ON SOME SUBSTITUTED THIAZOLIDINES.

by

Roy V. Maneval

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Approved by:

Instructor in Charge.

Head or Chairman of Department.

July, 1923.
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>PREPARATION OF P-BROM-ANILINE</td>
<td>3</td>
</tr>
<tr>
<td>PREPARATION OF P-BROM-PHENYL-AMINO-ETHANOL</td>
<td>4</td>
</tr>
<tr>
<td>PREPARATION OF PHENYL-AMINO-ETHANOL</td>
<td>6</td>
</tr>
<tr>
<td>PREPARATION OF P-TOLYL-AMINO-ETHANOL</td>
<td>7</td>
</tr>
<tr>
<td>PREPARATION OF ALPHA-NAPHTHYL-AMINO-ETHANOL</td>
<td>7</td>
</tr>
<tr>
<td>PREPARATION OF P-BROM-PHENYL MUSTARD OIL</td>
<td>8</td>
</tr>
<tr>
<td>PREPARATION OF ALPHA-NAPHTHYL MUSTARD OIL</td>
<td>9</td>
</tr>
<tr>
<td>SYNTHESIS OF ALPHA-P-BROM-PHENYL, BETA-ALPHA-NAPHTHYL THIOUREA</td>
<td>10</td>
</tr>
<tr>
<td>SYNTHESIS OF ALPHA-P-BROM-PHENYL, BETA-P-TOLYL THIOUREA</td>
<td>11</td>
</tr>
<tr>
<td>SYNTHESIS OF ALPHA-PHENYL, ALPHA-ETHANOL, BETA-P-BROM-PHENYL THIOUREA</td>
<td>12</td>
</tr>
<tr>
<td>SYNTHESIS OF ALPHA-P-BROM-PHENYL, ALPHA-ETHANOL, BETA-P-BROM-PHENYL THIOUREA</td>
<td>13</td>
</tr>
<tr>
<td>SYNTHESIS OF ALPHA-P-TOLYL, ALPHA-ETHANOL, BETA-P-BROM-PHENYL THIOUREA</td>
<td>14</td>
</tr>
<tr>
<td>SYNTHESIS OF ALPHA-P-BROM-PHENYL, ALPHA-ETHANOL, BETA-ALPHA-NAPHTHYL THIOUREA</td>
<td>15</td>
</tr>
<tr>
<td>SYNTHESIS OF ALPHA-P-BROM-PHENYL, ALPHA-ETHANOL, BETA-ALLYL, THIOUREA</td>
<td>16</td>
</tr>
<tr>
<td>SYNTHESIS OF 2-PHENYL-IMINO, 3-P-BROM-PHENYL, THIAZOLIDINE</td>
<td>17</td>
</tr>
<tr>
<td>PRODUCT FROM ETHYLENE DIBROMIDE AND ALPHA-P-BROM-PHENYL, BETA-PHENYL THIOUREA</td>
<td>18</td>
</tr>
</tbody>
</table>
SYNTHESIS OF 2-P-BROM-PHENYL-IMINO,3-PHENYL,
THIAZOLIDINE----------------------------------------19

SYNTHESIS OF 2-P-TOLYL-IMINO,2-P-BROM-PHENYL,
THIAZOLIDINE----------------------------------------20

PRODUCT FROM ETHYLENE DIBROMIDE AND ALPHA-P-BROM-
PHENYL,BETA-P-TOLYL THIOUREA------------------21

SYNTHESIS OF 2-P-BROM-PHENYL-IMINO,3-P-TOLYL,
THIAZOLIDINE----------------------------------------22

SYNTHESIS OF 2-ALPHA-NAPHTHYL-IMINO,5-P-BROM-
PHENYL, THIAZOLIDINE-------------------------------23

SYNTHESIS OF 2-P-BROM-PHENYL-IMINO,3-ALPHA
NAPHTHYL THIAZOLIDINE-------------------------------24

PRODUCT FROM ETHYLENE DIBROMIDE AND ALPHA-P-BROM-
PHENYL,BETA-ALPHA NAPHTHYL THIOUREA-------------25

SYNTHESIS OF 2-P-BROM-PHENYL-IMINO,3-P-BROM-
PHENYL THIAZOLIDINE-----------------------------26

SYNTHESIS OF 2-PHENYL-IMINO,3-P-BROM-PHENYL,
OXAZOLIDINE---------------------------------------27

SYNTHESIS OF 2-P-BROM-PHENYL-IMINO,3-PHENYL,
OXAZOLIDINE---------------------------------------28

SYNTHESIS OF 2-P-BROM-PHENYL-IMINO,3-P-TOLYL,
OXAZOLIDINE---------------------------------------30

SUMMARY------------------------------------------31

BIBLIOGRAPHY--------------------------------------32
INTRODUCTION.

Thiazolidines of the type

\[
\begin{array}{c}
\text{RN} \text{CH} \text{CH} \\
\text{RN-CH} \\
\text{S}
\end{array}
\]

have been prepared by Will and others by the action of ethylene dibromide upon the disubstituted thioureas.

Will\(^1\) found by treating molar amounts of thiocarbanilide with ethylene dibromide and by precipitating the free base, he was able to prepare the 2-phenyl-imino, 3-phenyl thiazolidine which melted at 135°.

\[
\text{C}_6\text{H}_5\text{NH} \text{SH} + \text{CH}_2\text{Br} \rightarrow \text{C}_6\text{H}_5\text{N} = \text{CH}_2
\]

Gabriel\(^2\) found that allyl thiourea when heated with concentrated hydrochloric under pressure, undergoes a rearrangement with ring closure for the thiazol. F. B. Dains\(^3\) found that the same thing happened when thioureas were heated with acetyl chloride in the absence of a solvent. This method was used by F. B. Dains, R. Q. Brewster, and J. S. Blair\(^3\) to prepare a number of thiazolidines. They found that phenyl allyl amine and phenyl mustard oil gave di-phe-

\(^1\) B. 14 (1861), 1490.
\(^2\) B. 82, 2985.
\(^3\) J. A. O. S., 44, 2647.
nal allyl thiourea. This, on ring closure with hydrochloric acid, gave 2-phenyl-imino, 5-methyl thiazolidine.

Dersin\(^4\) found that by treating amino dimethyl carbinoi with phenyl mustard oil, which on heating with hydrochloric acid at \(100^\circ\), he was able to form 2-phenyl-imino, 5-dimethyl thiazolidine.

Any of the foregoing methods can be used for the synthesis of the thiazolidines of the general type

\[
\begin{align*}
\text{R'} & \text{N} \quad \text{CH}_2 \\
\text{R} & \text{N} = \text{C} \quad \text{CH}_2 \\
& \text{S} \\
\end{align*}
\]

Only two of these methods were used in synthesizing the thiazolidines given in this paper. The general type reactions of these methods are the following:

I.
\[
\text{RNCS} + \text{R'}\text{NHCH}_2\text{CH}_2\text{OH} = \text{RNH} \quad \text{CN} \quad \text{CH}_2\text{OH} \\
\text{R'}\text{NCH}_2\text{CH}_2\text{OH} \\
\]

This on ring closure by the use of hydrochloric acid.

