ALLYL ANILINE

THE SYNTHESIS OF CERTAIN THIAZOLES

By

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1920.

Approved: [Signature]
Department of Chemistry.
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ALLYL ANILINE
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PART ONE.

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PART I.

INTRODUCTORY

It is a well known fact, discovered by Hoffman,¹ that secondary or tertiary alkyl aryl amines, when heated under pressure, either as the free base or as the hydrochloride, to about 300°C., undergo a molecular rearrangement. The products of such reactions are primary amines, the alkyl groups entering the benzene ring in the position para to the amino group, if unoccupied, otherwise in the ortho position. Thus methylaniline, heated to 300°C., rearranges to para-toluidine:

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 \\
\text{N} & \quad \text{H} \\
\text{H} & \quad \text{CH}_3 \\
\end{align*}
\]

Dimethylaniline or its hydrochloride, undergo the reaction with the formation of asymmetrical xylidine, the second methyl group entering the ring in the position ortho to the amino group. According to Hoffman, the re-

¹ Hoffman, Ber.² 720.
2.

action takes place quantitatively, there being few by-products.

Bamberger, in 1886, tried out the possibility of a similar reaction taking place in the case of certain alkyl phenyl ethers, such as anisole, phenetole, etc. He heated the ethers at various temperatures, the highest used in any of his experiments being 380°-400°. He found the sole products to be phenol and unsaturated hydrocarbons. There was no trace of any product in which the alkyl group had substituted itself for one of the hydrogens of the benzene nucleus. Thus anisole does not give a cresol but phenol and ethylene according to the reaction:

\[
\begin{align*}
2 \text{OCH}_3 & = 2 \text{HOH} + \text{C}_2\text{H}_4 \\
\end{align*}
\]

Phenetole also gives phenol and ethylene, the reactions in this case being monomolecular. Propyl phenyl ether gives phenol and propylene, etc.

It was therefore somewhat surprising when Claisen, in 1913, made the discovery that allyl ethers of phenols on simple boiling at atmospheric pressure, under-

2. Bamberger, Ber. 19, 1820.
3. went a rearrangement analogous with the Hoffman rearrangement of the nitrogen compounds, with the exception that the allyl group enters the ring in the position ortho to the hydroxyl group, even when the para position is unoccupied. Neither in his first paper nor in his second more detailed paper in which he worked with a large number of compounds and established the reaction on a firm footing, did he obtain the simple o-allyl phenol from allyl phenyl ether, but this has been done in this country by Jacobs and more recently by Roger Adams and R. E. Rindfusz, who obtained the compound in a purer state.

This fact is all the more interesting because compounds which contain the allyl group as a substituent in the benzene ring are rather rare and but few had, previously to Claisen's discovery, been prepared. Chojnacki, by distilling allyl iodide and benzene with

2. Claisen and Eisleb, Ann. 401, 73 (1913).
5. Chojnacki, Jahresbericht. 1873, 359.
zinc, thought he had obtained allyl benzene, but his compound later was found to be mostly the isomeric propenyl benzene. However, Tiffeneau later succeeded in preparing this compound by the action of magnesium on an ethereal solution of phenyl and allyl iodides. Some naturally-occurring products, such as estragol (p-allyl anisole) and eugenol (2-methoxy 4 allyl phenol) are known in which the allyl group is directly substituted in the benzene ring. Von Braun and Steindorff\(^1\) by the distillation of o-\(\text{CH}_3\)-propylbenzanilide under reduced pressure, were able to obtain a small yield of o-allyl benzanilide, from which, by hydrolysis with alcoholic sodium hydroxide, they obtained a small quantity of a base which they assumed to be o-allyl anilin, but their identification was not absolute on account of the small quantity available. They were able to reconvert it by means of benzoyl chloride, into the o-allyl benzanilide, which melts at 123°-124°.

2. Von Braun and Steindorff, Ber. 37, 4723-30 (1904)
From the above facts it was thought that an investigation into the behavior of allylaniline on heating under various conditions might be productive or interesting results. The possibilities in mind were:

1. Would the allyl group enter the ring?
   (a). If so, would the point of entrance be the position para to the amino group, as in the case of methylaniline?
   (b). Or would it enter, analogously to the allyl phenyl ether rearrangement, ortho to the amino group?

2. If the allyl group should fail to enter the ring, would there be a possibility of the interaction of two mols with the formation of one mol of anilin and one of diallylanilin?

3. Or would the allyl group, which is known to be loosely attached to nitrogen, simply split

\[ \text{H} \text{C}_3\text{H}_5 \text{N} = \text{H} \text{H} \text{N} + \text{C}_3\text{H}_5 \text{C}_3\text{H}_5 \]
(3-continued).

off, giving anilin and unsaturated hydrocarbons, in a manner somewhat analogous to the behavior of alkyl phenyl ethers on heating, as found by Bamberger.

Allylaniline was first made by Schiff by the direct action of allyl iodide on anilin. He describes the compound as a yellow oil, soluble in dilute acids, of specific gravity 0.985 and whose boiling point is 208-90 C. It was later prepared by Zander who gives its boiling point as "about 220°". It was prepared in much purer form in 1903 by E. Wedekind, by the action of allyl iodide on the sodium salt of formanilide, and subsequent hydrolysis with hydrochloric acid. He then purified the base from anilin by conversion of the crude secondary amine to the nitrosamine and subsequent reduction. As this is the method of preparation used in this investigation it will be described in detail in the experimental part of this paper. Wedekind

1. Schiff, A. Sp. 3, 364.
3. Wedekind, Ber. 364, 3791(1903).
gives the boiling point as being $217^\circ-19^\circ$ at 736 mm. pressure. He does not describe the preparation in detail but states that the synthesis is long and the yield is not good.
PART ONE—--- EXPERIMENTAL 8.

THE SODIUM SALT OF FORMANILIDE.

100 grams of redistilled aniline were refluxed with 100 grams of 50% formic acid for four hours. The mixture was then distilled and the portion boiling above 200° was collected as crude formanilide. This portion weighed 131 grams. It is a heavy yellow oil, which turns darker on standing, and shows no tendency to crystallize, although a portion dissolved in hot dilute alcohol deposits the white crystalline modification on cooling. M.P. 45°-60°. The oil was dissolved in alcohol and slowly added with constant stirring to 50 grams of sodium hydroxide dissolved in alcohol. A finely divided, white precipitate appeared which on standing over night settled to a thick cream-colored paste, which was filtered at the pump and washed with alcohol, in which it was almost insoluble, although it is very soluble in water. It was dried in the oven at 85° and powdered. During the drying the odor of phenyl isocyanide was very noticeable. Yield from the 131 grams of formanilide was 85 grams. In another experimen-
9.

ment 500 grams of aniline yielded 355 grams of the sodium salt.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{H}_2\text{CHO} \\
\text{+HCOOH=} & \quad \text{H}_2\text{O} \\
\text{H}_2\text{CHO} & \quad \text{HCOH} \\
\text{N} & \quad \text{N} \\
\text{= NaOH =} & \quad \text{Na}_2\text{SO}_4 \\
\text{H}_2\text{N} & \quad \text{H}_2\text{O}
\end{align*}
\]

ANALYSIS OF SODIUM FORMANILID.

The sodium salt of formanilid was analyzed by weighing a sample into a crucible, dissolving in water, adding sulphuric acid and evaporating to dryness, and weighing up the residue as sodium sulphate.

<table>
<thead>
<tr>
<th>Weight</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight crucible</td>
<td>6.0396</td>
</tr>
<tr>
<td>Weight crucible and sample.</td>
<td>6.7503</td>
</tr>
<tr>
<td>Weight crucible and Na(_2)SO(_4)</td>
<td>6.3625</td>
</tr>
<tr>
<td>Weight sample</td>
<td>.7107</td>
</tr>
<tr>
<td>Weight Na(_2)SO(_4)</td>
<td>.3229</td>
</tr>
</tbody>
</table>

\[
\frac{.3229 \times 46 \times 100}{.7107 \times 142} = 15.85\%\text{Na}
\]

Calculated for C\(_7\)H\(_6\)ON Na; Na 16.05\%
SODIUM FORMANILID AND ALLYL IODIDE.

30 grams of sodium formanilid were refluxed with 35 grams of allyl iodide for approximately eight hours. The completion of the reaction was shown by the change in character of the precipitate from the pasty mass of sodium formanilid, which sticks to the flask, to the more crystalline precipitate of sodium iodide. The whole mixture was then boiled with 50 c.c. water and 50 c.c. conc. HCl until a clear solution was obtained. This was transferred to a one-liter balloon flask, made strongly alkaline with NaOH, and liberated base distilled with steam. The oil as it comes over was nearly colorless and was lighter than water. Yield 20.7 grams. Boiling point was $200^\circ - 225^\circ$. This was the second repetition of the experiment. On the first trial the yield from 10 grams of the sodium salt was 5.4 grams, boiling point, $200^\circ - 220^\circ$. In a third synthesis 355 grams of the sodium salt yielded 190 grams boiling from $200^\circ - 245^\circ$, and 25 grams of a substance which was the last to distill with steam and was found to be formanilid, showing that the action of the allyl halide (in this case allyl bromide was used) was
incomplete, as well as the hydrolysis with dilute acid. The allylaniline obtained in this way was never found to be free from anilin, due probably to the fact that the reaction

\[
\begin{align*}
\text{HCONa} & \quad \text{HCOC}_3\text{H}_5 \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{C}_4\text{H}_5\text{I} = \quad \text{NaI} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]

does not go to completion.

\[
\begin{align*}
\text{HCOC}_3\text{H}_5 & \quad \text{C}_9\text{H}_5\text{CHO} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{C}_3\text{H}_5\text{CHO} = \quad \text{C}_3\text{H}_5\text{H} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]

The allylaniline as obtained in this way was used without further purification in the synthesis of thiazoles (Part II.).
Although the allylaniline as obtained above showed by its large range of boiling point and by the fact that it gave the bleaching powder and carbylamine tests for the presence of a primary amine, that it was impure, yet from the fact that it gave a pure trisubstituted thiourea with phenyl mustard oil, showing that aniline was not present in very great concentration, it was hoped that it was pure enough so that after heating at various temperatures, any product of a molecular rearrangement might be identified by means of its derivatives, and the change might be shown by a change in boiling point.

