The action of sulphuryl chloride upon naphthylamines

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for the Degree of

MASTER OF SCIENCE

-by-

CLIVE MORRIS ALEXANDER

June, 1913.
- THE ACTION OF SULPHURYL CHLORIDE UPON NAPHTHYLAMINES -

- Introduction -

Previous investigations have shown that sulphuryl chloride acts chemically in three ways to form sulphonation, chlorination, and oxidation products.

- Sulphonation -

The Action of Sulphuryl Chloride upon Ammonia

Thus Regnault\(^1\), one of the first investigators of the action of sulphuryl chloride, found that sulphamide was formed by the action of sulphuryl chloride on ammonia.

Traube\(^2\) obtained similar products by saturating a solution of sulphuryl chloride in chloroform with ammonia according to the equations:

1. J. pr. Chem. 18, 98.
2. B. 25, 2472 (1892); 26, 607 (1893).
SO₂Cl₂ + 4NH₃ = 2NH₄Cl + SO₂(NH₂)₂ (sulphamide)
SO₂Cl₂ + 3NH₃ = 2NH₄Cl + SO₂NH (sulphimide)
2SO₂Cl₂ + 7NH₃ = 4NH₄Cl + HN(SO₂NH₂)₂ (imido-disulphamide)

Hantzsch and Holl¹ also proved the same reactions, but that the sulphimide formed was a polymer.

SO₂Cl₂ + 4NH₃ = 2NH₄Cl + SO₂(NH₂)₂
3SO₂Cl₂ + 12NH₃ = 6NH₄Cl + (SO₂NNH₄)₃
3SO₂(NH₂)₂ = (SO₂NNH₄)₃ = 3NH₃ + (SO₂NH)₃ (trisulphimide)

Ephraim and Michel² state that when sulphuryl chloride is treated with an excess of ammonia in a ligroin solution surrounded by ice, the reaction is not the same as when sulphuryl chloride is used in excess; little or no sulphamide or trisulphimide is formed, but instead imido sulphamides and probably other long chain compounds with (NHSO₂) groups are formed.

SO₂Cl₂ + 4NH₃ = 2NH₄Cl + SO₂(NH₂)₂
SO₂Cl₂ + SO₂(NH₂)₂ = H₂NSO₂NHSO₂Cl + HCl
H₂NSO₂NHSO₂Cl + 2NH₃ = NH₄Cl + H₂NSO₂NHSO₂NH₂

H₂NSO₂NHSO₂NH₂
H₂NSO₂NHSO₂NHSO₂NH₂

-etc.-

1. B. 34,3430 (1901).
2. B. 42,3833 (1909); 43,138 (1910).
The Action of Sulphuryl Chloride upon Amines

Franchimont\(^1\) states that sulphuryl chloride acts normally with primary aliphatic amines to form sulphamides.

Behrend\(^2\) found that sulphuryl chloride with secondary amines gave sulphamides \(\text{SO}_2(\text{NR}_2)_2\) and amid sulphuryl chlorides \(\text{R}_2\text{NSO}_2\text{Cl}\). A chloroform solution of sulphuryl chloride and dimethyl amine react in the cold to form tetramethyl sulphamide. He assumes that dimethyl sulphamic chloride is the intermediate product.

\[
\text{SO}_2\text{Cl}_2 + 2\text{HN(CH}_3)_2 = (\text{CH}_3)_2\text{NSO}_2\text{Cl} + (\text{CH}_3)_2\text{NHCl} + (\text{CH}_3)_2\text{NH}
\]

Even the hydrochloride of dimethyl amine is acted upon similarly by sulphuryl chloride to form the sulphamic acid chloride which in turn will react with ammonia or an amine of the aliphatic or aromatic series forming sulphamides.

\[
\text{SO}_2\text{Cl}_2 + (\text{CH}_3)_2\text{NHCl} = (\text{CH}_3)_2\text{NSO}_2\text{Cl} + 2\text{HCl}
\]