II.

\[
\begin{align*}
\text{RNH} & \quad \text{CH}_2\text{Br} \\
\text{R'} & \text{NH} \quad \text{CH}_2\text{Br} \\
\end{align*}
\]

\(\text{R'}\text{N} \quad \text{CH}_2\text{Br} \\
\text{R'} & \text{N} = \text{C} \quad \text{CH}_2 \\
& \text{S} \\
\]

\(^4\)B. 26 (1903), 1281.
In the case of method II, if \( R \) and \( R' \) are different, two thiazolidines are possible. The problem of determining what influence the nature of the groups \( R \) and \( R' \) would have on the resulting thiazolidine has been the subject of a general investigation carried on at this University under the direction of Dr. F. B. Dains.

The method of proving the constitution of the thiazolidines made by the second method was by making the thiazolidines of known constitution by the first method.

**PREPARATION OF \( p \)-BROM-ANILINE.**

The following method was found to be the most economical. One hundred thirty-five grams of acetanilid were put into two liters of water and to this, with stirring, was added one hundred sixty grams of bromine dissolved in glacial acetic acid. The addition of the bromine being gauged by the way the acetanilid takes it up, trying all the while to prevent the formation of lumps of the \( p \)-bromacetanilid. Generally the addition of the bromine takes about an hour. The solution is then filtered and the residue which is \( p \)-bromacetanilid is dried and weighed. It is then hydrolysed by boiling the following under a reflux: eighteen grams of \( p \)-bromacetanilid, thirty-five cubic centimeters of alcohol, and twenty cubic centimeters of hydrochloric acid. As soon as some of the solution does not form a precipitate in water, the hydrolysis is complete, the alcohol is distilled off, and, after cooling, made alkaline with sodium hydroxide and
oil separates out to the bottom, which is the desired p-brom-aniline in the impure form. The p-bromaniline may then be purified by steam distillation or by recrystallizing from gasoline, however, the former method gives the better product as it is much whiter.

1. \( \text{CH}_3\text{CONHCH}_2\text{H}_2 + \text{Br}_2 = \text{CH}_3\text{CONHCH}_2\text{HBr} + \text{HBr} \)

2. \( \text{CH}_3\text{CONHCH}_2\text{HBr} + \text{HOH} = \text{p-BrC}_6\text{H}_4\text{NH}_2 + \text{CH}_3\text{COOH} \)

The above method is a modification of that found in Uhlmann in that the acetanilid is not dissolved in acetic acid. It was found that this method was much cheaper than any other method that could be worked out in the laboratory. If benzene were the starting point, probably the method of brominating the benzene, nitrating and reducing would be the best, but in case a method such as that, the percentage yield is not so good and takes a longer time.

The acetanilid used was of technical grade, the bromine was the chemically pure product, the acetic acid was commercial, the hydrochloric acid was technical and the sodium hydroxide was the ordinary caustic soda. The yield by the procedure above is about seventy-two per cent and the product melts at 66°.

**PREPARATION OF P-BROM-PHENYL-AMINO-ETHANOL.**

**First Method.**

Two moles of p-brom-aniline and one mole of ethylenechlor-hydrin were heated on an oil bath for ten hours under a reflux condenser at 120 - 130°. It was then made al-
kaline with sodium hydroxide and the excess p-brom-aniline was removed by steam distillation. The oil was then taken up with ether and dried with anhydrous sodium sulphate, the ether was then distilled off. It was thought that the remaining oil could be purified by distilling under a vacuum. It was found, however, that under the lowest vacuum obtainable in the laboratory that the oil decomposed when reaching the temperature of about 120°. It was noticed that some long needles separated out of the water of the flask after steam distilling. These needles proved to be the desired compound. It was found that the ethanol was only slightly soluble in the cold water. Quinoline and pyridine were tried as the base for taking up the HCl formed in the reaction. It was found that quinoline was much better than pyridine.

\[
2p{-}\text{BrC}_6\text{H}_4\text{NH}_2 + \text{CH}_2\text{CH}_2\text{CH}_3\text{OH} \rightarrow p{-}\text{BrC}_6\text{H}_4\text{NNCH}_2\text{CH}_3\text{OH} + p{-}\text{BrC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}
\]

Second Method

Miller\(^1\) has shown that the amino ethanols could be made by passing ethylene oxide into the amine and heating under pressure. This was tried in the case of para-brom aniline and it was found that it was much better than the first method tried. The ethylene oxide is made by allowing ethylene chlorhydrin react with potassium hydroxide, the gas is then passed into the amine. The solution is

\(^1\)Miller, 1923, "The Action of Ethylene Dibromide upon Substituted Thioureas."
heated under pressure. In the case a pressure of ninety centimeters of mercury was put on the amine and it was
heated to 75°. The oxide slowly reacts with the amine and
the pressure goes down. The ethanol thicourea is then se-
parated from the unchanged amine by crystallizing from hot
water. The yield was about thirty per cent of the theore-
tical, the product melting at 93°.

\[
p-\text{BrC}_{6}\text{H}_{4}\text{NBr} + \text{CH}_{2} \rightarrow p-\text{BrC}_{6}\text{H}_{4}\text{NECH}_{2}\text{CH}_{2}\text{OH}
\]

Analysis: Calculated for C_{6}H_{10}ONBr

Nitrogen = 6.48%. Found N = 6.29%, 6.25%.

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<thead>
<tr>
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<th>I</th>
<th>II</th>
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</thead>
<tbody>
<tr>
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<tr>
<td>Vol. Acid used by sample</td>
<td>10.45</td>
<td>10.40</td>
</tr>
</tbody>
</table>

1 cc. acid = .0012043 gms. of N = 1 cc base.

\[
\text{I } \frac{10.45 \times .0012043 \times 100}{.2000} = 6.29\%
\]

\[
\text{II } \frac{10.40 \times .0012043 \times 100}{.2000} = 6.25\%
\]

Preparation of Phenyl-Amino-Ethanol.

Previous work in this laboratory has shown that the
method used by Thompson\(^1\) gave the best yield. Two moles
of aniline and one mole of ClCH_{2}CH_{2}OH were heated under a

\(^1\) Thompson, 1922, "The Synthesis of Thicourea
Ethers and Thiolsidines."
reflux for ten hours at 120-130° and then made alkaline. The excess aniline was then removed by steam distillation, the oily layer was separated and the remaining solution extracted with ether. After drying with anhydrous sodium sulphate, it was purified by distilling under reduced pressure. The purpose of the extra mole of the aniline is to take up the mole of HCl that is formed by the reaction. The product obtained was a thick yellow liquid boiling at 201° at 70 mm. pressure. The yield of the ethanol was 65% of the theoretical. Upon exposure to the air, the product changes from a yellow to a dark purple.