I. Boiling at atmospheric pressure.

25 c.c. of the allylanilin (B.P. 200°-220°) were boiled for two days. At the end of that time the boiling point was 190°-225°. A few drops of the original substance and a few drops of the substance after boiling were dissolved in dilute HCl and treated after cooling in an ice bath, with NaNO₂ solution, then coupled
with α-naphthol in alkaline solution. The original substance gave a light yellow precipitate, while that which had been boiled gave a deep reddish-brown, indicating that primary amines were present in greater concentration after boiling.

II. Heating at Higher Temperatures.

(a). 5 c.c. of the allylanilin were heated in a sealed tube at 250° for eight hours. On opening the tube there was so much gas dissolved in the liquid that the latter foamed out of the tube. The liquid exhibited a reddish-green fluorescence. It was treated with phenyl mustard oil and dissolved in alcohol, but no crystals could be obtained. However, on evaporating off the alcohol and extracting the tarry residue with gasoline, a small quantity of a light yellow substance was obtained, which showed itself by its melting point to be very impure. M.P. 119-130.

(b). 15 c.c. of the allylanilin were heated in a sealed tube for eight hours. Arrangements were made to collect the gas formed by the reaction. A
portion of this was shaken up in a Schiff nitrometer with bromine water to determine whether or not it was unsaturated. Absorption took place with the formation of an oily substance which floated on the surface of the water in the eudiometer.

Volume of gas formed .....270 c.c. (approx.)
Volume of gas taken for analysis ........... 20 c.c.
Volume of air originally in the tube ........... 130 c.c. (approx.)
Volume of gas remaining unabsorbed ........... 9.8 c.c.

Calculated amount of the original air which would be present in the 20 c.c. taken for analysis:

\[
\frac{20 \times 130}{270} = 9.63 \text{ c.c.}
\]

This would show, roughly, that all of the gas formed by the reaction was unsaturated.

The remaining liquid was fractionated at ordinary atmospheric pressure, and derivatives were made of the various fractions with acetyl chloride, benzoyl chloride, and phenyl mustard oil.

B.P. of the original substance, before heating, 200-240°.

Weight of liquid recovered from the tube 14.49 gms.
Volume 14.40 c.c. Density 1.06

The liquid was fractionated into small tared
graduates:

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. of boiling</td>
<td>170°-205°</td>
<td>205-240°</td>
<td>240°-300°</td>
<td>300°-330°</td>
</tr>
<tr>
<td>2 wt. graduate</td>
<td>28.63</td>
<td>29.93</td>
<td>25.22</td>
<td>29.65</td>
</tr>
<tr>
<td>1 wt. graduate</td>
<td>24.21</td>
<td>27.30</td>
<td>22.00</td>
<td>26.64</td>
</tr>
<tr>
<td>Wt. fraction</td>
<td>4.42</td>
<td>1.63</td>
<td>3.22</td>
<td>3.01</td>
</tr>
<tr>
<td>Vol. fraction</td>
<td>4.36</td>
<td>1.77</td>
<td>3.13</td>
<td>2.68</td>
</tr>
<tr>
<td>Density fraction</td>
<td>1.01</td>
<td>0.92</td>
<td>1.03</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Fraction I.

(a) Plus phenyl mustard oil and recrystallized from alcohol, melted at 149°-150° (Thiocarbanilide 154°).

(b) Plus benzoyl chloride and recrystallized from alcohol, melted at 154°-155° (Benzanilide 160°-1°).

(c) Plus acetyl chloride and recrystallized from water, melted at 113°.0; mixed with acetanilide, at 113°.5

Fraction II.

(a) Plus phenyl mustard oil and recrystallized from alcohol, softened at 90°, completely melted at about 141°-2°. By fractional crystallization from alcohol, the less soluble fraction was found to be thiocarbanilide, the more soluble, allyl diphenyl thiourea.

(b) Plus benzoyl chloride and recrystallized
twice from alcohol, melted at 163°. Note: In the work with pure allyl anilin, page 31, it was found impossible to isolate a solid benzoyl derivative.

Fractions III and IV.

These fractions were only partially soluble in dilute acids, and neither a solid acetyl or benzoyl derivative nor a thiourea with phenyl mustard oil could be isolated from them.

In order to help determine the nature of fraction IV, its molar weight was determined by determining the freezing point of its solution in benzene. A small graduated pipette was used which, in giving the volume of sample used in the two check experiments, gave also the weight after the density had been determined.

**MOLAR WEIGHT OF THE FOURTH FRACTION.**

I. Density determination.

Vol. fraction in pipette.............0.775

Wt. pipette and fraction...........12.2429

Wt. pipette........................11.4607

Weight fraction.................... .7822
Density fraction .782/.775

2. Weight benzene used. (15 c.c.)

Wt. freezing point tube and benzene........52.48
Wt. freezing point tube........39.25
Weight benzene................13.23

3. Freezing point determinations.

Vol. of fraction added. Reading of Beckmann.
(a) (b) (c)
Pure benzene.........2.91 2.908 2.91
I. Added 0.187 c.c........2.49 2.49 2.49
   Depression............0.42 0.42 0.42
II. Added 0.568 c.c......1.67 1.67 1.67
   Depression............1.24 1.24 1.24

I. Molar weight \( \frac{5000 \times 0.187 \times 0.782}{0.42 \times 13.23 \times 0.775} \) = 171
II. Molar weight \( \frac{5000 \times 0.568 \times 0.782}{1.24 \times 13.23 \times 0.775} \) = 174

The fraction was also analyzed for nitrogen by a Kjeldahl determination.

**NITROGEN IN FRACTION IV.**

The benzene solution from the freezing point determination was used as the sample, containing \( \frac{0.568 \times 0.782}{0.775} = 0.573 \text{ gms} \) of the fraction.
Volume of HCl used for titrating 24.92 c.c.
Normality HCl .4079

Volume NaOH used in titrating. 18.16 c.c.
Normality NaOH .4350

Nitrogen in fraction:

\[
1.4 \times \frac{(24.92 \times .4079 - 18.16 \times .4350)}{.573} = 5.49\%
\]

CONCLUSION:

Fraction I is almost certainly practically entirely aniline.

Fraction II is a mixture of aniline and allylaniline. From the low percentage of nitrogen, from the high density and molar weight, and from the fact that it is only partially soluble in acid, and gives none of the derivatives an amine would be expected to give, Fraction IV, and also Fraction III, would seem to be polymerization products of the unsaturated hydrocarbons previously shown to have been formed, together with a nitrogenous base which is soluble in acid.

The possibility of the formation of diallylaniline, or even of a product of molecular rearrangement, has not been precluded by this experiment. The change in
boiling point and the isolation of anilin derivatives render it extremely probable that aniline has been formed from allylaniline by the heating at 250°, but from the fact that the allylaniline used was not free from aniline in the first place, this could not be said to have been absolutely proven.

The previous experiments had made it evident that allylaniline would have to be obtained in a purer state before positive results could be obtained as to the products formed on heating. Proceeding on the assumption that allylaniline is stable toward boiling at atmospheric pressure, 190 grams of the crude allylaniline of boiling point 200°-245°, were fractionated:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling Interval</th>
<th>Weight fraction</th>
<th>Wt. and flask.</th>
<th>Wt. flask.</th>
<th>Wt. fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>195-215</td>
<td>44.7</td>
<td>21.8</td>
<td>22.9</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>215-220</td>
<td>48.3</td>
<td>26.1</td>
<td>22.2</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>220-230</td>
<td>64.0</td>
<td>28.2</td>
<td>35.8</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>230-240</td>
<td>76.9</td>
<td>22.3</td>
<td>54.6</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>240-250</td>
<td>48.8</td>
<td>21.5</td>
<td>27.3</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>250-265</td>
<td>49.4</td>
<td>33.6</td>
<td>15.8</td>
<td></td>
</tr>
</tbody>
</table>

Total weight recovered 178.6

The change in boiling point indicates that the
same change takes place even on boiling at atmospheric pressure as occurs on heating at higher temperatures, and this method is therefore not available for purification. Fractions V and VI were not entirely soluble in dilute acid.