2. Ann. 222, 116; B. 14, 722, 1810 (1881); 15, 1610 (1882)
Wohl and Koch\(^1\) state that when sulphuryl chloride acts on a large excess of aniline, dry ether being used as a solvent, the sulphanilide is formed.

\[
\text{SO}_2\text{Cl}_2 + 4\text{C}_6\text{H}_5\text{NH}_2 = 2\text{C}_6\text{H}_5\text{NH}_2\text{HCl} + (\text{C}_6\text{H}_5\text{NH})_2\text{SO}_2
\]

If moist ether is employed the product consists of aniline phenyl sulphamate.

\[
\text{C}_6\text{H}_5\text{NHSO}_2\text{OH}, \text{C}_6\text{H}_5\text{NH}_2
\]

Ephraim and Lasocki\(^2\), in their work with sulphuryl chloride and hydrazine, made sulphohydrazide \(\text{SO}_2(\text{NHNH}_2)_2\).

- Chlorination -

The Action of Sulphuryl Chloride upon Amines

Wenghoffer\(^3\) found that trichlor aniline was formed by the action of sulphuryl chloride upon aniline; and mono- and dichlor acetanilid from acetanilid. The ethereal solution of aniline was added in small quantities to sulphuryl chloride.

\[
\text{C}_6\text{H}_5\text{NH}_2 + 3\text{SO}_2\text{Cl}_2 = \text{C}_6\text{H}_2\text{Cl}_3\text{NH}_2 + 3\text{SO}_2 + 3\text{HCl}
\]

1. B. 43, 3295 (1910).
2. B. 44, 395 (1911).
3. B. 11, 149 (1878); J. pr. Chem. (2) 16, 448.
Wohl and Koch\textsuperscript{1} find that nitraniline, acetanilide, and aniline hydrochloride become exclusively chlorinated.

Behrend\textsuperscript{2} states that sulphuryl chloride chlorinates secondary aromatic amines. With diphenyl amine, tetrachlor diphenyl amine is formed.

Wenghoffer\textsuperscript{3} found that sulphuryl chloride acts upon dimethyl aniline to form dichlor dimethyl aniline.

The Action of Sulphuryl Chloride upon Other Compounds

Dubois\textsuperscript{4} states that sulphuryl chloride reacts with benzene when heated to give mono-chlor benzene, and with phenol when cooled to give chlor-phenol.

Reinhard\textsuperscript{5} investigated its action with resorcin and obtained mono-, di-, and trichlor resorcin.

Allihn\textsuperscript{6} finds that with acetoacetic ester it gives mono- and dichlor acetoacetic ester.

1. B. 43, 3295 (1910).
4. Z. (1866), 705.
5. B. 10, 1525 (1877); 11, 1381 (1878).
Norris, Thomas, and Brown found that by boiling sulphuryl chloride with tetraphenyl ethylene, tetraphenyl ethylene dichloride was formed. 

\[(\text{C}_6\text{H}_5)_2\text{CCl}_2-\text{CCl}(\text{C}_6\text{H}_5)_2\]

Tohl and Eberhard state that with benzenes and naphthylenes, chlorinated products are obtained, chlorination taking place both in the nuclei and side chain.

Peratoner and Geuco determined that sulphuryl chloride chlorinates phenols. With hydroquinone, dichlor hydroquinone is formed.