**PREPARATION OF P-TOLYL-AMINO-ETHANOL.**

One hundred ten grams of para-toluidine and forty grams of ethylene chlorhydrin were heated on an oil bath under a reflux for ten hours at 130-140°.

$$2 \text{p-}C_7H_7\text{NH}_2 + \text{ClCH}_2\text{CH}_2\text{OH} = \text{p-}C_7H_7\text{NCH}_2\text{CH}_2\text{OH} + \text{p-}C_7H_7\text{NCl}$$

The product was then neutralized with sodium hydroxide and steam distilled to remove the excess amine. The oil was separated and dried with anhydrous sodium sulfate, then purified by distilling under reduced pressure. A thick, oily, straw colored, liquid is distilled over, which becomes darker on exposure to light. The oil boiled at 209° at 73 m.m. and the yield was seventy per cent of the theoretical.

**PREPARATION OF ALPHA-NAPHTHYL-AMINO-ETHANOL.**

One hundred five grams of alpha-naphthylamine and thirty grams of chlorhydrin were heated under a reflux on an oil
bath for ten hours keeping the oil bath at the temperature of 120-130°. It was very noticeable in the flask when the reaction had started for the hydrochloride of the naphthylamine separated out and made the oil partially a solid.

\[2 \alpha C_{10}H_7NH_2 + C_6H_5CH_2OH = \alpha C_{10}H_7NHCH_2CH_2OH + \alpha C_{10}H_7NH_2HCl\]

The product was made alkaline and steam distilled to remove the excess amine. The oil was then taken up with ether and dried with anhydrous sodium sulphate. After distilling off the ether, the oil was then purified by distilling under reduced pressure. The product is an oil that darkens on exposure to air and light, its constitution can be proven by its action with phenyl mustard oil with which its forms an ethanol thiourea with a melting point of 163°. The boiling point of this oil is 258° at 68 m.m., the yield was seventy per cent of the theoretical.

**PREPARATION OF P-BROM-PHENYL MUSTARD OIL.**

In this case, the stirrer was arranged as in the preparation of the p-toly1 mustard oil. Thirty grams of carbon disulphide and forty grams of ammonia were used and to this was added small portions of a solution composed of forty-five grams of para-brom-aniline and forty-five cubic centimeters of alcohol. About an hour was required for the addition of the solution of the amine, stirring all the while, the solution thus formed was stirred for an additional hour. After allowing the solution to stand overnight the thiocarbamate separated out, it was dissolved in about a liter of
water and the solution filtered to recover the unchanged amine. A solution of eighty-seven grams of lead nitrate dissolved in a liter of water was then added to the thio-carbamate solution and then steam distilled. The yield of the mustard oil in this case was found to be about thirty-one per cent of the theoretical.

The yield of the above method was found to be increased by allowing the solution, after being stirred, to be surrounded by ice for twenty-four hours. More crystals of the salt seemed to separate out and the yield was brought up to forty-four per cent. The product melts at 66°.

1. \( p-BrC_6H_4NH_2 + CS_2 + NH_2OH = p-BrC_6H_4NHCSSNH_2 + H_2O \)
2. \( p-BrC_6H_4NHCSSNH_2 + Pb(NO_3)_2 = p-BrC_6H_4NCS + NH_4NO_3 + HNO_3 + PbS \)

**PREPARATION OF ALPHA NAPHTHYL MUSTARD OIL.**

Forty grams of alpha naphthylamine dissolved in forty cubic centimeters of alcohol were added slowly to a mixture of fifteen grams of carbon bisulphide and forty-four grams of ammonia, stirring all the while with the flask in an ice bath. After about two hours stirring, only a few crystals separated out. The flask was then set in an ice box for twelve hours and the whole became solid with crystals. The crystals were then dissolved in water, filtered to remove the excess amine, then added to a solution of ninety-three grams of lead nitrate dissolved in four hundred cubic centimeters of water. A heavy precipitate of lead sulphide
is formed, this is extracted with alcohol. filtering by decantation, the mustard oil crystallizing from the alcohol. The product melts at 35°.

It was found that the above method was much better than the ordinary method, in that by keeping the stirred mixture in a low temperature for some time and in this way the salt seemed to be crystallized out better.

1. \[ \text{C}_{10} \text{H}_7 \text{NH}_2 + \text{CS}_2 + \text{NH}_4 \text{OH} = \text{C}_{10} \text{H}_7 \text{NHCSSNH}_4 + \text{H}_2 \text{O} \]

2. \[ \text{C}_{10} \text{H}_7 \text{NHCSSNH}_4 + \text{Pb(NO}_3)_2 = \text{C}_{10} \text{H}_7 \text{NCS} + \text{NH}_4 \text{NO}_3 + \text{HNO}_3 + \text{PbS} \]

**SYNTHESIS OF ALPHA-P-BROM-PHENYL, BETA- ALPHA-NAPHTHYL THIOUREA.**

Molecular proportions of alpha naphthylamine and para-brom-phenyl mustard oil were heated in an alcohol solution. The solution was then allowed to stand overnight and during that time the thio urea crystallized out. It was then recrystallized from alcohol, forming small white granules. The yield was ninety-five per cent and the products melts at 168°.

\[ \alpha \text{C}_{10} \text{H}_7 \text{NH}_2 + \text{p-BrC}_6 \text{H}_4 \text{NCS} = \alpha \text{C}_{10} \text{H}_7 \text{NH} \text{p-BrC}_6 \text{H}_4 \text{NCS} \]

**Analysis:** Calculated for \( \text{C}_{17} \text{H}_{12} \text{N}_2 \text{SBr} \)

Nitrogen = 7.63%  Found N = 7.38%, 7.41%.
Analysis Nitrogen

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<td>Volume of acid</td>
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<td>Volume of alkali</td>
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<td>Weight of sample</td>
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<tr>
<td>Vol. of acid neutralized</td>
<td>12.2</td>
<td>12.25</td>
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</table>

1 cc acid = .0012043 grams of Nitrogen = 1 cc base

\[ \frac{12.2 \times 0.0012043 \times 100}{2000} = 7.38\% \]

\[ \frac{12.25 \times 0.0012043 \times 100}{2000} = 7.41\% \]

SYNTHESIS OF ALPHA-P-BROM-PHENYL, BETA-P-TOLYL THIOUREA.

Molecular proportions of p-brom-aniline and p-tolyl mustard were put into an alcohol solution and on the application of a small amount of heat the reaction proceeded with the evolution of heat. The thiourea was crystallized from hot alcohol, it forming white plates with melting point of 184°. The yield was nearly theoretical.

\[ \text{p-BrC}_6\text{H}_4\text{NH}_2 + \text{p-C}_7\text{H}_7\text{NCS} = \text{p-BrC}_6\text{H}_4\text{NH} \]

\[ \downarrow \text{CS} \]

\[ \text{p-C}_7\text{H}_7\text{NH} \]

Analysis: Calculated for C_{14}H_{13}N_{2}SBr

Nitrogen = 8.73% Found N = 8.56%, 8.75%
Analysis Nitrogen.