Fraction I was redistilled and the portion boiling above 210° was added to fractions II and III and these portions of fractions IV and V which when redistilled boiled below 230°. A portion of this was used in making the hydrochloride (page 33), and the results showed that the base thus obtained was heavily contaminated with aniline.

Recourse was therefore had to the purification of allylaniline by the nitrosamine reaction, as mentioned by Wedekind¹ and described in connection with the purification of methylaniline by Nölting and Byasson².

**PURIFICATION OF ALLYLANILINE.**

As this experiment was repeated three times, a

¹ Loc. cit.
general description of the method will be given, with a summary of yields at the end.

The crude allylaniline, containing, as made by the sodium formanilide method, aniline, allylaniline, formanilide, and possibly diallylaniline, was dissolved in dilute HCl and cooled in an ice-and salt-bath. A saturated solution of sodium nitrite was then added in small quantities, the mixture being well shaken after each addition and kept well cooled. The reaction is complete when a test for free nitrous acid is given with potassium iodide-starch paper. The aniline is thus converted into phenyl diazonium chloride, which remains in solution, together with the para nitroso diallyl aniline from any diallyl aniline that may have been present. The allylaniline was converted into allyl phenyl nitrosamine, which is precipitated as an oil, reddish-yellow at first but later becoming almost black.
The nitrosamine was extracted with ether and was purified by steam distillation, which was the cause of the low yields obtained, as the nitrosamine was not very volatile and the distillation had to be kept up for days. It also appeared to undergo some kind of a decomposition during the process, as while coming over at first as a golden yellow oil, it later came over black and rather viscous, and at the end of the distillation a considerable amount of black tarry material remained in the flask.

The nitrosamine thus obtained was reduced with tin and hydrochloric acid, using an excess of each. After addition of all the acid, the solution was heated on a water bath for several hours to complete the reaction. On cooling, a heavy black oil separated out, which was evidently the double salt of tin and allylaniline. A large excess of sodium hydroxide was added
to dissolve up stannic hydroxide, and the liberated allyl anilin was distilled with steam.

\[ \text{C}_3\text{H}_5\text{NO} + 3\text{H}_2 \rightarrow \text{C}_3\text{H}_5\text{H} + \text{N}_2 + 2\text{H}_2\text{O} \]

Summary of yields:

2. " " " 84.5" " 18.9 "
3. " " " 269 " " 88.0 "

The steam distillate was extracted with ether, and distilled under reduced pressure.

Boiling Point:

133°-135° at 28 mm.Hg.

111° at 9 mm.Hg.

The pure product is a yellow oil, which does not become darker with time, is completely soluble in dilute acid, and does not give a test for primary amine with bleaching powder nor with chloroform and KOH. Some derivatives were made. (Pages 31-37)
I. BOILING AT ATMOSPHERIC PRESSURE.

(a) A few c.c. of the pure product, which gave no test with bleaching powder, were boiled in a test-tube for ten minutes. At the end of that time a decided positive test was obtained with bleaching powder.

(b) 25 c.c. of the pure product were boiled at atmospheric pressure under a reflux condenser for three hours, and then fractionated under reduced pressure in a Brühl apparatus.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>1 wt. tube</th>
<th>2 wt. tube</th>
<th>B.P. and Bleaching Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt.</td>
<td>fract.</td>
<td>Pressure</td>
</tr>
<tr>
<td>I</td>
<td>15.4</td>
<td>19.2</td>
<td>3.8</td>
</tr>
<tr>
<td>II</td>
<td>14.75</td>
<td>19.3</td>
<td>4.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>15.60</td>
<td>22.6</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>14.4</td>
<td>16.4</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>15.25</td>
<td>16.5</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As shown, whenever the receptacles were changed, trouble was experienced in keeping the pressure constant.
ures are given in parentheses below the boiling points. The number of + signs in the bleaching powder column indicate the relative intensity of the color produced. Fraction V when dissolved in dilute acid, gave a solution that was slightly cloudy, indicating incomplete solubility.

Fractions I, III, and V were treated with phenyl mustard oil. Thioureas were obtained from I and III only. Melting points of the thioureas:

\[
\begin{align*}
\text{Fraction III} & : 91.0^\circ\text{C}-91.5^\circ\text{C} \\
\text{Fraction I} & : 91.0^\circ\text{C}-98.0^\circ\text{C}
\end{align*}
\]

The thiourea of fraction I was made again on a larger scale and recrystallized from a comparatively large volume of alcohol. On cooling crystals were obtained which were found by the mixed melting point with thio-carbanilide, to be thiocarbanilide.

\[
\begin{align*}
\text{M.P. } & : 148^\circ\text{C}-150^\circ\text{C} \\
\text{Of Mixture} & : 148^\circ\text{C}-153^\circ\text{C}
\end{align*}
\]

The conclusion was that Fraction I was a mixture of aniline and allylaniline, and that Fraction III was allylaniline, and that Fraction V was a mixture of
allylaniline and the tarry products previously met with. There was the possibility that Fraction V might contain diallyl aniline, which would also cause the rise in boiling point, but its quantity was so small that the base could not be separated from the tarry acid-insoluble material and tested.

It was also thought since this material had received the same treatment (two or three hours boiling) as that which had caused the rearrangement of the allyl phenyl ethers, that Fraction III might contain, in addition to allylaniline, a primary amine caused by a similar rearrangement, whose boiling point might be the same as that of the secondary amine, which would not necessarily give a test with bleaching powder (viz. P.-toluidine), and whose thiourea might have been "lost in the shuffle".

In order to settle this question, Fraction III was tested with d-naphthyl sulphone chloride for the
presence of a primary amine.¹

4.8 grams of Fraction III (1 mol., if allylanilin or an isomer) 4 mols. of NaOH solution were added followed by the addition of 12.2 grams (1.5 mols) of the naphthalene q-sulphone chloride. On acidifying with dilute HCl a pink oil was precipitated. This was extracted with chloroform (it was not very soluble in ether); the chloroform was evaporated off and the oil treated with a solution of 4 grams sodium in 80 grams absolute alcohol, and the alcoholic solution refluxed for four hours. 100 c.c. of water were then added and the alcohol was distilled off, which precipitated the oily allyl phenyl sulphonamide. The clear alkaline supernatant liquid, which should contain in solution the sodium salt of the sulphonamide of any primary amine present, gave no precipitate when acidulated with HCl, indicated the total absence of any primary amine.

The refluxing with sodium ethylate was for the purpose of converting any disulphonamide which might be formed from a primary amine, and which, as well as the sulphonamide of a secondary amine, would be insoluble in alkali, into the soluble monosulphone derivative.

2-HEATING AT HIGHER TEMPERATURES.

30 c.c. of the pure allylaniline were heated at 250° for eight hours. On opening the tube with a flame, the gaseous hydrocarbons were ejected, burning with a blue flame. The liquid in the tube was extracted with dilute acid, which showed the presence of a large amount of acid-insoluble tarry material. The acid solution was made alkaline, the liberated bases extracted with ether, and fractionated under reduced pressure.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Pressure</th>
<th>Boiling-point</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>9 mm.</td>
<td>93-97</td>
</tr>
<tr>
<td>II</td>
<td>8.5</td>
<td>97-110</td>
</tr>
<tr>
<td>III</td>
<td>8.5</td>
<td>110-112</td>
</tr>
</tbody>
</table>

The rise in boiling point from 97° to 110° was very
sudden, most of Fraction II boiling at about 97°. Benzanilide and thiocarbanilide were isolated from fractions I and II, and allyl diphenyl thioureia from fraction III. The residue in the flask was very small in quantity, and could not be driven over by raising the temperature of the oil-bath to 170°.

The absence of any acid-soluble material boiling above 112°, which is the boiling point of allylanilin at 9 mm., renders the formation of diallylaniline extremely improbable.

3.--HEATING THE HYDROCHLORIDE.

It was thought that the behavior of the hydrochloride of allylanilin on heating (page 34) might be different from that of the free base. Accordingly, 5 grams of the pure hydrochloride were heated in a sealed tube at 200° for four hours. On opening the tube no pressure was observed and no gases were evolved, and on attempting to dissolve the product in dilute acid it was found that practically complete decomposition had taken place as the quantity of
material dissolved was small, and on neutralizing the acid solution with NaOH only a very small quantity of a base, too small for identification, was liberated. When liberated it appeared to have some tarry material in solution, as it would not dissolve up again completely on acidifying, and when first thrown down had the appearance of a solid.

**CONCLUSION.**

The following conclusions as to the behavior of allylanilin on heating would seem to be justified:

1. Allylanilin, on boiling at atmospheric pressure, undergoes the same decomposition, with the formation of the same products, as when heated at higher temperatures.

2. These products, in either case, are:
   
   (a) Aniline.
   (b) Gaseous unsaturated hydrocarbons.
   (c) Tarry polymerization products, of high molar weight, probably hydrocarbons.

3. The hydrochloride is more unstable toward heat than the free base.
4. Neither diallyl aniline, nor bases formed by molecular rearrangement, are formed.

**SIMPLE DERIVATIVES OF ALLYLANILIN.**

With the exception of the chlorplatinate, which had been prepared by Schiff, no of the salts, of allylanilin with mineral acids have been prepared, and no reference to any other simple derivative, such as the acetyl or benzoyl derivatives, has been found in the literature.

