THESIS
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By
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THE MOBILITY OF SEMICYCLIC TRIAD SYSTEMS CONTAINING AN OXAZOLE RING.
Author's note

The experiments described in this thesis were carried out by myself under the directions of Professor R.F. Hunter, and Dr. R.D. Desai, in the chemical laboratories of the Muslim University, Aligarh, during the years 1933-1936.

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(1). 5-Bromo-1-aminobenzoxazole, 6-bromo-1-hydroxybenzoxazole and 5-bromo-1-mercapto-benzoxazole have been methylated. In each case the methylation took place at the nuclear N, like their parent compounds.

(2). Derivatives of 2-amino-1-naphthol.

The following have been prepared and their methylation studied: i. 1-aminoo-2-naphthoxazole, ii. 1-hydroxy-2-naphthoxazole, iii. 1-anilino-2-naphthoxazole iv. 1-mercapto-2-naphthoxazole.

In i and ii methylation took place at N and only one isomer was obtained. Whereas iii iv gave each two isomers. The constitutions of all these methylation products have been discussed in the theoretical.

(3). Derivatives of 1-amino-2-naphthol.

All these derivatives have been prepared according to identical methods. They have also been methylated, their behaviour is exactly similar to the a-series.
It appeared of particular interest from the point of view of the theory of sextuple group stability to compare the behaviour of semicyclic triad systems containing an oxazole ring \( (I \rightarrow II) \) with that of thiazole derivatives (Hunter, J.C., 1926, 1585; 1930, 125; Hunter and Jones, ibid., 241, 2190).

\[
\begin{align*}
\left| \begin{array}{c}
0 \\
\end{array} \right> & \quad e^x \left| \begin{array}{c}
[H] \\
\end{array} \right> \\
\left| \begin{array}{c}
0 \\
\end{array} \right> & \quad e^{-x} \left| \begin{array}{c}
[H] \\
\end{array} \right>
\end{align*}
\]

\( (H) \) mobile hydrogen atom.

This theory, which attributes the stability of aromatic systems to the formation of a highly stable, sextuple valency group was first advanced by Pemberger (Ber., 1891, 24, 1758; 1893, 26, 146; Annalen, 1893, 273, 373) is expressed in one form in the centric formula for benzene and in another in the Thiele partial valency formula.

which may, as Professor Ingold has pointed out (Annual Report of the Chemical Society, 1928, 119), be regarded as the classic representatives of the two views that the association is central and peripheral respectively. The main evidence in favour of this idea was given by Pemberger himself who pointed out that pyrroles are weak bases because the salt forming valencies are wanted in the formation of the sextuple group.
while pyridines are strong bases because this can be formed without calling on the additional valencies of the ring nitrog atom.

This conception may be represented in the modern way by the formula (III) and (IV) suggested by Ingold and Goss (J.C.S., 1928, 1266) in which each arrow represents a contributing electronic supplent.

![Diagram](image)

The application of these ideas to thiophene (Ingold and Goss loc cit) and to thiazole (Hunter, J.C.S., 1930, 125; Parrot and Hunter, J. Ind. Chem. Soc., 1932, 2, 545) seem obvious. In thiophene a lone pair of electrons of the ring sulphur atom is wanted for the completion of sextuple group, which brings about the inertness of the sulphur atom towards bromine and alkyl halides as compared with divalent sulphur in the dialkyl sulphides.

![Diagram](image)

Similarly in thiazole ring sulphur atom contributes the pair of electrons necessary for the sextuple group which is thereby completed without calling on the lone pair of electrons of the nitrogen atom which are therefore reactive.

![Diagram](image)

The thiazoles therefore show the greatest resemblance to the pyridines and give rise to addition products with bromine and
alkyl halides on account of the reactivity of the lone pair of electrons of nitrogen:

\[ \geq N: + Br_2 \rightarrow \geq N < Br_r \]

\[ \geq N: + R^+ \quad \left[ \geq N R \right] ^+ \]

Considerable support has been given to the sextuple group theory by Heitler's wave mechanical analysis of the benzene molecule (Z. Physik., 1931, 70, 204). Thus it has been shown that a system of six electrons constitutes a "closed ring" somewhat analogous to the duplet of helium and the octet of neon, which are the basis of the electronic theories of valency. Although the effect of distributed symmetry in heterocyclic compounds of the type of pyridine and thiophene cannot be calculated, it is reasonable to suppose that the importance of the sextuple group still persists in relation to the chemical behaviour (compare Farooq and Hunter, loc cit).