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<tr>
<th></th>
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<td>Weight of sample</td>
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<tr>
<td>Vol. of net acid neutralized</td>
<td>14.2</td>
<td>14.5</td>
</tr>
</tbody>
</table>

1 cc acid = 0.0012043 grams of Nitrogen = 1cc base

\[
\text{I } \frac{14.2 \times 0.0012043 \times 100}{2000} = 8.56\%
\]

\[
\text{II } \frac{14.5 \times 0.0012043 \times 100}{2000} = 8.75\%
\]

SYNTHESIS OF ALPHA-PHENYL, ALPHA-ETHANOL, BETA P-BROM-PHENYL THIOUREA

Molar proportions of phenyl-amino-ethanol and p-brom phenyl mustard oil in an alcohol solution were heated for one hour on a water bath and then were allowed to stand for a day. The product came down as an oil and was first crystallized from alcohol but a much better product was obtained by recrystallizing from benzene. The crystals were of granular form and melted at 131°. The yield was nearly theoretical.

\[
\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_2\text{OH} + p-\text{BrC}_6\text{H}_4\text{NCS} = \text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_2\text{OH}_2\text{CS} \text{p-BrC}_6\text{H}_4\text{NH}
\]

Analysis: Calculated for \(\text{C}_{16}\text{H}_{25}\text{N}_2\text{OBrs}\) Nitrogen = 7.98%

Found N = 7.88%, 7.83%
Analysis Nitrogen

<table>
<thead>
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<td>Volume of alkali</td>
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<tr>
<td>Vol. acid used by sample</td>
<td>13.1</td>
<td>13.00</td>
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1 cc acid = .0012043 grams of N = 1 cc base

I \[ \frac{13.1 \times .0012043 \times 100}{.2000} = 7.88\% \]

II \[ \frac{13.0 \times .0012043 \times 100}{.2000} = 7.85\% \]

SYNTHESIS OF ALPHA P-BROM-PHENYL, ALPHA ETHANOL, BETA PHENYL THIOUREA.

Equal molecular parts of p-brom-amino-ethanol and phenyl-mustard oil were heated in an alcohol solution on a water bath for one-half hour, the thiourea crystallizing as white granules while still hot. The product was recrystallized from dilute alcohol. The product thus obtained had a melting point of 99°.

\[
p-\text{BrC}_6\text{H}_4\text{NHCH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{NCS} = \text{p-BrC}_6\text{H}_4\text{NHCH}_2\text{CH}_2\text{OH}
\]

\[
\text{C}_6\text{H}_5\text{NH}
\]

Analysis: Calculated for \( \text{C}_{15}\text{H}_{15}\text{N}_{2}\text{OBrS} \), \( \text{N} = 7.98\% \)

Found \( \text{N} = 7.81\%, 7.74\% \)

Analysis Nitrogen

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<td>.5</td>
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</table>
Weight of Sample
Vol. acid used by sample

\[
\begin{align*}
\text{Weight of Sample} & \quad .2000 \quad .2000 \\
\text{Vol. acid used by sample} & \quad 12.95 \quad 12.90
\end{align*}
\]

\[
1 \text{ cc acid} = .0012043 \text{ grams of } N = 1 \text{ cc base}
\]

\[
\begin{align*}
\text{I} & \quad \frac{12.95 \times .0012043 \times 100}{.2000} = 7.68\% \\
\text{II} & \quad \frac{12.90 \times .0012043 \times 100}{.2000} = 7.77\%
\end{align*}
\]

SYNTHESIS OF ALPHA-P-TOLYL, ALPHA-ETHANOL, BETA-P-BROM-PHENYL

Molecular portions of p-tolyl-amino ethanol and p-brom-phenyl mustard oil were put in an alcohol solution and heated on a water bath for one-half hour. After standing over night white granular crystals began to form, which were recrystallized from alcohol. The yield was nearly theoretical and the product melts 137°.

\[
p-C_7H_7NOCH_2CH_2OH + p-BrC_6H_4NCS = p-C_7H_7NOCH_2CH_2OH + p-BrC_6H_4NH
\]

Analysis: Calculated for C\textsubscript{16}H\textsubscript{17}ON\textsubscript{2}Br S

\[
\text{Nitrogen} = 7.68\% \quad \text{found } N = 7.78\% \quad 7.81\%
\]

\[
\begin{array}{ccc}
\text{Analysis Nitrogen} & \text{I} & \text{II} \\
\text{Volume of acid} & 20.0 & 20.0 \\
\text{Volume of alkali} & 5.15 & 5.00 \\
\text{Correction for blank} & 2.10 & 2.10 \\
\text{Weight of sample} & .2000 & .2000 \\
\text{Vol. of acid used by sample} & 12.75 & 12.90 \\
\end{array}
\]

\[
1 \text{ cc acid} = .0012043 \text{ grams of Nitrogen} = 1 \text{ cc base}
\]

\[
\begin{align*}
\text{I} & \quad \frac{12.75 \times .0012043 \times 100}{.2000} = 7.68\% \\
\text{II} & \quad \frac{12.90 \times .0012043 \times 100}{.2000} = 7.77\%
\end{align*}
\]
SYNTHESIS OF ALPHA-P-BROM-PHENYL, ALPHA ETHANOL, BETA

ALPHA NAPHTHYL THIOUREA.

Molecular proportions of p-brom-amino-ethanol and alpha-naphtyl mustard oil were put in an alcohol solution and heated for one hour on the water bath. The solution was then filtered to remove some of the lead salts that were in the mustard oil and the solution cooled in ice. The thiourea separated out in small needles. After several crystallizations the product melted at 60°. The yield of the product was sixty per cent of the theoretical.

\[ p\text{-Br}-C_6H_4NCH_2CH_2OH + \alpha C_{10}H_7NCS = \]
\[ p\text{-Br}-C_6H_4NCH_2CH_2OH \]
\[ \alpha C_{10}H_7NH \]

Analysis: Calculated for C\(_{19}\)H\(_{17}\)O\(_2\)BrS

Nitrogen = 6.98%  Found Nitrogen: = 6.79%, 6.82%

Analysis Nitrogen

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of acid</td>
<td>20.0</td>
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<td>Volume of alkali</td>
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<td>Correction for blank</td>
<td>.7</td>
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<tr>
<td>Vol. acid used by sample</td>
<td>11.25</td>
</tr>
</tbody>
</table>

1 cc acid = .0012043 grams of Nitrogen = 1 cc base

I \[ 11.25 \times .0012043 \times 100 = 6.78\% \]
\[ .2000 \]

II \[ 11.45 \times .0012043 \times 100 = 6.92\% \]
\[ .2000 \]
SYNTHESIS OF ALPHA-p-BROM-PHENYL, ALPHA-ETHANOL, BETA-ALLYL, THIOUREA.