Paul Behrend finds that sulphuryl chloride acts as an acid chloride upon alcohols.

\[\text{SO}_2\text{Cl}_2 + \text{ROH} = \text{ROSO}_2\text{Cl} + \text{HCl}\]

\[\text{ROSO}_2\text{Cl} + \text{ROH} = \text{ROSO}_2\text{OR} + \text{HCl}\]

- Oxidation -

Sulphuryl chloride in some cases also acts as an oxidizing agent, but these reactions are few so far as the literature shows. In fact, when sulphuryl chloride acts as an oxidizing agent, the reaction is usually a side reaction to some other main one; as in the

1. B. 43, 2949 (1910).
2. B. 26, 2940 (1893).
4. B. 9, 1354 (1876).
action of sulphuryl chloride upon aniline not only sulphanilide, the main product, is formed, but also some azo benzene, as a side product, if ether is the solvent; some blue dye if benzene is the solvent; and some brown dye if chloroform or carbon tetrachloride is the solvent. In the last case the product is possibly some tri-anilido benzene $C_6H_3(NHC_6H_5)_3$. Monomethyl aniline is oxidized to a dark green dye.

As a result of the above investigations it is quite conclusive that the more basic the compound is, the greater the tendency to form sulphonation products; while the more acidic the compound is, the greater the tendency to form chlorination or oxidation products. The former reaction is favored by having the compound, basic in nature, in excess during the reaction. The latter reaction is favored by the reverse conditions, i.e., adding the compound to the sulphuryl chloride. The solvents used govern the products and yields of the reaction, but do not in general alter its direction, i.e., sulphonation, chlorination, or oxidation.

1. B. 43, 3295 (1910).
The reaction of sulphuryl chloride with the naphthylamines seems never to have been studied. In view of this fact, it was the object of this investigation to determine the action of sulphuryl chloride upon α- and β-naphthylamines. The possibilities of this reaction as deduced from those of similar bodies lie in three directions; the formation of sulphonation, chlorination, or oxidation products.
Upon the addition of sulphuryl chloride directly to either α- or β-naphthylamine, a very energetic exothermal reaction took place, evolving irritating gases and leaving a dark-colored mass. The reaction was more energetic with α-naphthylamine than with β-naphthylamine and also left a more colored mass. Consequently it was decided advisable to try the action in the presence of a solvent as a diluent to moderate the reaction.

- Experiment I. -

α-Naphthylamine

The first experiment was conducted at room-temperature. The sulphuryl chloride and α-naphthylamine were used in the proportion of one mole to four moles respectively. Dry diethyl ether was used as the solvent. A solution of 10 grams of sulphuryl chloride in 200 cc. of ether contained in a dropping funnel was dropped slowly into a solution of 42.5 grams of α-naphthylamine in 400 cc. of ether contained in a 1,500 cc. flask. The reaction mixture was constantly and rapidly
stirred by a mechanical stirrer. Upon addition of the sulphuryl chloride solution, a yellowish precipitate commenced immediately to form. This precipitate and solution became orange in color as the reaction proceeded. After the reaction mixture had stood for twenty-four hours, it was filtered and the precipitate washed with ether.

The precipitate was a light purple color. It dissolved almost completely in hot water with the exception of a little dark purple sticky oil. After purification, the substance soluble in water was found to be α-naphthylamine hydrochloride, which was identified by its properties and by converting into the free naphthylamine.

The filtrate was allowed to evaporate in the open and gave a dark purple sticky residue. This residue was almost insoluble in water, but very soluble in most organic solvents to a dark purple solution. Several solvents and means of purification were tried, but these were all unsuccessful in converting this sticky residue into crystalline products. This substance was also treated with dilute alkali solution in order to extract any sulphamide, if present,
but none was found.

Further investigations on \( \alpha \)-naphthylamine were abandoned at this point and \( \beta \)-naphthylamine taken up.

- Experiment II. -

\( \beta \)-Naphthylamine

Two experiments were tried with sulphuryl chloride and \( \beta \)-naphthylamine in the proportions one mole to four and six moles respectively. The same conditions and manipulations were used as with \( \alpha \)-naphthylamine. In this case the reaction mixture, after standing twenty-four hours, was not so colored as with \( \alpha \)-naphthylamine. After filtering and washing, the precipitate was a pale yellow and the filtrate a bright red.

The precipitate was soluble in water and by further treatment was found to be \( \beta \)-naphthylamine hydrochloride.