I. Attempt to prepare allyl phenyl benzamide.

One c.c. of the pure allylanilin was suspended in 20% NaOH solution and about one c.c. of benzoyl chloride added. The solution was shaken until the odor of benzoyl chloride had disappeared, and allowed to stand over night. The product was washed with water, which left a heavy oil undissolved. This was extracted with ether, and the ethereal solution allowed to evaporate at room temperature. No crystals could be observed.

1. Loc. Cit.
32.
The oily residue was dissolved in hot alcohol, but again no crystals were formed, either on cooling or on iso-thermal evaporation, nor on cooling in an ice-bath. As the oil was insoluble in dilute acid, the conclusion is that the benzanilid is formed but is an oil at ordinary temperatures.

2. Attempt to prepare allyl phenyl acetamide.

When acetyl chloride was added to about one c.c. of pure allylanilin, there occurs a slight red evolu- tion of heat but much less than in the case of anilin, for instance. The excess acetyl chloride was decomposed with water and the product dissolved in boiling water. An oil separated on cooling, which seemed to be partially soluble in acid, due probably to partial hydrolysis. On another attempt, after decomposing the excess acetyl chloride with water, this was decanted off, and the oil was dissolved in hot alcohol. No crystals were obtained.

3. Allyl phenyl naphthalene sulphonamide.
As has been already mentioned,(page 27) this product
33.

comes down as an oil, and did not crystallize, although kept for several weeks, and although an attempt was made to crystallize it from alcohol.

4. Allyl aniline hydrochloride.

(a) 5 grams of the crude allylanilin(page 20) were dissolved in dry benzene and HCl dried by passage through conc. H₂SO₄ was passed in until precipitation seemed complete. The salt came down at first as a dark red oil but after standing a few minutes and shaking it formed red crystals of a slushy character. These were washed several times by decantation with petroleum ether, when the crystals became light yellow in color. Dried in a dessicator they melted from 89⁰ to 160⁰, showing great impurity and the presence of aniline hydrochloride.

(b) A few drops of pure allylanilin were dissolved in fairly concentrated HCl. No crystals could be obtained in this way by salting out with concentrated HCl.
(c) 10 grams of pure allylanilin were dissolved in petroleum ether and HCl, dried as before, was passed through. The salt came down as a cream-colored paste which soon became crystalline. It was washed several times with petroleum ether and dried in a dessicator over CaCl₂. Melting point, sharply at 110°. The crystals are soluble in hot benzene and some well-formed crystals were obtained by recrystallizing from a mixture of benzene and petroleum ether, but deliquescence was taking place all the time and not enough product was obtained even for a melting point. The salt was analyzed by titration:

**ANALYSIS OF ALLYLANILINE HYDROCHLORIDE.**

<table>
<thead>
<tr>
<th>Wt. bottle and sample</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. bottle</td>
<td>13.4466</td>
<td>12.3196</td>
<td>11.6703</td>
</tr>
<tr>
<td>Wt. sample</td>
<td>1.1105</td>
<td>.5593</td>
<td>.2893</td>
</tr>
<tr>
<td></td>
<td>I.</td>
<td>II.</td>
<td>III.</td>
</tr>
<tr>
<td>-------</td>
<td>-----</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>NaOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower reading</td>
<td>49.80</td>
<td>38.90</td>
<td>26.30</td>
</tr>
<tr>
<td>Upper reading</td>
<td>0.40</td>
<td>0.14</td>
<td>1.20</td>
</tr>
<tr>
<td>Total NaOH</td>
<td>49.40</td>
<td>38.76</td>
<td>25.10</td>
</tr>
<tr>
<td>Normality</td>
<td>0.0885</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower reading</td>
<td>20.00</td>
<td>16.70</td>
<td>23.00</td>
</tr>
<tr>
<td>Upper reading</td>
<td>19.85</td>
<td>19.95</td>
<td>16.70</td>
</tr>
<tr>
<td>Total HCl</td>
<td>0.15</td>
<td>1.75</td>
<td>6.30</td>
</tr>
<tr>
<td>Normality</td>
<td>0.0887</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

I.  \(HCl = \frac{72.55 \times 0.0885 \times 36.46}{1.1105} = 21.08\%\)

II. \(HCl = \frac{37.01 \times 0.0885 \times 36.46}{0.5593} = 21.39\%\)

III. \(HCl = \frac{18.80 \times 0.0885 \times 36.46}{0.2894} = 21.21\%\)

Calculated for \(C_{9}H_{12}NC1;\) \(HCl \ 21.77\%\)

Phenolphthalein was used as the indicator but the end-point was not particularly sharp and there was the free base in suspension which helped to obscure the end-point.

5. Allyl aniline monoxalate.

To 2 grams allylaniline, dissolved in ether, an
ethereal solution of oxalic acid was added until precipitation seemed complete. The finely divided white precipitate was filtered, washed with ether, and recrystallized from acetone, M.P. 119-120°.

Analyzed by dissolving a sample in water, making alkaline with NaOH and evaporating nearly to dryness three times, which procedure in effect steam distills off the allylanilin, the acidifying with dilute sulphuric acid and titrating with KMnO₄.

ANALYSIS OF ALLYLANILINE ACID

<table>
<thead>
<tr>
<th>Wt. bottle and salt</th>
<th>11.1654</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. bottle</td>
<td>10.9689</td>
</tr>
<tr>
<td>Wt. sample</td>
<td>.1965</td>
</tr>
</tbody>
</table>

| KMnO₄ | 25.30 |
| Upper reading | 7.68 |

Volume KMnO₄ 17.62

\[
\frac{90 \times 100 \times 0.0986 \times 17.62}{2 \times 1000 \times 0.1965} = 40.49\% (COOH)_2
\]
Calc. for $\text{COOH} \cdot \text{NH}_2 \text{C}_3\text{H}_5 \text{COOH} \cdot \text{NH}_2 \text{C}_6\text{H}_5$; $(\text{COOH})_2$ 40.35%

Calc. for $\text{COOH} \cdot \text{NH}_2 \text{C}_3\text{H}_5 \text{COOH} \cdot \text{NH}_2 \text{C}_6\text{H}_5$; $(\text{COOH})_2$ 25.28%
PART TWO

THE SYNTHESIS OF CERTAIN THIAZOLES.
PART TWO

INTRODUCTORY

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α Allyl α paratolyl β phenyl thiourea;
   Synthesis............................................. 49
   Analysis................................................ 49

2-phenylimido 3-paratolyl 5-methyl 4,5-dihydro thiazole;
   Synthesis............................................. 50
   Analysis................................................ 50

α Allyl α phenyl β parabromphenyl thiourea;
   Synthesis............................................. 52
   Analysis................................................ 52

2-Parabromphenylimido 3-phenyl 5-methyl 4,5-dihydro thiazole;
   Synthesis............................................. 53
   Analysis................................................ 53
PART TWO (continued).

\[ \text{Allyl } \alpha \text{ paratolyl } \beta \text{ parabromphenyl thiourea; } \]
Synthesis.................................54
Analysis..................................54

2-parabromphenylimido 3-paratolyl 5-methyl 4,5-dihydro thiazole;
Synthesis.................................55
Analysis..................................55

\[ \text{Allyl } \alpha \text{ phenyl } \beta \text{ paratolyl thiourea; } \]
Synthesis.................................57
Analysis..................................57

2-paratolylimido 3-phenyl 5-methyl 4,5-dihydro thiazole(?). ..........58

\[ \text{Allyl } \alpha \beta \text{ d}-\text{paratolyl thiourea; } \]
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Summary of thiazole synthesis..............................63

Attempted reactions..............................64-70
The fact that allyl thiourea, or thiosinamine, when heated with concentrated hydrochloric acid under pressure, undergoes a rearrangement with ring closure to form a thiazole, was discovered in 1889 by S. Gabriel.

A representation of the course of the reaction, showing the similarity in structure of the enol form of the thiourea with that of the thiazole, may be given as follows:

\[
\begin{align*}
\text{Thiourea} & \quad = \quad \text{Thiazole} \\
\text{Isothiourea} & \quad \text{Isothiourea} \quad \text{Thiazole}
\end{align*}
\]

B. Prager, who was working with Gabriel, has carried out the analogous experiment in the case of symmetrical allyl phenyl thiourea, using hydrochloric acid under pressure.

Dr. F. B. Dains, in 1900, made the discovery that

1. S. Gabriel, Ber. 22, 2986;
2. B. Prager, Ber. 22, 2992.
allyl phenyl thiourea, when heated with acetyl chloride in the absence of a solvent, rearranges in the same way as with HCl under pressure. Dains and Brewster\(^1\) have further continued the investigation of the action of acetyl and benzoyl chlorides on a variety of disubstituted thioureas of the type

\[
\begin{align*}
\text{HN} & \quad \text{CH}_2 \\
\text{C} & \quad \text{CH=CH}_2 \\
\text{RN} & \quad \text{SH}
\end{align*}
\]

by the rearrangement of mono- or di-substituted thioureas, there is a possibility of two structural formulae, I and II. Young and Crookes\(^2\) have succeeded in methylating this thiazole and have shown that the methyl group is attached to the nitrogen at 2, indicating that the thiazole has here a structure corresponding to II. This does not, however, preclude the possibility of tautomeric equilibrium between the two forms.