Molecular proportions of p-brom-α-methyl-ethanol and allyl mustard oil were put into an alcohol solution and heated on a water bath for half an hour. The product thus formed could not be crystallized from alcohol but by dissolving the substance in benzene and letting the benzene evaporate slowly, colorless plates were obtained which has a melting point of 96°. The yield was about seventy-five per cent.

\[
p-\text{Br-C}_6\text{H}_4\text{NHCH}_2\text{CH}_2\text{OH} + \text{C}_2\text{H}_5\text{NCS} = \]

\[
p-\text{Br-C}_6\text{H}_4\text{NHCH}_2\text{CH}_2\text{OH}
\]

\[
\text{C}_2\text{H}_5\text{NH}
\]

Analysis: Calculated for \( \text{C}_12\text{H}_{14}\text{OH}_2\text{SBr} \)

Nitrogen = 8.88%  Found N = 8.83%

Analysis Nitrogen

| Volume of acid | 20.0 | 21.0 |
| Volume of alkali | 4.65 | 5.95 |
| Correction for blank | .5 | .5 |
| Weight of sample | 2000 | 2000 |
| Vol. of acid used by sample | 14.75 | 14.65 |

1 cc acid = .0012043 grams of N = 1 cc base

I \[
14.75 \times .0012043 \times 100 = 8.90% \]

II \[
14.65 \times .0012043 \times 100 = 8.83% \]
It was found that the above thiourea seemed to decompose on heating with hydrochloric acid. The thiazolidine was attempted by the ethylene dibromide method, the product obtained being a sticky mass which would not form good crystals in any manner, even by forming the picrate or the perchlorate, which was probably due to a mixture of compounds.

**SYNTHESIS OF 2-PHENYL-IMINO, 3-P-BROM-PHENYL THIAZOLIDINE.**

Alpha-phenyl, beta-ethanol, beta-p-brom-phenyl was heated with concentrated hydrochloric acid for one-half hour on the water bath; all of the thiourea reacted and formed the soluble HCl salt of the thiazolidine. The free base was precipitated by adding ammonia until the solution was alkaline; the free base came down as a sticky mass; it was then crystallized from alcohol in the form of flakes. After several recrystallizations a pure product was obtained which melted at 113°. The yield was about eighty per cent.

\[
\begin{align*}
\text{p-Br-C}_6\text{H}_4\text{N} & \quad \text{CH}_2 \\
\text{C}_6\text{H}_5\text{N} & \quad \text{C}_6\text{H}_5\text{N} \\
\text{CH}_2\text{OH} & \quad \text{S} \quad \text{CH}_2 \\
\end{align*}
\]

Analysis: Calculated for C\textsubscript{15}H\textsubscript{13}H\textsubscript{2}BrS

Nitrogen = 8.41%  
Found N = 8.25  8.53

Analysis Nitrogen

| Volume of acid | 21.0 | 21.0 |
| Volume of alkali | 6.35 | 6.80 |
Correction for blank 50 50
Weight of sample 2000 2000
Vol. used by sample 14.15 13.70

1 cc acid = .0012043 grams of N = 1 cc base

I \(\frac{14.15 \times .0012043 \times 100}{2000} = 8.53\%\)

II \(\frac{13.7 \times .0012043 \times 100}{2000} = 8.25\%\)

PRODUCT FORMED FROM ETHYLENE DIBROMIDE AND ALPHA-P-BRON-PHENYL, BETA-PHENYL THIOUREA.

The thiourea was formed by heating phenyl mustard oil and p-brom-aniline in an alcohol solution. The thiourea is of granular form and melts at 165°. Molecular proportions of the thiourea and ethylene dibromide were heated on an oil bath for one hour at 130°. The excess ethylene dibromide was distilled off and the free base came down as a sticky mass but was crystallized from alcohol, giving flakes which melted at 113°.

By the mixed melting points this product proved to be 2-phenyl-imino, 3-phenyl thiazolidine. The yield of this product was forty per cent of the theoretical.

\[
\begin{align*}
\text{p-BrC}_6\text{H}_4\text{NH} \quad \text{CH}_2\text{Br} & \quad \text{p-BrC}_6\text{H}_4\text{N-OH}_2 \\
\text{C}_6\text{H}_5\text{N} \quad \text{CH}_2\text{Br} & \quad \text{C}_6\text{H}_5\text{N-SCH}_2
\end{align*}
\]
SYNTHESIS OF 2-P-BROM PHENYL-IMINO, 3-PHENYL
-THIAZOLIDINE.

Alpha-phenyl, alpha-ethanol, beta para-brom-phenyl thiourea was warmed on the water bath with concentrated hydrochloric acid. The solution is then filtered and the free base precipitated by making the solution alkaline with ammonia. It was obtained in a purer form by again dissolving in acid and precipitating with ammonia, however it still came down as a gummy precipitate but was obtained in the crystalline form by recrystallizing from alcohol. The crystals were of flakelike form and melted at 112°. The yield was about seventy per cent.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{N}\cdots \text{CH}_2 \hspace{1cm} \text{p-BrC}_6\text{H}_4\text{C} \hspace{.5cm} \text{CH}_2 \hspace{.5cm} \text{OH} \hspace{1cm} \text{S} \hspace{1cm} \text{CH}_2 \\
\text{C}_6\text{H}_5\text{N} \cdots \text{CH}_2 \hspace{1cm} \text{p-BrC}_6\text{H}_4\text{C} \hspace{.5cm} \text{CH}_2 \hspace{.5cm} \text{OH} \hspace{1cm} \text{S} \hspace{1cm} \text{CH}_2
\end{align*}
\]

Analysis: Calculated for C_{15}H_{13}N_{2}BrS

\[N = 8.41\%\]

\[\text{Found } N = 8.62 , 8.54\%\]

Analysis Nitrogen

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of acid</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Volume of alkali</td>
<td>5.05</td>
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</tr>
<tr>
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<td>.65</td>
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</tbody>
</table>
Vol. acid used by sample

14.30
14.15

1 cc acid = .0012043 grams of nitrogen = 1 cc base

I 14.3 \times .0012043 \times 100 = 8.62\%
\frac{2000}

II 14.15 \times .0012043 \times 100 = 8.54\%
\frac{2000}

SYNTHESIS OF 2-P-TOLYL IMINO, 3-P-BROM-PHENYL THIAZOLIDINE.

