1893

Phenylbromethylbenzenesulfonamid and phenylbromethylamin

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Phenylbromethylbenzenesulfonanilide

and

Phenylbromethylamin

A Thesis

By Carl L. Enke

Class 1893

S.W. I.
The amino derivatives include a class of very basic compounds, called organic bases or alkaloids. They all contain nitrogen and are looked upon as derivatives of ammonia, which accounts for their basic properties. One, two or three of the hydrogen atoms being replaceable by alkyls, gives rise respectively to primary, secondary and tertiary amines.

\[ \text{N} \text{H}_2 \cdot \text{CH}_3 \quad \text{Primary methylamine} \]
\[ \text{N} \text{H} \cdot (\text{CH}_3)_2 \quad \text{Secondary} \]
\[ \text{N} (\text{CH}_3)_3 \quad \text{Tertiary} \]

There are likewise derivatives corresponding to \( \text{N} \) \( \text{H}_4 \), \( \text{Cl} \) and hypothetical \( \text{N} \) \( \text{H}_4 \), \( \text{OH} \):
\[ \text{N}(\text{CH}_3)_4 \cdot \text{Cl} \quad \text{Tetramethylammonium chloride} \]
\[ \text{N}(\text{CH}_3)_4 \cdot \text{OH} \quad \text{Tetramethylammonium hydroxide} \]
The amines are formed by heating the alkyl halides or nitrates with ammonia, under pressure. The following consecutive reactions take place:

1. \( \text{C}_2\text{H}_5\text{Cl} + \text{NH}_3 = \text{NH}_2\text{C}_2\text{H}_5 + \text{HCl} \)

2. \( \text{C}_2\text{H}_5\text{Cl} + \text{NH}_2\text{C}_2\text{H}_5 = \text{NH}_2\text{C}_2\text{H}_5\text{C}_2\text{H}_5 + \text{HCl} \)

3. \( \text{C}_2\text{H}_5\text{Cl} + \text{NH}_2\text{C}_2\text{H}_5\text{C}_2\text{H}_5 = \text{NH}_2\text{C}_2\text{H}_5\text{C}_2\text{H}_5 \text{C}_2\text{H}_5 + \text{HCl} \)

Those containing the lower members of the series of alkyls are gaseous at the ordinary temperatures, those containing the higher members are usually liquid. They have a peculiar ammoniacal smell, which is usually accompanied by a fish-like odor. Many metallic salts are thrown down, from solutions, by them and they combine directly with acids to form crystalline compounds. Their chlorides combine with muriatic chloride, as does \( \text{NH}_4\text{Cl} \), and
their sulphates with aluminium sulphate to form alums.

For distinguishing the primary, secondary and tertiary amines, nitrous acid is used, it being applied indirectly. The salt of the amine treated with KMnO₄. In the case of a primary amine, as CH₃.NH₂, this reaction takes place:

\[ CH₃.NH₂ + KMnO₄ \rightarrow CH₃.OH + N₂ + N₂O \]

giving the alcohol, free nitrogen and water.

In the case of secondary amines

\[ (CH₃)₂NH + KMnO₄ = (CH₃)₂N - N = O + N₂O \]

giving us a nitrosoamine, which is an oily body insoluble in water.

The tertiary amines give no reaction whatever with KMnO₄. They readily combine with alkyl halides, giving an iodide of a compound ammonium, as \( N(CH₃)_4 \) or Tetramethylammonium iodide.
They separate, like Na+ Cl- into their constituents upon heating, but recombine again upon cooling. Most silver oxide converts them into hydrates, which are strong alkalis like NaOH or KOH, readily soluble in water, form crystalline salts, throw down many metals from solutions as hydrates, destroy animal matter, such as skin, and saponify fats.

The possible isomers of the amines are very numerous; they are determined not only by the isomers of the alkyls, but also by the number of replacing groups, as the following examples will show.

\[
\begin{align*}
N\text{H}_2\text{C}_3\text{H}_7 & \quad \text{Propyl and Isopropylamine} \\
N\text{H}_1\text{C}_2\text{H}_5 & \quad \text{Methylisobutylamine} \\
N\text{H}_1\text{C}_3\text{H}_3 & \quad \text{Trimethylamine}
\end{align*}
\]
They can be distinguished by the action of 
C₂H₅. I; the primary amines can receive two, 
the secondary, one additional ethyl group; 
the tertiary amines form ammonium bases 
directly.