In the case of trisubstituted thioureas, however,

\[\text{I} \quad \text{II.}\]

as there is only one mobile hydrogen atom, there is only one possibility for the structure of the isothiourea and hence for the thiazole formed by its rearrangement. The trisubstituted thioureas formed by the action of mustard oils on secondary allyl amines would then rearrange as follows:

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

It was then with the intention of synthesizing a variety of trisubstituted thioureas, of this type, of rearranging them to the thiazoles, and of determining some of the properties of the latter that this work was undertaken.

It was intended to make the nine thiazoles formed by the rearrangement of the thioureas produced by the action of phenyl mustard oil, p-tolyl mustard oil, and p-brome-phenyl mustard oil on each of the three amines; allyl amine, allyl p-toluidine, and allyl p-bromphenyl amine. This program, however, only was partially success-
ful, as may be shown by a comparison with the diagrammatic summary of experimental work, page 63.
Part Two
Experimental

Synthesis of the secondary allylamines.

(a) Allylaniline. The preparation of this substance has been described in the first part of this paper.

(b) Allyl p-toluidine.

160 grams p-toluidine were refluxed with a solution of 100 grams 90% formic acid in 160 c.c. water for six hours. The product was distilled and that fraction boiling above 220° was collected as form-p-toluidine. Yield 148 grams. This was dissolved in alcohol and slowly added to 44 grams NaOH, also dissolved in alcohol. The white sodium salt of the toluidine separated out and was filtered at the pump and washed with alcohol. Yield when dry, 70 grams. In appearance it greatly resembled the corresponding salt of formanilide.

The 70 grams of the salt was placed in a two-liter balloon flask and refluxed with 65 grams of allyl bromide until the pasty appearance of the toluidine salt was replaced by the more crystalline appearance of sodium bromide. 100 c.c. conc. HCl in 200 c.c. water was
then added and the mixture refluxed until the solution was practically clear, which required about eight hours. An excess of saturated NaOH solution was then added and the liberated base distilled with steam. The steam distillate was extracted with ether, which was distilled off and the allyl p-toluidine used in this condition, without distilling, as it had been found in the case of allylaniline that the product was sufficiently pure for thiourea synthesis. It was identified by the preparation of the acid oxalate, which has been prepared by Wedekind. About one c.c. of the amine was dissolved in ether and an excess of an ethereal solution of oxalic acid added. When filtered and washed with ether the small white crystals which were precipitated melted at 147-8°. When crystallized from acetone the melting-point was 149°-150°. Given by Wedekind, 150°-1°. The yield of the allyl p-toluidine was 48 grams.

(c). Attempt to synthesize allyl b-brom aniline.

125 grams of p-bromaniline were refluxed for

.............

1. E. Wedekind and F. Oberheide, Ber. 37, 2720 (1904)
four hours with 125 grams of 90% formic acid, and then poured into cold water. The p-brom formanilid separated out as cream-colored needles. It was well washed with water, then with dilute HCl, then again with water. Yield 127 grams. A small portion was washed with alcohol. M. p. 115-117°. Given in Beilstein: 119°. The product was dissolved in alcohol and slowly added to 25.4 gram of NaOH dissolved in alcohol. A white salt separated out which was considerably more crystalline in appearance than in the case of formanilide or of form-p-toluidine. Yield of the salt, 120 grams.

The 120 grams of the salt were refluxed with 75 grams (molar quantity would be 67 grams) of allyl bromide until the changing appearance of the precipitate indicated that it was the end of the reaction. 150 c.c. conc. HCl and 150 c.c. water were then added and the whole brought to a boil under a reflux condenser. Within a few minutes after the boiling point had been reached the mixture turned black with the formation of a large quantity of tarry viscous material. When the boiling had been continued for perhaps half an hour the mixture was cooled and made alkaline with NaOH. A small
quantity of a base was liberated in the supernatant liquid above the tar. The mixture was subjected to a steam distillation. The dark-colored oil which came over was only partially soluble in dilute acid. That which was insoluble was separated by extraction with chloroform. The remaining acid solution was made alkaline with NaOH and extracted with ether. On evaporating off the ether a brown oil remained which was still not entirely soluble in dilute acid, the solution being cloudy. The oil gave a carbylamine test for primary amine, but no test with bleaching-powder. It gave a benzoyl derivative which after recrystallization from alcohol melted at 202°-3°. The melting point of N-p-bromphenyl benzamide is given in Beilstein to be 202°, showing the basic substance to be p-bromaniline.

The conclusion is that allyl p-brom formanilide is unstable towards hydrolysis by boiling with dilute acids, with the probable formation of p-bromaniline as one of the decomposition products.

An attempt was then made to synthesize allyl p-brom aniline by the direct action of allyl bromide on p-brom aniline. 25 grams of pure p-brom aniline were treated with 22 grams (25% excess) of allyl bromide in the cold. There
was no apparent reaction, which is entirely different from
the action of allyl bromide on aniline. The flask was
placed on a steam bath for a few seconds, when the whole
mixture turned black with the formation of a tarry product.
The reaction did not appear to be violent and there was
not much heat evolved. The amount of material which was
soluble in dilute acid was very slight.

It may be that by the use of a different method of
hydrolysis of the allyl p-brom formanilid, or by the use
of a solvent, in the direct action of allyl bromide on
p-brom aniline, allyl p-brom aniline may be obtained, but
time was lacking for a repetition of the experiment.

SYNTHESIS OF THE MUSTARD OILS.

Para tolyl mustard oil was made by a method suggested
by Fry, who although he did not make any, got some analy-
tical results to indicate that by varying the proportions
of the reagents, mustard oils and not thioureas may be pro-
duced by the action of carbon disulfide on primary amines
in the presence of pyridine and iodine, the reaction
following equation 2 instead of I.

I. $2RNH_2 + CS_2 + 2C_5H_5N + I_2 = RNHCSNHR + 2C_5H_5NHI + S$
2. $RNH_2 + CS_2 + 2C_5H_5NN + I_2 = RNCS + 2C_5H_5NHI + S$

1. H. S. Fry, J. A. C. S., 35, 1543 (1913).
In this case it was found, by using the proportions indicated by the second equation, that both p-tolyl mustard oil and di-p-tolyl thiourea were formed.

Para-bromphenyl mustard oil was made by making the thiourea by Fry's method. 168 grams of the crude product, containing sulfur, and melting, when recrystallized from alcohol, at 177°-179° (Beilstein 180°) was refluxed for four hours with 75 c.c. of acetic anhydride, and then distilled with steam. The mustard oil was very volatile in steam, solidifying in the receiver and condenser to a cream-colored solid, with a strong cheese-like odor. M.P. 60-61°. Given in Beilstein 62°. Yield 20.1 grams.

2 PHENYLIMIDO 3PHENYL 5METHYL 4,5 DIHYDRO THIAZOLE.

This compound was made by the rearrangement of α-allyl αβdiphenyl thiourea formed by the action of phenyl mustard oil on allylaniline. M. P. of the thiourea, 91°. The urea is known.

(a) With acetyl chloride.

9.8 grams of the thiourea were heated with 10 cc. acetyl chloride on a water-bath for about half an hour. The product was dissolved in 50% alcohol and made alkaline with Na₂CO₃ solution. A base was liberated which at first
had the appearance of a solid precipitate but on standing came down as an oil. However, on extraction with ether and evaporation at room temperature large white plates were formed. M. P. 98°.

(b) With hydrochloric Acid.

30 grams of the thiourea were heated with 75 c.c. concentrated hydrochloric acid in a pressure bottle in a water bath until the solution was clear, which required about two hours. A few drops of a clear oil were left which seemed to be unaffected even after several hours heating. The solution was then diluted with 50% alcohol and made alkaline with Na₂CO₃ solution. The thiazole came down as a white flocculent precipitate which was recrystallized from a mixture of alcohol and ether. It had a tendency to come down as an oil from alcohol alone. M.P. 98°. A mixture of the products(a) and (b) melted at 98°. The picrate forms yellow needles from alcohol, M.P. 168-9°. The thiazole is soluble in benzene, alcohol, ether and acetone, and completely so in dilute hydrochloric acid.
ANALYSIS. CARIUS FOR SULPHUR.¹

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. tube and sample</td>
<td>2.7365</td>
<td>3.3219</td>
</tr>
<tr>
<td>Wt. tube</td>
<td>2.5393</td>
<td>3.0927</td>
</tr>
<tr>
<td>Wt. thiazole</td>
<td>.1972</td>
<td>.2292</td>
</tr>
<tr>
<td>Wt. cruc. and BaSO₄</td>
<td>14.8982</td>
<td>17.9583</td>
</tr>
<tr>
<td>Wt. crucible</td>
<td>14.7264</td>
<td>17.7527</td>
</tr>
<tr>
<td>Wt. BaSO₄</td>
<td>.1718</td>
<td>.2056</td>
</tr>
</tbody>
</table>

Percentage sulphur 11.92 12.31
Calculated for C₁₅H₁₆N₂S; S 11.93%

ANALYSIS. KJELDAHL FOR NITROGEN.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Wt. bottle</td>
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<td>12.2627</td>
</tr>
<tr>
<td>2. Wt. bottle</td>
<td>12.2627</td>
<td>11.6096</td>
</tr>
<tr>
<td>Wt. thiazole</td>
<td>.9873</td>
<td>.6531</td>
</tr>
</tbody>
</table>

Total cc.HCl used 75.10 75.00
Normality .1035 .1035
Total c.c.KOH used 7.15 33.00
Normality .0887 .0887

I. \[
\frac{(75.10 \times 0.1035 - 7.15 \times 0.0887) \times 14 \times 100}{0.9873 \times 1000} = 10.13\% 
\]

II. \[
\frac{(75.00 \times 0.1035 - 33.00 \times 0.0887) \times 14 \times 100}{0.6531 \times 1000} = 10.19\% 
\]
Calculated for C₁₅H₁₅N₂S; N 10.44%

¹ Analysis for sulphur made by W. F. Asendorf.
15 grams of allyl p-toluidine were heated for a few minutes on the water bath with 13.8 grams of phenyl mustard oil. The product was dissolved in boiling alcohol and allowed to cool. The thiourea separated out as an oil but on placing in a freezing mixture 11.6 grams of a white crystalline product was obtained. When recrystallized from alcohol the melting point was 91°.5-92°. Soluble in ether, chloroform, and hot alcohol; only moderately soluble in cold alcohol and in benzene, even when hot. The oily residue after standing for several days deposited a further small crop of crystals.