After the filtrate had evaporated in the open, a dark purple sticky residue remained. This was found to contain a little free \( \beta \)-naphthylamine, but the main part could not be purified and identified as was the case with
the similar product from α-naphthylamine.

- Experiment III. -

An investigation of the reaction when an ethereal solution of β-naphthylamine was added to an ethereal solution of sulphuryl chloride was now taken up.

A solution of 14.3 grams (one mole) of β-naphthylamine in 400 cc. dry ether, contained in a dropping funnel, was dropped slowly into a solution of 27 grams (two moles) of sulphuryl chloride in 400 cc. dry ether contained in a 1,500 cc. flask surrounded by ice. The reaction mixture was constantly and rapidly stirred by a mechanical stirrer. Some hydrogen chloride and a little sulphur dioxide were given off during addition, but precipitation did not take place immediately. The reaction mixture was not appreciably colored after standing several hours. After filtering the precipitate was white and the filtrate almost colorless.

The precipitate dissolved easily in hot water. This water solution gave tests for
chlorides and also a precipitate when neutralized with dilute alkali solution. This latter precipitate was found to be free $\beta$-naphthylamine. Further tests and properties showed that the precipitate formed during the above reaction was $\beta$-naphthylamine hydrochloride.

The filtrate after evaporation on the water bath gave a slightly colored residue which was found to crystallize well from benzine (60-70°) in clusters of colorless needles melting at 105°C. It was also found that the filtrate contained no excess sulphuryl chloride.

- Experiment IV. -

Another experiment was made with the following proportions: 14.3 grams (one mole) of $\beta$-naphthylamine in 400 cc. dry ether and 54 grams (4 moles) sulphuryl chloride in 400 cc. dry ether. Considerable hydrogen chloride and a little sulphur dioxide were given off. In this case the precipitation did not commence until about two-thirds of the amine had been added. The same products were obtained.
from the reaction mixture, but with different yields. The quantity of \( \beta \)-naphthylamine hydrochloride was decreased, and the compound melting at 105°C. obtained from the filtrate was increased.

- Experiment V. -

It was now decided to determine what proportions would be necessary to just prevent any permanent precipitate during the reaction. This investigation showed that the proportion of one mole of the amine to five moles of the sulphuryl was necessary.

Preparation

The best conditions and manipulations for the reaction were as follows: 67.5 grams (five moles) of sulphuryl chloride was dissolved in 400 cc. dry diethyl ether and placed in a 1,500 cc. flask containing a mechanical stirring device and surrounded by ice. 14.3 grams (one mole) of \( \beta \)-naphthylamine was dissolved in 400 cc. of dry diethyl ether and placed in a dropping funnel. The ethereal solution of the \( \beta \)-naphthylamine was now dropped slowly into
the ethereal solution of the sulphuryl chloride, which was constantly and rapidly stirred. The rate of addition of sulphuryl chloride was so regulated that at no time was there any appreciable quantity of precipitate present in the reaction mixture. In case a quantity of precipitate did form, the addition of sulphuryl chloride was stopped until the precipitate redissolved. About two hours were required for complete addition. Considerable hydrogen chloride but very little sulphur dioxide was given off during the reaction.

The solution was now placed in a distilling flask and the ether distilled on the water bath until only about 50 cc. of the solution remained. This last portion was further distilled under low pressure at room-temperature to dryness. Later, it was found advisable to distill the whole at room-temperature (about 20°C, or below) under low pressure, as a little better yield and a more nearly pure product could be obtained. During distillation, some hydrogen chloride and large quantities of sulphur dioxide were given off.
Properties

The product thus obtained from this reaction crystallized in clusters of colorless needles from benzine (60-70°). A good yield resulted. The purified compound melted at 105°C, and contained nitrogen and chlorine.