**Methylamin** N₂H₂ · CH₃

The best method for its preparation is by 
heating bromacetanilid with KOH

\[ \text{Br} \quad \text{N} - \text{H} + 3 \text{KOH} \rightarrow \text{CH₃NH₂} \cdot \text{K₂CO₃} + \text{KBr} + \text{H₂O} \]

It is a colorless gas with an ammoniacal odor, 
condenses to a liquid at minus 6° and is 
combustible, which distinguishes it from N₂H₃.

At 12° one volume of water dissolves 1150 volumes 
of the gas, giving a solution which shows all
The properties of aqueous NH₃, except that it does not dissolve the oxides of cobalt, nickel, and cadmium. Its solution gives with I and Br red precipitates; conducted over heated potassium it decomposes into KCN and hydrogen.

Ethylamine  C₂H₅-NH₂

It is a mobile liquid, boiling at 18°, base
sp. gr. of 0.696 at 8° and mixes with water in all proportions. It acts precisely like ammonia, except that it will drive out NH₃ from its salts and redissolve aluminium hydrate when in excess.

Dimethylamine  N H (CH₃)₂

It is a gas readily soluble in water. Cold
condenses it into a liquid, which boils at 7.2.

The easiest way of obtaining it, is by boiling
Nitrodimethylanilin or dinitrodimethylanilin with KOH.

Diethylamin N H (C₂ H₅)₂
It is a liquid, which boils at 6.6°, is readily soluble in water and gives an HCl-salt fusing at 216° and boiling at 325°.

The Amides.

In ammonia the hydrogen atoms may be replaced by acid radicals, instead of alkyls. Such NH₃ derivatives are termed amides, to distinguish them from amines. Analogous to the amines, as one, two or three of the hydrogen atoms are replaced we have primary, secondary or tertiary amides.

There are several general methods for
Preparing them, which are as follows:

1st. By the action of acid chlorides upon aqueous ammonia

\[ C_2H_3O.Cl + 2 NH_3 = C_2H_3O.NH_2 + NH_4Cl \]

Acetanilid.

2nd. By the action of \( NH_3 \) or ammonia upon the esters. The action frequently takes place in the cold, but it is best to apply heat to the alcoholic solution.

\[ C_2H_3O.O.C_2H_5 + NH_3 = C_2H_3O.NH_2 + C_2H_5.OH \]

Acetanilid.

\[ C_2H_3O.O.C_2H_5 + C_2H_5.NH_2 = C_2H_3O.NH + C_2H_5.OH \]

Ethyl acetanilid.

3rd. By the dry distillation of ammonium salts of the fatty acids. This method is best adapted to the preparation of volatile amides. A mixture of the sodium salt with \( NH_4.Cl \) may be substituted for the ammonium salts.
The latter will first be formed in the reaction, which takes place.

\[ \text{C}_2\text{H}_3\text{O} \cdot \text{O} \cdot \text{UN}_4 = \text{C}_2\text{H}_3\text{O} \cdot \text{UN}_2 + \text{N}_2\text{O} \]

4th By distillation of the fatty acids with potassium sulfocyanide

\[ 2 \text{C}_2\text{H}_3\text{O} \cdot \text{OH} + \text{CN} \cdot \text{SK} = \text{C}_2\text{H}_3\text{O} \cdot \text{UN}_2 + \text{C}_2\text{H}_3\text{O} \cdot \text{OK} + \text{CO}_5 \]

5th By hydrolyzing the nitriles of the acids.

\[ \text{CH}_3 \cdot \text{CN} + \text{N}_2\text{O} = \text{CH}_3 \cdot \text{CO} \cdot \text{NH}_2 \]

Acetonitrile Acetamide

These methods given, do not give secondary and tertiary amides. They are obtained by heating the alkyl cyanides with acids or acid anhydrides to 200°.

\[ \text{CH}_3 \cdot \text{CN} + \text{CH}_3 \cdot \text{CO} \cdot \text{OH} = \text{CH}_3 \cdot \text{CO} \cdot \text{NH} \]

\[ \text{CH}_3 \cdot \text{CO} \cdot \text{NH} \]

Diacetamide

\[ \text{CH}_3 \cdot \text{CN} + (\text{CH}_3 \cdot \text{CO})_2 = (\text{CH}_3 \cdot \text{CO})_3 \text{N} \]

Acetic anhydride Triacetamid
The amides of the fatty series are usually solid, crystalline bodies, soluble in both alcohol and ether. The lower members are usually soluble in water and distill over without decomposition. On account of their containing the basic amido group, they will unite directly with acids to form salt-like compounds, thus:

\[ \text{C}_2\text{H}_3 \cdot \text{NH}_2 + \text{HNO}_3 = \text{C}_2\text{H}_3 \cdot \text{NH}_2 \cdot \text{NO}_3 \cdot \text{H} \]

These are however very unstable, the basic character of the amido group being neutralized by the acid radical. Added to this the presence of the acid radical makes the one hydrogen atom of the \(\text{NH}_2\) group replaceable by a weakly basic metal, such as mercury, forming a salt (\(\text{C}_2\text{H}_3 \cdot \text{Co} \cdot \text{NH}_2 \cdot \text{H}\)) called mercury acetamid.