Molecular proportions of p-brom phenyl amino ethanol and p-tolyl mustard oil were put into an alcohol solutions and heated on the water bath for half an hour. It was then found that the thiourea could not be crystallized out of the ordinary solvents.

\[
p-\text{BrC}_6\text{H}_4\text{NHCH}_2\text{CH}_2\text{PH} + p-\text{C}_7\text{H}_7\text{NCS} = p-\text{BrC}_6\text{H}_4\text{NCH}_2\text{CH}_2\text{OH}
\]
\[
p-\text{C}_7\text{H}_7\text{NH} \quad \text{(oil)}
\]

The thiourea as an oil was converted into the thiazolidine by heating with concentrated hydrochloric acid for a short time. The ring closes and forms the hydrochloride of the thiazolidine which is soluble. The free base was then precipitated by the addition of ammonia which throws down the free base as a sticky mass. The free base was then crystallized from alcohol from which it forms white, lustrous leaves which melt at 145°. The yield of the product was eighty per cent of the theoretical.

\[
p-\text{BrC}_6\text{H}_4\text{N} - \text{CH}_2
\]
\[
p-\text{C}_7\text{H}_7\text{N}=\text{C} + \text{CH}_2\text{OH}
\]

\[
p-\text{BrC}_6\text{H}_4\text{N} - \text{CH}_2
\]
\[
p-\text{C}_7\text{H}_7\text{N}=\text{C} + \text{CH}_2\text{OH}
\]

Analysis: Calculated for C_{16}H_{15}N_2SBr

Nitrogen = 8.07\% \quad \text{Found N} = 8.23\% , 8.20\%
Analysis Nitrogen

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
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<tbody>
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<td>Volume of acid</td>
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</tr>
<tr>
<td>Volume of alkali</td>
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<td>Correction for blank</td>
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<tr>
<td>Vol. acid used by sample</td>
<td>13.75</td>
<td>13.60</td>
</tr>
</tbody>
</table>

1 cc acid = .0012043 grams of N = 1 cc base

II

\[
\text{II} \quad 13.60 \times \frac{.0012043 \times 100}{2000} = 8.20\%
\]

PRODUCT FORMED FROM ETHYLENE DIBROMIDE AND ALPHA-PARA-BROM-PHENYL, BETA-PARA-TOLYL THIOUREA.

Molecular proportions of alpha-para-brom-phenyl, beta-para-tolyl thiourea and ethylene dibromide were heated on an oil bath for one hour at the temperature of 130°. The excess ethylene dibromide was then removed by steam distillation, the solution filtered and the free base precipitated by the addition of ammonia. The free base came down as a sticky mass but was crystallized from alcohol giving small plates which melted at 145°. The yield of the product was sixty per cent of the theoretical.

\[
p\text{-BrC}_6\text{H}_4\text{NH}_2 \text{CSH} + \text{CH}_2\text{Br} = p\text{-BrC}_6\text{H}_4\text{N} \rightleftharpoons \text{CH}_2
\]

\[
p\text{-C}_7\text{H}_7\text{N} + \text{CH}_2\text{Br} = p\text{-C}_7\text{H}_7\text{N} \rightleftharpoons \text{S} \left\langle \text{CH}_2
\]
SYNTHESIS OF 2-P-BROM-PHENYL-ININO, 3-P-TOLYL-
THIAZOLIDINE.

Alpha-p-tolyl, alpha-ethanol, beta-p-brom-phenyl, thiourea
was heated with hydrochloric acid for one-half hour on the wa-
ter bath, the solution was then filtered to remove any unchanged
thiourea and ammonia added to precipitate the free base. The
precipitate came down as a gummy oil, but was crystallized from
alcohol in the form of long needles. The product melted at
97°, and the yield was eighty per cent.

\[
\begin{align*}
\text{p-C}_7\text{H}_7\text{N}-\text{CH}_2 & \quad \text{p-C}_7\text{H}_7\text{N}\text{CH}_2 \\
\text{p-BrC}_6\text{H}_4\text{N}-\text{CH}_2\text{OH} & \quad \text{p-BrC}_6\text{H}_4\text{N}-\text{CH}_2 \\
\end{align*}
\]

Analysis calculated for C\(_{16}\)H\(_{15}\)NBrS
Nitrogen = 8.07%  Found N = 8.11%, 7.96%

Analysis Nitrogen

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of acid</td>
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</tr>
<tr>
<td>Volume of alkali</td>
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<tr>
<td>Weight of sample</td>
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</tr>
<tr>
<td>Vol. acid used by sample</td>
<td>13.45</td>
<td>13.2</td>
</tr>
</tbody>
</table>

1 cc acid = .0012043 grams of N = 1 cc base

\[
\begin{align*}
\text{I: } 13.45 \times \frac{.0012043 \times 100}{2000} & = 8.11% \\
\text{II: } 13.20 \times \frac{.0012043 \times 100}{2000} & = 7.96%
\end{align*}
\]
SYNTHESIS OF 2-ALPHA-NAPHTHYL-IMINO, 3-P-BROM-PHENYLTHIAZOLIDINE.

Alpha-p-brom-phenyl, alpha-ethanol, beta alpha naphthyl thiourea was heated with hydrochloric acid for one-half hour on the water bath. This converts the thiourea to the hydrochloride of the thiazolidine. The solution is filtered and the free base precipitated by the addition of ammonia. The free base is precipitated as very irregular crystals, some of the clumping together, all finally settling to the bottom of the beaker, it is then crystallized from alcohol forming small needles which melt at 127°C. The yield of this product was forty percent of the theoretical.

\[
\begin{align*}
\text{p-BrC}_6\text{H}_4\text{N} & \quad \text{CH}_2 \\
\text{C}_{10}\text{H}_7\text{N} & \quad \text{CH}_3\text{OH}
\end{align*}
\]

Analysis: Calculated for \( C_{19}H_{15}N_2BrS \)

Nitrogen = 7.28%  
Found \( N = 7.04\% \), 7.11%

Analysis Nitrogen

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of acid</td>
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<tr>
<td>Volume of alkali</td>
<td>7.65</td>
<td>7.55</td>
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<tr>
<td>Correction for blank</td>
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<td>.7</td>
</tr>
<tr>
<td>Vol. of acid used by sample</td>
<td>11.65</td>
<td>11.76</td>
</tr>
</tbody>
</table>

1 cc acid = .0012043 grams of nitrogen = 1 cc base

I \[ \frac{11.65 \times .0012043 \times 100}{.2000} = 7.04\% \]

II \[ \frac{11.75 \times .0012043 \times 100}{.2000} = 7.11\% \]
SYNTHESIS OF 2-P-BROM-PHENYL-IMINO, 3-ALPHA NAPHTHYL THIAZOLIDINE.