Analysis

A quantitative analysis gave the following results:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found</th>
<th>Cal.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (1) 0.3000 gm.</td>
<td>CO₂ 0.4139 gm.</td>
<td>C 37.64%</td>
</tr>
<tr>
<td>(2) 0.3000 gm.</td>
<td>CO₂ 0.4174 gm.</td>
<td>C 37.93%</td>
</tr>
<tr>
<td>H (1) 0.3000 gm.</td>
<td>H₂O 0.0530 gm.</td>
<td>H 1.97%</td>
</tr>
<tr>
<td>(2) 0.3000 gm.</td>
<td>H₂O 0.0550 gm.</td>
<td>H 2.03%</td>
</tr>
<tr>
<td>Cl (1) 0.2000 gm.</td>
<td>AgCl 0.4510 gm.</td>
<td>Cl 55.80%</td>
</tr>
<tr>
<td>(2) 0.2000 gm.</td>
<td>AgCl 0.4513 gm.</td>
<td>Cl 55.80%</td>
</tr>
<tr>
<td>N (1) 0.5172 gm. .1N H₂SO₄ 16.17 cc.</td>
<td>N 4.38%</td>
<td>4.36% 4.42%</td>
</tr>
<tr>
<td>(2) 0.6566 gm. .1N H₂SO₄ 20.29 cc.</td>
<td>N 4.34%</td>
<td>99.95 100.00</td>
</tr>
</tbody>
</table>

The above percentage composition showed that the empirical formula of the compound was C₁₀H₆NCl₅.

2. Kjedehl Method.
By the freezing-point method its molecular weight determined in benzene gave 310; calculated for \( \text{C}_{10}\text{H}_6\text{NCl}_5 \) it should be 317.3.

Solubility

Very soluble in ethyl alcohol.

" " " methyl alcohol.

" " " diethyl alcohol.

" " " carbon tetrachloride.

" " " benzene.

" " " chloroform.

" " " ethyl acetate.

" " " acetone.

" " " toluene.

" " " glacial acetic acid.

Much more soluble in hot than in cold benzine.

" " " " " " " dilute acetic acid.

Insoluble in water.

" " dilute alkali.

" " dilute mineral acids.

After treating the compound \( \text{C}_{10}\text{H}_6\text{NCl}_5 \) with water or dilute alkali solution, no chlorides could be found in the filtrate, which showed that it undoubtedly was not an hydrochloride of a chlor \( \beta \)-naphthylamine.
Oxidation

Upon oxidation of the compound with chromic acid a mono-basic acid was obtained.

The following mixture:

20 grams of the compound
50 cc. of conc. sulphuric acid
100 cc. of water
50 grams of sodium dichromate

was placed in a 300 cc. flask to which was attached a reflux condenser and boiled with a free flame for four or five hours. This mixture was then filtered, the filtrate discarded, and the resulting greenish residue extracted with boiling water. The water extract, upon cooling, gave fine colorless needles which after recrystallization melted at 118-119°C.

This oxidation product was readily soluble in cold dilute alkali. When titrated with tenth normal alkali, it gave 0.473% acid hydrogen. .0930 gm. compound required 4.40 cc. .1N NaOH; (acid) H 0.473%.

Qualitative tests showed that chlorine was present.
A quantitative analysis of this acid gave:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found</th>
<th>Cal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>.2700 gm.</td>
<td>CO₂ .4908 gm.</td>
</tr>
<tr>
<td>H</td>
<td>.2700 gm.</td>
<td>H₂O .0677 gm.</td>
</tr>
<tr>
<td>Cl</td>
<td>.1870 gm.</td>
<td>AgCl .2486 gm.</td>
</tr>
<tr>
<td>O (by difference)</td>
<td>0</td>
<td>14.78%</td>
</tr>
</tbody>
</table>

These percentages correspond to a dichlor mono-basic acid of the empirical formula C₉H₆O₂Cl₂ or C₆H₅Cl₂COOH, but no such compound melting at 118-119° could be found in the literature. It is possible that this compound may be o-dichlor vinyl benzoic acid², which melts at 120-121°, or one of a similar type. Further work is in progress to determine the validity of this assumption.