The union between the amido group and the acid radical, in the amido is much weaker, than between the alkyls and the amido group in the
Ammon: hence the former are easily decomposed, by heating with water or still more easily, by boiling with alkalies or acids.

\[ \text{CN}_3 \cdot \text{CO} \cdot \text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{CN}_3 \cdot \text{CO} \cdot \text{H} + \text{NH}_3 \]

**Formamid** \( \text{CN} \cdot 0 \cdot \text{NH}_2 \)

It is the amid of formic acid and is obtained by heating ammonium formate to 230° or ethyl-formic ether with alcoholic \( \text{NH}_3 \) to 100° or by boiling formic acid with ammonium sulfocyanate. It is a liquid readily soluble in water and alcohol and boils at 192°–195° with partial decomposition. Rapid heating breaks it up into \( \text{CO} \) and \( \text{NH}_3 \) and with \( \text{P}_2\text{O}_5 \) gives HCN.

**Acetamid** \( \text{C}_2\text{H}_3 \cdot 0 \cdot \text{NH}_2 \)

It is the amid of acetic acid and is formed by heating a mixture of dry sodium acetate and \( \text{NH}_3 \cdot \text{Cl} \) or by digesting acetic ether with alcoholic \( \text{NH}_3 \).
It crystallizes in long needles, melts at 82°-83° and boils with decomposition at 222°. It readily dissolves in water and alcohol and when boiled with alkalies or acids decomposes into acetic acid and NO₃.

The Sulfonamides.

According to Nyberg (see Liebig's Annalen Vol. 265, S. 178 and Vol. 272, S. 229) the amides of benzenesulfonic acid, especially benzenesulfonamid and the benzenesulfonamides of the primary bases are distinguished from almost all other acid amides by the fact that they are strong acids and give with the alkalies easily soluble salts, whose stability is so great, in the presence of an excess of alkali, that they may be boiled for hours with concentrated NaOH or KOH without being affected.
The benzenesulfonamides of the primary bases owe their relatively great reactive power, to the readiness with which they form stable and easily soluble salts. Accordingly several of them are changed by oxidizing agents, in alkaline solution; others react with Br_2 in the presence of an alkali, forming substituted nitrogen bromides. The salts of the primary benzenesulfonamides in aqueous solution universally give with the halogens of the fatty series and in a few cases of the aromatic series, reactions such that benzenesulfonamides of the secondary bases are formed:

\[
C_6H_5SO_2NRK + R_1Cl \rightarrow C_6H_5SO_2NR_1 + KCl.
\]

This reaction can be made use of for forming mixed secondary amin bases. It has the advantage over other methods, such as that of Keff, in that it is generally applicable and gives almost quantitative results, if by-products are avoided.

As an example, suppose we wish to produce
the base NHR. First prepare the benzene-
sulfonanilid C₆H₅SO₂NHR, which is best done
by benzene-sulfonating the primary amine base
NHR. This sulfonanilid is dissolved in dilute
alkali with the addition of a little alcohol, and is
then treated with the halogen alkyl RCl and
warmed on the water-bath for several hours.
The sulfonanilid C₆H₅SO₂NHR, thus formed,
needs only to be split up with concentrated HCl at
a temperature of 15°0, to obtain the chloride of
the mixed secondary base.

Experimental

The following are the steps for preparing from
sodium benzene sulfonate, phenylbromomethylbenzene-
sulfonanilid and from it phenylbromomethylamin

1) C₆H₅SO₂ONa + RCl = C₆H₅SO₂Cl + NaCl

Benzensulfoclorid
(2) \( C_6H_5-SO_2-Cl + 2 C_6H_5 NH_2 = C_6H_5-SO_2 NH C_6H_5 + C_6H_5 NH_2 HCl \)

Aminin \hspace{1cm} Benzene sulfonamid.

(3) \( C_6H_5-SO_2 NH C_6H_5 + NaOH + Br_2 C_6H_4 Br = C_6H_5-SO_2 NH + NaBr + H_2O \)

Phenylbromomethylbenzene sulfonamid.

Hydrolyzing with fuming HBr

(4) \( C_6H_5-SO_2 NH C_6H_5 Br + H_2O + HBr = C_6H_5-SO_2 OH + HBr C_6H_5 \)

Bromomethylphenyl-

ammoniumbromid.