### ANALYSIS

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Wt. bottle</td>
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<td>12.5473</td>
</tr>
<tr>
<td>Wt. sample</td>
<td>.8091</td>
<td>.5218</td>
</tr>
<tr>
<td>Total c.c. HCl</td>
<td>74.69</td>
<td>74.36</td>
</tr>
<tr>
<td>Normality</td>
<td>.0885</td>
<td>.0885</td>
</tr>
<tr>
<td>Total c.c. KOH</td>
<td>14.00</td>
<td>34.14</td>
</tr>
<tr>
<td>Normality</td>
<td>.0887</td>
<td>.0887</td>
</tr>
</tbody>
</table>

I. \( \frac{(74.69-14.00) \times 0.0885 \times 14 \times 100}{0.8091 \times 1000} \) 9.31%

II. \( \frac{(74.36-34.13) \times 0.0885 \times 14 \times 100}{0.5218 \times 1000} \) 9.59%

III. \( \frac{(73.79 \times 0.1035-39.05 \times 0.0900) \times 14 \times 100}{0.5872 \times 1000} \) 9.81%

Calculated for \( \text{C}_{17}\text{H}_{18}\text{N}_{2}\text{S}; \ N 9.93\% \)
50.

2PHENYLIMIDO-3PARATOLYL-5METHYL-4,5 DIHYDRO THIAZOLE.

\[
\text{CH}_3\text{C}_6\text{H}_4\text{N} - \text{CH}_2 \quad \text{CH}_3\text{C}_6\text{H}_4\text{N} - \text{CH}_2 \\
\text{C}_6\text{H}_5\text{N} - \overset{\text{SH}}{\text{C}} - \text{CH} = \text{CH}_2 \quad \text{C}_6\text{H}_5\text{N} - \overset{\text{S}}{\text{C}} - \text{CH}_3 \text{CH}_3
\]

5 grams of the \(\alpha\)-allyl \(\alpha\)-paratolyl \(\beta\) phenyl thiourea were heated with about 50 c.c. conc. HCl in a pressure bottle on the water bath for two hours. The solution was clear but on diluting with water a slight cloudiness appeared. Alcohol was added in excess of that required to clear up the solution. Addition of NaOH caused the appearance of a white lumpy precipitate, which was filtered off and recrystallized from alcohol. M. P. 72°-73°. In appearance the thiazole resembled acetonilide, crystallizing in large white flakes. Yield 3.8 grams. Easily soluble in ether, chloroform, benzene and hot alcohol; only moderately soluble in cold alcohol. Picrate; yellow needles from alcohol, M. P. 164-6°.

**ANALYSIS.**

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Wt. bottle</td>
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</tr>
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<td>2 Wt. bottle</td>
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<td>Wt. sample</td>
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<td>.7786</td>
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**KJELDAHL.**
<table>
<thead>
<tr>
<th></th>
<th>Total c.c. HCl</th>
<th>Normality</th>
<th></th>
<th>Total c.c. KOH</th>
<th>Normality</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>72.98</td>
<td>0.0885</td>
<td>II</td>
<td>75.66</td>
<td>0.0885</td>
</tr>
<tr>
<td></td>
<td>33.89</td>
<td>0.0887</td>
<td></td>
<td>17.11</td>
<td>0.0887</td>
</tr>
</tbody>
</table>

I. \[
\frac{(72.98 - 33.89) \times 0.0885 \times 14 \times 100}{5648 \times 1000} = 9.62\%
\]

II. \[
\frac{(75.66 - 17.11) \times 0.0885 \times 14 \times 100}{7786 \times 1000} = 9.35\%
\]

Calculated for C_{17}H_{18}N_{2}S; \quad N \quad 9.93\%
52.

PARA BROMPHENYL MUSTARD OIL AND ALLYL ANILINE.

5 grams of allylaniline were heated with 9.4 grams of the mustard oil for a few minutes at about 120°. The product was dissolved in hot alcohol which on cooling deposited light cream-colored needles. M. P. 122°-123°. Yield 7.0 grams. A portion again recrystallized from alcohol was still cream-colored, M. P. 123°. Easily soluble in chloroform and hot alcohol. Moderately soluble in ether, benzene, and cold alcohol.

ANALYSIS.

COMBUSTION FOR NITROGEN.1

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. boat and sample</td>
<td>3.7745</td>
<td>3.6155</td>
</tr>
<tr>
<td>Wt. boat</td>
<td>3.5618</td>
<td>3.3402</td>
</tr>
<tr>
<td>Wt. sample</td>
<td>.2127</td>
<td>.2753</td>
</tr>
<tr>
<td>Vol. nitrogen (over KOH)</td>
<td>16.25</td>
<td>18.40</td>
</tr>
<tr>
<td>Barometer</td>
<td>73.70</td>
<td>73.70</td>
</tr>
<tr>
<td>Temperature</td>
<td>30°C</td>
<td>30°C</td>
</tr>
<tr>
<td>Percentage nitrogen</td>
<td>8.65</td>
<td>7.56</td>
</tr>
</tbody>
</table>

Calculated for C\textsubscript{16}H\textsubscript{15}N\textsubscript{2}SBr; N 8.07%

KJELDAHL FOR NITROGEN.

<p>| | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>1 wt. bottle</td>
<td>11.3877</td>
</tr>
<tr>
<td>2 wt. bottle</td>
<td>10.6426</td>
</tr>
<tr>
<td>Wt. sample</td>
<td>.7451</td>
</tr>
<tr>
<td>Total vol. HCl</td>
<td>75.70</td>
</tr>
<tr>
<td>Normality</td>
<td>.0885</td>
</tr>
<tr>
<td>Total vol. KOH</td>
<td>26.05</td>
</tr>
<tr>
<td>Normality</td>
<td>.0887</td>
</tr>
</tbody>
</table>

\[
\frac{(75.70 - 26.50) \times 0.0885 \times 14 \times 100}{.7451 \times 1000} = 8.25\%
\]

1. Combustions made by R.M. Buffington.
2-PARABROMPHENYLIMIDO 3-PHENYL 5-METHYL 4,5 DIHYDRO THIAZOLE.

4.5 grams of the allyl phenyl parabromphenyl thiourea were heated with about 50 c.c. concentrated HCl in a pressure bottle in a water bath for about three hours. The solution was diluted with water and alcohol added until the solution was clear, then made alkaline with NaOH. The precipitate which appeared was recrystallized from alcohol. Small glistening pink flakes, easily soluble in chloroform, ether and hot alcohol. Only moderately soluble in cold alcohol and in benzene.


ANALYSIS.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt. bottle</td>
<td>12.6726</td>
<td>12.2938</td>
</tr>
<tr>
<td>2 wt. bottle</td>
<td>12.2938</td>
<td>11.9940</td>
</tr>
<tr>
<td>Wt. sample</td>
<td>.3788</td>
<td>.2998</td>
</tr>
<tr>
<td>Total vol. HCl</td>
<td>51.00</td>
<td>50.40</td>
</tr>
<tr>
<td>Normality</td>
<td>.1035</td>
<td>.1035</td>
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KJELDAHL.

<table>
<thead>
<tr>
<th></th>
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<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>24.65</td>
<td></td>
</tr>
<tr>
<td>Total vol. KOH</td>
<td>I</td>
<td>II Control.</td>
</tr>
<tr>
<td>---------------</td>
<td>-----</td>
<td>-------------</td>
</tr>
<tr>
<td></td>
<td>31.95</td>
<td>37.20</td>
</tr>
<tr>
<td>Normality</td>
<td>.0887</td>
<td>.0887</td>
</tr>
<tr>
<td></td>
<td>.0887</td>
<td>.0887</td>
</tr>
</tbody>
</table>

Control yields \(24.65 \times .1035 - 27.00 \times .0887 = .160\) c.c normal nitrogen.

\[
\text{I.} \quad (51.00 \times .1035 - 31.95 \times .0887 - .16) \times 14 \times 100 = 8.48\% \\
\quad .3788 \times 1000
\]

\[
\text{II.} \quad (50.40 \times .1035 - 37.20 \times .0887 - .16) \times 14 \times 100 = 8.23\% \\
\quad .2998 \times 1000
\]

Calculated for \(C_{16}H_{15}N_2SBr\); \(N\) 8.07\%
PARABROMPHENYL MUSTARD OIL AND ALLYL PARATOLUIDINE.