Additional Properties of the Compound C₁₀H₆NCl₅

Some properties of the initial compound C₁₀H₆NCl₅ which aid in determining the exact structure are as follows:

The compound when heated alone on the water bath gave off hydrogen chloride and left as a residue, a reddish brown sticky mass.

2. C₁H₅=C(Cl)₅H₄COOH
   Zincke, B. 20, 2895 (1887); 21, 3556 (1888).
This in all probability showed that some of the chlorine atoms were additive.

Furthermore, the compound when warmed with concentrated hydrochloric acid gave off free chlorine slowly. An alcoholic solution of the compound, when acidified with concentrated hydrochloric acid, and potassium iodide added, liberated free iodine. This was also the case when a glacial acetic acid solution was treated with potassium iodide. The iodine in this experiment was readily liberated, and after diluting with a large quantity of water was titrated with a standard sodium thiosulphate solution.

1.000 gm. of compound required 66.00 cc. of 0.1N Na₂S₂O₃ = .2340 gm. Cl.

Cl Found, 23.40%. Cal., 22.36%.

The result of this titration showed the quantity of iodine liberated was equivalent to two chlorine atoms. Upon diluting the acetic acid solution, a white precipitate was formed. This precipitate, when recrystallized from dilute acetic acid, gave colorless needles; their composition and melting point were not determined. This property of liberating
chlorine with hydrochloric acid and iodine with hydriotic acid is a common property of chlorine atoms\(^1\) attached to the nitrogen, and hence points to a dichlor amine.

An alcoholic solution of the compound \(\text{C}_10\text{H}_6\text{NCl}_5\) reacted in the cold with alcoholic soda. Sodium chloride was precipitated and an orange red solution formed. The formation of color here pointed to a reaction of the alkali with the dichlor amine group to form a nitroso group, at the same time precipitating sodium chloride. The amount of sodium chloride precipitated was approximately determined by filtering and weighing. This determination gave results much too large for a reaction with only two chlorine atoms, and hence pointed to a reaction of the alkali with chlorine additive

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1. Kohler, B. 12, 771, 1870 (1879).
   Bamberger and Renauld, B. 28, 1683 (1895).
   Berg, A. ch. (7) 3, 318; B. 26 (2), 188 (1893); Bl. (3) 3, 687 (1890).
   Tscherniak, B. 9, 146 (1876); 12, 2129 (1879); 32, 3582 (1899).
   Seliwanow, B. 25, 3621 (1892).
   Lippmann and Regensdorfer, B. 30, 2053 (1899).
   Baeyer, A. 107, 261.
   Pierson and Heumann, B. 16, 1047 (1883).
   Paloma, B. 32, 3343 (1899).
   Brühl, Ph. Ch. 16, 214 (1895).
atoms\(^1\) which would also give a precipitation of sodium chloride. In view of these results with alcoholic soda, the validity of a dichlor amine and also chlorine additive atoms was further confirmed. Absolute proof on the other hand only lies in determining the derivatives thus formed by these reactions.

- Experiment VI. -

In the preparation of the compound \(C_{10}H_6NCl_5\) it was found that if the solvent, ether, was not dry, a more exothermal reaction took place and the reaction mixture became quite colored. The reaction mixture was allowed to stand several hours, after which the ether was distilled off. The resulting reddish brown residue was only partially soluble in hot benzine. From the benzine extract a colorless compound crystallizing in elongated prisms was obtained. It melted at 112-113\(^\circ\) and gave tests for chlorine, but not for sulphur or nitrogen.