The last compound is the hydrobromid of the mixed secondary amine sought for.

The sodiumbenzencesulfonate is prepared from benzene by treating it with chlorosulfonic acid and the precipitating with a saturated solution of NaCl. The flask with a long tube condenser, in which the operation was carried on, was kept cool by constantly shaking under a water tap. The sodiumbenzencesulfonate is purified and freed from the diphenylsulfone, formed at the same time, by dissolving in hot water, filtering,
The diphenylsulfone \((\text{C}_6\text{H}_5\cdot)_2\text{SO}_2\) recrystallized from alcohol has a melting point of 125°.

**Benzene sulfochlorid** \(\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{Cl}\)

First dry in a nickel dish, thoroughly and carefully, over an argand-burner, the sodium benzene sulphonate. Then transfer to a flask with long tube condenser and gradually add the calculated amount of \(\text{POCl}_3\), with constant shaking and careful heating over an argand. Continue heating until reaction is completed, distill off \(\text{POCl}_3\) formed and allow the mass to thoroughly cool. Then add cracked ice and a little water and shake well until all is dissolved that will dissolve. (The temperature must be kept down so as to prevent any of the benzene sulfochlorid from changing back to the sodium salt) add enough dry benzene to dissolve out all the benzene sulfochlorid and separate
the same from the water; filter benzene solution
to get rid of the slimy mass, transfer filtrate
to a bottle and dry with CaCl₂.

170 gms. C₆H₅·SO₂·O. Na gave about 105 gms.
of C₆H₅·SO₂·Cl.

Benzeneanisidid C₆H₅·SO₂·NH·C₆H₅

Mix, in a mortar, the benzene solution of
benzeneanisidid with a slight excess of
anilin; (add the latter gradually and work up the mass
well) add water to dissolve out the anilin hydrochlorid
formed and if the solid separates well, pour off the
liquid, if not, first distill off the benzene. Tack out
the excess of anilin by means of dilute HCl. Purify
the product, by dissolving it in twice molecular NaOH
or KOH and reprecipitate with HCl, or by simply
washing with gasoline. The product recrystallized
from alcohol melts at 108°.
Average of four (4) analyses.

**Found**

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<td>C</td>
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**Calculated**

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<tr>
<td>C</td>
<td>61.84</td>
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Phenylbromomethylenesulfonamide

\[ C_6H_5 \cdot SO_2 \cdot NH \cdot C_2H_4Br \]

Take the benzene sulphonamide and treat with NaOH and \( \text{BrC}_2\text{H}_4\text{Br} \), the latter in about 10% excess and heat over an acid burner, shaking well if bumping is too strong. It seems to be best to add the required amount of NaOH in separate portions, about one half first and after boiling a while, the other half. The heating is continued until the alkaline reaction has about disappeared. The operation is best carried on in a round bottom flask with reflex condenser. Next the excess of \( \text{BrC}_2\text{H}_4\text{Br} \) is removed by passing steam through the mass, until there can be no odor of the bromide detected. The syrupy mass is then
allowed to run into a mortar and is worked up several times with alcohol and finally with a twice molecular NaOH solution, after this it is filtered off and washed with water.

The residue is a white mealy mass from which the phenyl(trimethyl)benzenesulfonanilid is extracted in an extractor, by means of gasoline which distills over under 80°. It readily crystallizes out from the gasoline in beautiful, fine, colorless needles.

From the NaOH washings the dissolved and uncharged benzenesulfanilid, can be recovered by precipitating with an acid. The alcohol is distilled off from the alcohol washings; the residue is worked up again, in a similar way, with a small amount of alcohol and then NaOH and lastly is extracted with gasoline the same as the other.

The product thus obtained melts at 88°.
The average of two analyses.

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The portion insoluble in gasoline has not yet been examined, and its composition determined. It melts at about 215°, turning dark at the same time.

The last step, that of forming phenyl-bromomethylammonium from phenylbromomethylbenzene-sulfonamid, I have not as yet been able to carry out, for want of time.

The method used in making the hydrogen and carbon determinations, was that of Dudley (see Am. Chem. Journ. Vol. 10 - Pg 433). According to it, manganese dioxide, prepared from the nitrate, is used instead of copper oxide.
In determining nitrogen the Kjeldahl-Dunning method was used (see Fres. Jtech., Vol. 28 - P 188) for converting the nitrogen into ammonia. Then the ammonia was distilled off with an excess of NaOH and collected in tenth (1/10) normal acid and the unneutralized acid titrated with an alkali solution.