Molecular proportions of alpha naphthyl amino ethanol and p-brom-phenyl mustard oil were put in an alcohol solution and heated for a half-hour on the water bath. It was then tried to crystallize the thiourea thus formed; alcohol and benzene were used but the thiourea could not be crystallized as it came down as an oil. It was then converted into the thiazolidine by boiling the thiourea with concentrated hydrochloric acid for an hour. The boiling converted it into the hydrochloride of the thiazolidine. The free base was precipitated by the addition of ammonia, throwing down the free base as a gummy mass. It was then dissolved in alcohol from which came out fine needlelike crystals of the thiazolidine which melted at 165°. The yield of this product was fifty per cent.

\[
C_{10}H_7NHCH_2CH_2OH + p-BrC_6H_4NCS = C_{10}H_7NHCH_2CH_2OH
\]

\[
p-BrC_6H_4NH \quad \text{(oil, not)}
\]

Analysis: Calculated for \( C_{19}H_{15}N_2BrS \)

Nitrogen = 7.28% Found N = 7.06%, 7.21%
Analysis Nitrogen

<table>
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<tr>
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<th>I</th>
<th>II</th>
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<tbody>
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</tr>
<tr>
<td>Vol. acid used by sample</td>
<td>11.7</td>
<td>11.95</td>
</tr>
</tbody>
</table>

\[
1 \text{ cc acid} = 0.0012043 \text{ grams of } N = 1 \text{ cc base}
\]

\[
\text{I: } \frac{11.7 \times 0.0012043 \times 100}{2000} = 7.06\%
\]

\[
\text{II: } \frac{11.95 \times 0.0012043 \times 100}{2000} = 7.21\%
\]

**PRODUCT FORMED FROM ETHYLENE DIBROMIDE AND ALPHA-PARA-BROM-PHENYL BETA, ALPHA NAPHTHYL, THIOUREA.**

Molecular proportions of the above thiourea and ethylene dibromide were heated under a reflux for one hour at 130°. The excess ethylene dibromide was then removed by steam distilling the solution. The solution was then filtered to remove any unchanged thiourea and the free base precipitated by the addition of ammonia. The free base comes down as a sticky mass but can be crystallized from alcohol in the form of needles which melt at 165°. By making mixed melting points this product was proven to be 2-para-brom-phenyl-imino, 3-alpha-naphthyl, thiazolidine. The yield was thirty per cent of the theoretical.

\[
\begin{align*}
\text{C}_7\text{H}_7\text{NH} \quad \text{CH Br} & \quad \text{C}_{10}\text{H}_7\text{N} \quad \text{CH}_2 \\
\text{p-BrC}_6\text{H}_4\text{H} & \quad \text{CH}_2\text{Br} \quad \text{p-C}_{6}\text{H}_4\text{N} = \text{O} \quad \text{S} \quad \text{CH}_2
\end{align*}
\]
SYNTHESIS OF 2-P-BROM-PHENYL IMINO, 3-P-BROM-PHENYL THIAZOLIDINE.

Di-Para-brom phenyl thiourea was prepared by allowing molecular proportions of para-bromanilin and p-brom-phenyl mustard oil to react in an alcohol solution. The thiourea crystallizes in the form of small, white needles which melt at 178°.

The thiourea thus formed was heated with ethylene dibromide under a reflux. A temperature of 130° was maintained for one hour, then putting the solution into a flask and steam distilling to remove the excess ethylene dibromide. The solution then contained the hydrobromide salt of the thiazolidine which was soluble in water, the solution was then filtered and the free base precipitated by the addition of ammonia. The free base came down as a sticky mass but was crystallized from alcohol in small granules which melted at 128°. The yield of the product was sixty per cent of the theoretical and it was found that it was very soluble in hot alcohol or benzene.

\[ \text{p-BrC}_6\text{H}_4\text{NH}_2 + \text{p-BrC}_6\text{H}_4\text{NOS} = \text{p-BrC}_6\text{H}_4\text{NH} \]

\[ \text{p-BrC}_6\text{H}_4\text{NH} \quad \text{Br} \quad \text{CH}_2 \quad \text{p-BrC}_6\text{H}_4\text{N} \quad \text{CH}_2 \]

Analysis: Calculated for \( \text{C}_{15} \text{H}_{13} \text{N} \text{Br}_2 \text{S} \)
Nitrogen = 6.87%  Found N = 6.78%  6.68%

Analysis Nitrogen

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
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</thead>
<tbody>
<tr>
<td>Volume of acid</td>
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<td>20.0</td>
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<tr>
<td>Volume of alkali</td>
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<td>Weight of sample</td>
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<tr>
<td>Vol. acid used by sample</td>
<td>11.25</td>
<td>11.05</td>
</tr>
</tbody>
</table>

1 cc acid .0012043 grams of N = 1 cc of base

I  \( \frac{11.25 \times 0.0012043 \times 100}{2000} = 6.78\% \)

II  \( \frac{11.05 \times 0.0012043 \times 100}{2000} = 6.68\% \)

SYNTHESIS OF 2-PHENYL-IMINO, 3-P-BROM-PHENYL
OXAZOLIDINE.

Alpha-p-brom-phenyl, alpha-ethanol, beta-phenyl thiourea was heated in a benzene solution with the addition of molecular quantity of yellow mercuric oxide. After heating for one hour the benzene solution was filtered several times and the benzene allowed to evaporate off. The crystals thus formed were recrystallized from alcohol where they formed white flakes. It was found that it was very difficult to remove all of the mercuric sulphide formed by the reaction but after the filtering mentioned above, using a tight filter paper, the big share of the sulphide was removed. The yield was fifty per cent of the theoretical and melted at 149°.
\[
\begin{align*}
\text{p-Br-C}_6\text{H}_4\text{N} \equiv \text{CH}_2 &= \text{p-Br-C}_6\text{H}_4\text{N} \equiv \text{CH}_2 \\
\text{C}_6\text{H}_5 = \text{C} \equiv \text{CH}_2\text{OH} \equiv \text{H}_2\text{O} &= \text{C}_6\text{H}_5 = \text{C} \equiv \text{O} \equiv \text{CH}_2
\end{align*}
\]

Analysis: Calculated for \( \text{C}_{15}\text{H}_{13}\text{N}_2\text{Br}_0 \)

Nitrogen = 8.83% \quad Found N = 8.94%, 8.79%

Analysis Nitrogen

<table>
<thead>
<tr>
<th></th>
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<th>II</th>
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<tbody>
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<td>Volume of alkali</td>
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<tr>
<td>Vol. of acid used by sample</td>
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<td>14.4</td>
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</table>

\[
\text{I atm acid} \cdot 0.012043 \text{ grams of } N = 1 \text{ cc of base}
\]

\[
\begin{align*}
\text{I} & \quad 14.85 \times 0.012043 \times 100 = 8.94\% \\
\text{II} & \quad 14.4 \times 0.012043 \times 100 = 8.79\%
\end{align*}
\]

**SYNTHESIS OF 2-P-BROM-PHENYL, IMINO, 3-PHENYL, OXAZOLIDINE.**

Alpha-phenyl, alpha imino, beta-p-brom-phenyl thiourea was heated in a benzene solution on a water bath, with the addition of molecular quantity of yellow mercuric oxide. After heating for one hour the solution is removed and filtered several times through a tight filter, this is supposed to filter off all of the mercuric sulphide but sometimes some
of the sulphide comes through the best of filters. After the solution was filtered, the benzene was evaporated off and crystals of the oxazolidine were left, but a better product was obtained by recrystallizing from alcohol. This product is very soluble in hot or cold benzene, soluble in hot alcohol but very insoluble in cold alcohol. The yield was thirty-five per cent of theoretical. It formed in small needles, and melted at 138°.