1. Fischer, B. 11, 735; 11, 1411 (1878).
   Armstrong and Wynne, B. 24 (2), 713 (1891).
   Widman, Bl., 28, 506 (1895).
   Atterberg and Widman, B. 10, 1842 (1877).
A quantitative analysis gave the following results:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found</th>
<th>Cal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C  .3000 gm.</td>
<td>CO₂ .4128 gm.</td>
<td>C 37.54% 37.70%</td>
</tr>
<tr>
<td>H  .3000 gm.</td>
<td>H₂O .0443 gm.</td>
<td>H 1.64% 1.57%</td>
</tr>
<tr>
<td>Cl².2000 gm.</td>
<td>AgCl.4530 gm.</td>
<td>Cl 56.00% 55.71%</td>
</tr>
<tr>
<td>O (by difference)</td>
<td>0</td>
<td>4.82% 5.02%</td>
</tr>
</tbody>
</table>

These results correspond to a compound of the empirical formula C₁₀H₅OCl₅, but an identical compound cannot be found in the literature.

Properties

Quite soluble in diethyl ether
" " ethyl alcohol
" " carbon tetrachloride
" " benzene

Insoluble in water, hot or cold

It dissolved readily in warm dilute alkali, forming a green solution while hot and a brown while cold. This solution, when neutralized with dilute nitric acid, gave a light brown precipitate. The compound C₁₀H₅OCl₅ is probably a keto compound of the

type made by Zincke\textsuperscript{1} which split with alkali to form a monobasic acid. This product was not further studied, as very small yields were obtained.

1. B. 20, 2890 (1888); 21, 3540 (1889).
(1) Sulphuryl chloride and either \( \alpha \)-or \( \beta \)-naphthylamine in the absence of a solvent react energetically, resulting in the formation of a dark-colored product.

(2) A solution of sulphuryl chloride in dry diethyl ether, when added to an excess of a solution of \( \alpha \)-or \( \beta \)-naphthylamine in dry diethyl ether, reacts to form the naphthylamine hydrochloride and a dark purple viscous substance of unknown composition.

(3) A solution of \( \beta \)-naphthylamine in perfectly dry diethyl ether, when added to a solution of sulphuryl chloride in dry diethyl ether, reacts with an evolution of hydrogen chloride and sulphur dioxide and with the formation of colorless chlorination products. If the \( \beta \)-naphthylamine and sulphuryl chloride are in the proportion one mole to five moles respectively, the chlorination product formed has the empirical formula \( \text{C}_10\text{H}_6\text{NCI}_5 \), melts at 105\( ^\circ \)C., and crystallizes in clusters of colorless needles from benzine. This product seems to have two chlorine atoms attached to the
nitrogen and the others additive. It gives upon oxidation with sulphuric acid and sodium dichromate mixture, a dichlor monobasic acid which has the empirical formula C$_9$H$_5$O$_2$Cl$_2$ or (C$_9$H$_5$Cl$_2$COOH), melts at 118-119° and crystallizes from water in colorless needles.

If the β-naphthylamine and sulphuryl chloride are used in the proportion one mole of the former to less than five moles of the latter, β-naphthylamine hydrochloride is also formed.

(4) A solution of β-naphthylamine in moist ether, when added to a solution of sulphuryl chloride in moist ether, reacts forming the compound C$_{10}$H$_5$OCl$_5$, which melts at 112-113° and crystallizes in elongated prisms from benzine, and a dark-colored viscous product which was not further studied.

- Acknowledgement -

The writer desires to express his gratitude to Dr. William J. Karslake, at whose suggestion and under whose supervision this investigation was carried out.
Clive Morris Alexander was born in Leon, Iowa, April 28, 1889, and there received his public school education, graduating from the Leon High School in May, 1907. He entered the State University of Iowa in September, 1907, and graduated from that institution in June, 1911, receiving the degree of Bachelor of Science in Chemistry. At the State University of Iowa, during the Summer Session of 1909, he was store-keeper in the Department of Chemistry, and during the Summer Session of 1911, Assistant in Chemistry. He studied in Harvard University at the Summer Session of 1912. The two years 1911-12 and 1912-13 were spent in graduate work and as Assistant Instructor in Chemistry at the State University of Iowa. He is a member of the Sigma Xi and the American Chemical Society.