7 grams of allyl paratoluidine were heated with 10.15 grams of the mustard oil for a few minutes at about 120°. The product was dissolved in hot alcohol from which the thiourea was deposited on cooling. On a second recrystallization from alcohol the melting point was 120°-1°. Cream-colored needles easily soluble in chloroform, hot benzene and hot alcohol. Moderately soluble in ether, cold alcohol and cold benzene. Yield 10.3 grams.

ANALYSIS.  

<table>
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<th>I</th>
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<td>1 Wt. bottle</td>
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<td>11.8106</td>
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<td>2 Wt. bottle</td>
<td>11.8106</td>
<td>11.2195</td>
</tr>
<tr>
<td>Wt. sample</td>
<td>.6377</td>
<td>.5911</td>
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<tr>
<td>Total cc. HCL</td>
<td>72.53</td>
<td>75.60</td>
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<tr>
<td>Normality</td>
<td>.0885</td>
<td>.0885</td>
</tr>
<tr>
<td>Total c.c. KOH</td>
<td>33.35</td>
<td>40.50</td>
</tr>
<tr>
<td>Normality</td>
<td>.0887</td>
<td>.0887</td>
</tr>
</tbody>
</table>

I. \( \frac{(72.53-33.35) \times .0885 \times 14 \times 100}{.6377 \times 1000} \) 7.64%

II. \( \frac{(75.60-40.50) \times .0885 \times 14 \times 100}{.5911 \times 1000} \) 7.35%

Calculated for \( \text{C}_{17}\text{H}_{17}\text{N}_{2}\text{SBr} \);  N 7.75%
55.

2-PARABROMPHENYLIMIDO 3-PARATOLYL 5-METHYL 4,5-DIHYDRO THIAZOLE.

5 grams of the allyl paratolyl parabromphenyl thiourea were heated for about four hours with about 50 c.c. conc. HCl in a pressure-bottle in a water bath. The solution was diluted with dilute alcohol and made alkaline with NaOH solution. The dark product was filtered, at the pump, during which operation due to clogging of the filter the filter flask (Erlenmeyer) broke and more than half the product was lost. The remainder was recrystallized from alcohol. Reddish-brown flakes, M. p. 79°-81°. The yield at this point was only about .5 gram, not permitting of a second recrystallization and only one sample was taken for analysis.

\[
\begin{align*}
\text{CH}_3\text{C}_6\text{H}_4\text{N} & \quad \text{CH}_2 \\
\text{BrC}_6\text{H}_4\text{N} & \quad \text{SCH}=\text{CH}_2
\end{align*}
\]

ANALYSIS.

<table>
<thead>
<tr>
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<tbody>
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</tr>
<tr>
<td>2. wt. bottle</td>
<td>12.0373</td>
</tr>
<tr>
<td>Wt. sample</td>
<td>.3883</td>
</tr>
</tbody>
</table>
ANALYSIS

Total cc. HCl 76.25
Normality .0885

Total cc. KOH 52.00
Normality .0887

\[
\frac{(76.25 - 52.00) \times 0.0885 \times 14 \times 100}{0.3883 \times 1000} = 7.73% \\
\]

Calculated for C_{17}H_{17}N_{2}SBr; N .7.75%
PARATOLYL MUSTARD OIL AND ALLYL ANILINE.

15 grams of allylaniline and 16.6 grams of paratolyl mustard oil were heated together at 120° for a few minutes. The product was dissolved in hot alcohol. On cooling an oil separated out, in which after standing for several days, some white crystals made their appearance. These were separated, again recrystallized from alcohol; white needles, M.P. 107°. Yield of the crystals, about two grams. Most of the product remained as an oil.

ANALYSIS.

<table>
<thead>
<tr>
<th></th>
<th>Kjeldahl I</th>
<th></th>
<th>Kjeldahl II</th>
<th></th>
</tr>
</thead>
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<tr>
<td>1 wt. bottle</td>
<td>11.7155</td>
<td>11.1392</td>
<td>11.1392</td>
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<td>2 wt. bottle</td>
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<td></td>
<td>10.6596</td>
<td></td>
</tr>
<tr>
<td>Wt. sample</td>
<td>.5763</td>
<td></td>
<td>.4796</td>
<td></td>
</tr>
<tr>
<td>Total c.c. HCl</td>
<td>74.36</td>
<td></td>
<td>74.25</td>
<td></td>
</tr>
<tr>
<td>Normality</td>
<td>.0885</td>
<td></td>
<td>.0885</td>
<td></td>
</tr>
<tr>
<td>Total c.c. KOH</td>
<td>28.50</td>
<td></td>
<td>37.05</td>
<td></td>
</tr>
<tr>
<td>Normality</td>
<td>.0887</td>
<td></td>
<td>.0887</td>
<td></td>
</tr>
</tbody>
</table>

I. \[ \frac{(74.36 - 28.50) \times 0.0885 \times 14 \times 100}{0.5763 \times 1000} = 9.85\% \]

II. \[ \frac{(74.25 - 37.05) \times 0.0885 \times 14 \times 100}{0.4796 \times 1000} = 9.63\% \]

Calculated for C_{17}H_{18}N_{2}S; N 9.93\%
As stated on the preceding page, not enough of the allyl phenyl paratolyl thiourea was obtained in the crystalline state to hope to accomplish the thiazole synthesis with it.

Therefore 8 grams of the oil from the thiourea synthesis were heated with HCl in a water bath for four hours. Solution in the acid was incomplete. The insoluble material was extracted with chloroform and the remaining clear acid solution made alkaline. A yellow tarry base was precipitated which could not be completely dissolved in dilute acid. The acid solution was again extracted with chloroform and made alkaline and the liberated base extracted with ether. No crystals but a yellow oil remained. The picrate of this basic substance was made; yellow needles from alcohol, M. P. 187-80. It was analyzed by the method of Busch.1

1M. Busch and G. Blume. Z. angew. Chem. 21, 354.
59.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
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</thead>
<tbody>
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<td>wt.</td>
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</tr>
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<td>2</td>
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<tr>
<td>wt.</td>
<td>picrate</td>
<td>picrate</td>
</tr>
<tr>
<td></td>
<td>.2786</td>
<td>.3018</td>
</tr>
<tr>
<td>wt.</td>
<td>Gooch and</td>
<td>nitron picrate</td>
</tr>
<tr>
<td></td>
<td>&quot;nitron&quot;</td>
<td>19.1682</td>
</tr>
<tr>
<td></td>
<td>Gooch</td>
<td>18.8696</td>
</tr>
<tr>
<td>wt.</td>
<td>&quot;nitron&quot;</td>
<td>picrate</td>
</tr>
<tr>
<td></td>
<td>.2986</td>
<td>.3194</td>
</tr>
</tbody>
</table>

I. \[
\frac{.2986 \times 229 \times 100}{.2786 \times 541} = 45.47\% \text{ picric acid.}
\]

II. \[
\frac{.3194 \times 229 \times 100}{.3018 \times 541} = 44.80\% \text{ picric acid.}
\]

Calculated for \(C_{23}H_{210}N_5S\); \(C_6H_3N_3O_7\) 44.82%
PARA TOLYL MUSTARD OIL AND ALLYL PARA TOLUIDINE.

10 grams allyl para toluidine and 10.1 grams of para tolyl mustard oil were heated together for a few minutes at about 120°. The product was dissolved in boiling alcohol. On cooling a red oil separated out. After standing several weeks without crystallizing, it was diluted with ether and allowed to evaporate at room temperature. After several trials of this method about 1.5 grams of crystals were finally obtained. (About half of the oil had been used in an attempt to make the thiazole.) M. P. of the crystals 88°-93°. On a second trial 5 grams of the mustard oil were treated with 5.2 grams of the amine, the mixture dissolved in alcohol and ether, and the solution seeded with a few crystals from the previous trial. By this method about 5 grams of a crystalline product were obtained, melting at 109°-113°. Again recrystallized, M. P. 113°. Mixed with the product melting at 88°-93° the melting interval was 88°-112°.

ANALYSIS.

<table>
<thead>
<tr>
<th>wt. bottle</th>
<th>KJELDAHL</th>
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</thead>
<tbody>
<tr>
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<td>13.8120</td>
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<tr>
<td>2 bottle</td>
<td>12.4586</td>
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(con).

**ANALYSIS.**

<table>
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<th>Wt. Sample</th>
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<tr>
<td>Total vol. HCl</td>
<td>110.40</td>
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<td>Normality</td>
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</tr>
<tr>
<td>Total vol. KOH</td>
<td>9.40</td>
</tr>
<tr>
<td>Normality</td>
<td>.0887</td>
</tr>
</tbody>
</table>

\[
\frac{(110.40 - 9.40) \times 0.0885 \times 14 \times 100}{1.3534 \times 1000} = 9.26\%
\]

Calculated for C_{18}H_{20}N_{2}S; N 9.46%
2-PARATOLYLIMIDO 3-P.ARATOLYL 5-METHYL 4,5-DIHYDRO THIAZOLE (DOUBTFUL).