\[
\text{C}_6\text{H}_5\text{N} \text{-CH}_2 \quad \text{C}_6\text{H}_5\text{N} \text{-CH}_2
\]

\[
p\text{-BrC}_6\text{H}_4\text{=}\text{C} \text{-CH}_2\text{OH} \quad \text{HgO} \quad p\text{-BrC}_6\text{H}_4\text{=}\text{C} \text{CH}_2\text{OH}
\]

Analysis: Calculated for C\text{H}_1\text{H}_2\text{OBr}

Nitrogen = 8.83%  Found = 8.97%, 8.74%

Analysis Nitrogen

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of acid</td>
<td>19.9</td>
<td>20.0</td>
</tr>
<tr>
<td>Volume of alkali</td>
<td>4.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Correction for blank</td>
<td>.5</td>
<td>.5</td>
</tr>
<tr>
<td>Volume of acid used by sample</td>
<td>14.9</td>
<td>14.5</td>
</tr>
</tbody>
</table>

1 cc acid = .0012043 grams of N = 1 cc base

\[
\text{I} \quad \frac{14.9 \times .0012043 \times 100}{.2000} = 8.97\%
\]

\[
\text{II} \quad \frac{14.5 \times .0012043 \times 100}{.2000} = 8.74\%
\]
SYNTHESIS OF 2-P-BROM-PHENYL-IMINO, 3-P-TOLYL, OXAZOLIDINE

To a benzene solution of alpha-p-tolyl, alpha-ethanol beta-p-brom-phenyl thiourea was added a molecular quantity of yellow mercuric oxide. The solution was then heated under a reflux on a water bath for one hour, after filtering several times the benzene was allowed to evaporate and the crystals thus formed were recrystallized from alcohol. They formed very slowly and belonged to the monoclinic system. The yield was seventy-five per cent of the theoretical. The product melted at 105°.

\[
\begin{align*}
\text{p-C}_7\text{H}_7\text{N} & \quad \text{CH}_2 \\
p-\text{BrC}_6\text{H}_4\text{N} & \quad \text{SH} \quad \text{C}_6\text{H}_4\text{N} \quad \text{O} \quad \text{CH}_2 \\
\end{align*}
\]

Analysis: Calculated for C_{16}H_{15}N_2OBr
Nitrogen = 8.72%  Found N = 8.57%, 8.50%

Analysis Nitrogen

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. of acid</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Vol. of alkali</td>
<td>3.70</td>
<td>3.60</td>
</tr>
<tr>
<td>Correction for blank</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Weight of sample</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>Vol. acid used by sample</td>
<td>14.20</td>
<td>14.10</td>
</tr>
</tbody>
</table>

\[
\text{1 cc acid} = .0012043 \text{ grams of } N = 1 \text{ cc base}
\]

\[
\begin{align*}
\text{I} & \quad 14.2 \times .0012043 \times 100 = 8.57\% \\
& \quad \frac{2000}{14.20}
\end{align*}
\]

\[
\begin{align*}
\text{II} & \quad 14.1 \times .0012043 \times 100 = 8.50\% \\
& \quad \frac{2000}{14.10}
\end{align*}
\]
### SUMMARY

R and R' as in general formula

\[
\begin{array}{c}
\text{R N} \\
\text{-- CH}_2 \\
\text{R' N = C} \\
\text{SH} \\
\end{array}
\]

<table>
<thead>
<tr>
<th>R  2</th>
<th>Ethanol Thioureas</th>
<th>Thiazolidines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M.P.</td>
<td>Calc.</td>
</tr>
<tr>
<td>p-BrC₆H₄</td>
<td>C₆H₅</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>C₆H₅</td>
<td>p-BrC₆H₄</td>
</tr>
<tr>
<td>p-BrC₆H₄</td>
<td>p-C₇H₇</td>
<td>oil</td>
</tr>
<tr>
<td>p-C₇H₇</td>
<td>p-BrC₆H₄</td>
<td>137</td>
</tr>
<tr>
<td>p-BrC₆H₄</td>
<td>αC₁₀H₇</td>
<td>60</td>
</tr>
<tr>
<td>αC₁₀H₇</td>
<td>p-BrC₆H₄</td>
<td>oil</td>
</tr>
<tr>
<td>p-BrC₆H₄</td>
<td>C₆H₅</td>
<td>96°</td>
</tr>
<tr>
<td>p-BrC₆H₄</td>
<td>p-BrC₆H₄</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>M.P.</th>
<th>Calc.</th>
<th>Found</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-BrC₆H₄</td>
<td>C₆H₅</td>
<td>149</td>
<td>8.83°</td>
<td>8.87</td>
<td>Oxazolidine</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>p-BrC₆H₄</td>
<td>138</td>
<td>8.83</td>
<td>8.85</td>
<td>&quot;</td>
</tr>
<tr>
<td>p-C₇H₇</td>
<td>p-BrC₆H₄</td>
<td>105</td>
<td>8.72</td>
<td>8.54</td>
<td>&quot;</td>
</tr>
<tr>
<td>p-BrC₆H₄</td>
<td>αC₁₀H₇</td>
<td>188</td>
<td>7.63</td>
<td>7.63</td>
<td>Thiourea</td>
</tr>
<tr>
<td>p-BrC₆H₄</td>
<td>p-C₇H₇</td>
<td>184</td>
<td>8.73</td>
<td>8.66</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

With ethylene dibromide the thioureas react thus:

\[
\begin{align*}
p-\text{BrC}_6\text{H}_4\text{NH}_2 & \quad p-\text{BrC}_6\text{H}_4\text{NH}_2 \\
\text{C}_6\text{H}_5\text{N} & \quad p-\text{C}_7\text{H}_7 \\
\text{CSH} & \quad p-\text{BrC}_6\text{H}_4\text{CSH} \\
\text{CSH} & \quad p-\text{C}_7\text{H}_7 \\
\text{CS} & \quad p-\text{BrC}_6\text{H}_4\text{CS} \\
\end{align*}
\]
In concluding this paper, the writer wishes to express his appreciation to Dr. F. B. Dains and Dr. R. Q. Brewster for the direction of this work and for their many helpful suggestions.

Chemical Laboratories
University of Kansas
July, 1923
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J.A.C.S. 42, 1725
B. 43, 370

Abbreviated Title

B.  
J.A.C.S.  
J. Pr. Chem.  
J. Bio. Chem.

Journal

Berichte der Deutschen Chemischen Gesellschaft
Journal of the American Chemical Society
Journal fur praktische Chemie
Journal of Biological Chemistry