3.3 grams of the crystalline α(allyl βdi-paratolyl thiourea were heated for one and one-half hours in a pressure bottle in a water bath. Solution in the acid was incomplete. The insoluble material was separated by extraction with ether, the solution made alkaline, and the liberated basic substance extracted with ether. Nothing but an oil could be obtained. The picrate was made, dark yellow needles from alcohol, M. P. 140°-141°. This was analysed for picric acid.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
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<td>1. Wt. bottle</td>
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</tr>
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<td>2. Wt. bottle</td>
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<td>12.6077</td>
</tr>
<tr>
<td>Wt. picrate</td>
<td>.5572</td>
<td>.3578</td>
</tr>
<tr>
<td>Wt. Gooch and &quot;nitron&quot; picrate</td>
<td>15.0159</td>
<td>16.4523</td>
</tr>
<tr>
<td>Wt. Gooch</td>
<td>14.4212</td>
<td>16.0772</td>
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<tr>
<td>Wt. &quot;nitron&quot; picrate</td>
<td>.5947</td>
<td>.3194</td>
</tr>
</tbody>
</table>

\[
\text{I. } \frac{.5947 \times 229 \times 100}{.5572 \times 541} = 45.2\% \text{ picric acid.}
\]

\[
\text{II. } \frac{.3751 \times 229 \times 100}{.3578 \times 541} = 44.4\% \text{ picric acid.}
\]

Calculated for \(\text{C}_2\text{H}_2\text{S}_7\text{N}_5\text{S; C}_6\text{H}_3\text{N}_3\text{O}_7\) 43.6%
<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>M.P.</th>
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</thead>
<tbody>
<tr>
<td>Thiourea</td>
<td><img src="image1" alt="Thiourea" /></td>
<td></td>
</tr>
<tr>
<td>C₆H₅NCS</td>
<td><img src="image2" alt="C₆H₅NCS" /></td>
<td>91°</td>
</tr>
<tr>
<td>Thiazole</td>
<td><img src="image3" alt="Thiazole" /></td>
<td>98°</td>
</tr>
<tr>
<td>Allylaniline</td>
<td><img src="image4" alt="Allylaniline" /></td>
<td>120-1</td>
</tr>
<tr>
<td>Allyl p-toluidine</td>
<td><img src="image5" alt="Allyl p-toluidine" /></td>
<td>91.05</td>
</tr>
<tr>
<td>Thiourea</td>
<td><img src="image6" alt="Thiourea" /></td>
<td></td>
</tr>
<tr>
<td>BrC₆H₄NCS</td>
<td><img src="image7" alt="BrC₆H₄NCS" /></td>
<td>123°</td>
</tr>
<tr>
<td>Thiazole</td>
<td><img src="image8" alt="Thiazole" /></td>
<td>106-7°</td>
</tr>
<tr>
<td>Picrate only</td>
<td><img src="image9" alt="Picrate" /></td>
<td></td>
</tr>
<tr>
<td>Thiourea</td>
<td><img src="image10" alt="Thiourea" /></td>
<td></td>
</tr>
<tr>
<td>CH₃C₆H₄NCS</td>
<td><img src="image11" alt="CH₃C₆H₄NCS" /></td>
<td>107°</td>
</tr>
<tr>
<td>Thiazole</td>
<td><img src="image12" alt="Thiazole" /></td>
<td></td>
</tr>
<tr>
<td>Picrate only</td>
<td><img src="image13" alt="Picrate" /></td>
<td>113°</td>
</tr>
</tbody>
</table>

Note: M.P. = Melting Point
ATTEMPTED REACTIONS.

1. Attempt to make the hydrochloride of 2-phenyl-imido 3-phenyl 5-methyl 4,5 dihydro thiazole.
   (a) 5 grams of the thiazole were dissolved in benzene which had been dried over calcium chloride and HCl gas, dried by passage through conc. H₂SO₄, was passed into the solution. A dark red oil was thrown down which would not solidify on washing with petroleum ether.
   (b) 2 grams of the thiazole were dissolved in ether which had been dried, first over CaCl₂, then over P₂O₅ and the dry HCl passed through. An abundance of a white flocculent precipitate appeared, which was quickly filtered at the pump, washed with the dry ether, and placed in a dessicator over sulphuric acid. The salt proved to be very deliquescent, and went over even in the dessicator, to a white pasty mass, which when exposed to air became a syrup.

2. Attempt to add ethyl iodide.

   One gram of the above thiazole was treated with one gram of ethyl iodide and the mixture brought to a boil on a hot plate. On cooling crystals were deposited
which melted at 98°. Mixed with the original thiazole the melting point was 98°. Evidently no reaction had ethyl taken place. The crystals were again treated with iodide, brought to a boil, and allowed to stand over night. Crystals which were deposited melted at 98°. No test for iodide ion was obtained from the filtrate when shaken with water and tested with AgNO₃. The conclusion is that the thiazole, although having the structure of a tertiary amine, will not add ethyl iodide to form the quaternary ammonium salt.

3. Attempt to substitute oxygen for the phenyl-imido group of 2-phenylimido 3-phenyl 5-methyl 4, 5 di-hydro thiazole by hydrolysis.

2 grams of the thiazole were heated in a sealed tube with a solution of 5 c.c. conc. H₂SO₄ in 20 c.c. of water. The temperature was kept at 140° for four hours. On making the solution alkaline with NaOH a base was liberated which melted at 96° without purification. A mixed melting point with some of the original thiazole was 96°-98°. The filtrate was tested for aniline with bleaching powder with negative results.
It was thought that there was a possibility of the following reaction taking place:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{N} & - \text{CH}_2 \quad \overset{+\text{H}_2\text{O}}{\longrightarrow} \quad \text{C}_6\text{H}_5\text{N} - \text{CH}_2 \\
\text{C}_6\text{H}_5\text{N} & = \text{C} \quad \text{CH}_2 \quad + \text{C}_6\text{H}_5\text{NH}_2
\end{align*}
\]

Three attempts at a higher temperature failed because of failure of the tube.

4. Attempt to substitute a phenyl group in 2-phenylimido 5-methyl 4,5 dihydro thiazole.

This thiazole was prepared by the rearrangement of symmetrical allyl phenyl thiourea as mentioned in the introduction. M. p. 118°-119°. There were theoretically two possibilities as to the position of substitution, if substitution should occur:

\[
\begin{align*}
\text{I.} & \quad \overset{+\text{C}_6\text{H}_5\text{I}}{\longrightarrow} \quad \text{C}_6\text{H}_5\text{N} - \text{CH}_2 \\
\text{C}_6\text{H}_5\text{N} & = \text{C} \quad \text{CH}_2 \quad + \text{HI}
\end{align*}
\]
It is evident that if the substitution should take place according to equation I, that the product would be thiazole which has been made by the rearrangement of allyl diphenyl thiourea. This would throw light on the structure of the original thiazole, in a way similar to the methylation experiment of Young and Crookes. 

(a) Molar quantities of the thiazole and phenyl iodide were dissolved in nitrobenzene with the addition of a small amount of copper powder and boiled under a reflux air condense for eleven hours. There was a thermometer suspended in the condenser but the temperature varied with the briskness of the boiling and varied from 150°-170°. The reaction mixture was subjected to steam distillation to remove the nitrobenzene. The residue in

1. Loc. cit.
the flask was made acid and the cloudy acid solution extracted with ether to remove acid-insoluble tar. It was made alkaline, which liberated a base, was again made acid and as the acid solution was not clear it was again extracted with ether, the base was again liberated with NaOH, filtered and recrystallized from acetone and water. White needles, M. P. 118°. Mixed with some of the original thiazole, M. P. 118°. Evidently a product in which substitution had taken place was not isolated, at least.

(b) The experiment was repeated under identical conditions except that the heating was continued for twenty-two hours. On removal of the nitrobenzene by steam distillation a large amount of tarry material remained in the flask and although a basic substance was present all attempts to get a pure crystalline product failed.

5. Attempt to make unsymmetrical allyl phenyl thio-urea and rearrange to the thiazole:
5 grams of allyl aniline were dissolved in dilute HCl and 5 grams of NH₄NCS added. The solution was evaporated on the water-bath. As the water was driven off a dark red oil began to appear together with some white crystals which were found to be ammonium chloride. A small amount of water was added and the oil extracted with ether. On evaporating off the ether at room temperature no crystals were deposited, the thiourea(?) coming out as an oil. This was transferred to a pressure bottle, heated open for a while in a water-bath to drive off the ether, then about 100 c.c. conc. HCl added, the bottle closed and heated in the bath for three or four hours. On diluting with dilute alcohol and making alkaline a base made its appearance which, however, could not be obtained in a crystalline form. It was extracted with benzene, the benzene solution dried
with $\text{Na}_2\text{SO}_4$ and dry HCl passed in to the clear solution. The salt came down as a dark red oil, which did not solidify, even when well washed with petroleum ether.
I wish to express my appreciation of the manner in which the work was directed by Dr. F. B. Dains, and of the interest which he took in its progress. I also wish to include Dr. R. Q. Brewster in this acknowledgement.