The sextuple valency group has been used to explain a number of points in connection with the behaviour of tautomeric compounds of the thiazole group (Hunter, loc cit). The behaviour of mobile semicyclic amidines of aminothiazole type (V \( \rightleftharpoons \) VI) may be taken as an example.

\[ (V) \quad S \quad C \quad N[H] \quad H \quad \left[ \geq N R \right] ^+ \]

\[ (VI) \quad S \quad C = N[H] \]

The aminothiazoles have an almost overwhelming tendency to
react in the amino aromatic form (V) except when strong 
conjugating influences which tend to draw the double bond into the positions are present. The greater stability of the amino aromatic form (V) than that of the imino dihydro phase (VI) has been explained on the basis of the sextuple group as shown in formula (V) (Hunter and Jones, J.C.S. 1930, 252, 2190; Choudhr, Desai and Hunter, J. Ind. Chem. Soc. 1935, 12, 638; compare also Parken thesis London, 1937).

It might therefore be expected that the oxazoles would show a striking similarity to their sulphur analogues and this is the case. They nevertheless retain certain distinctive features of the oxazole ring system, such as a much greater ease of hydrolysis.

**1-Aminophenoxazone** (VII = VIII) could not be obtained from phenylcarbamide and bromine under the usual conditions of thisazole cyclization of arylthiocarbamide, nuclear substitutio occurring with the production of p-brom-phenylcarbamide and then of 2:4 dibromphenylcarbamide. The base was obtained by the action of mercuric oxide on O-hydroxyphenylthiocarbamide and also by treatment of 1-thiophenoxazone with ammonia.

```
\[
\begin{align*}
\text{VII} & \xrightarrow{\text{H}^+} \text{H} \\
\text{VIII} & \xrightarrow{\text{H}^+} \text{H}\ \\
\text{VII} & \xrightarrow{\text{H}^+} \text{H} \\
\end{align*}
\]
```

The presence of the u-amino group was established by the formation of a dihydrogen chloride which coupled with alkaline
1-naphthol to give an azo dye, and was converted into 1-chloro benzoxazole by the Sandmeyer reaction.

\[
\text{C}_6\text{H}_4\text{NH} \xrightarrow{\text{NCl}} \text{C}_6\text{H}_4\text{NHCl} \xrightarrow{\text{HCl}} \text{C}_6\text{H}_4\text{N}^+\text{Cl}^- \xrightarrow{\text{MeOH}} \text{C}_6\text{H}_4\text{NMe}^+\text{Cl}^-
\]

On methylation it gave 1-imino-1-methyl-1:2-dihydrobenzoxazole (X), whose structure follows from its hydrolysis to 0-methyl aminophenol(XI).

No evidence was obtained of the formation of isomeric 1-methyl aminobenzoxazole (XII) which was synthesised from 1-thiobenz oxazole and mono methylamine.

Substitution of a hydrogen atom of the amino group by phenyl however, stabilises the imino dhydro form of the triad system (compare, Hunter and Jones, J.C.S., 1930, 2193), and the methylation of 1-anilino benzoxazole (XIII \xrightarrow{\text{MeOH}} XIV) gave rise to a mixture of 1-phenylmethylaminobenzoxazole (XVI), in which the former isomeride derived from the amino aromatic form (Turtle and Pyman, J.C.S., 1928, 123, 362; Hunter and Stiles, J.C.S., 1928, 3019) was present in larger amount (Rasan, Hunter and Khalidi, J.C.S., 1934, 1196).
1-Hydroxybenzoxazole (XVII) was obtained by the action of carbonyldichloride on 0-aminophenol and by the hydrolysis of 1-chlorobenzoxazole:

\[
\begin{align*}
\text{C}_6\text{H}_4 < \overset{\circ}{\text{N}} > \cdot \text{C} \cdot \text{N} > & \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_4 < \overset{\circ}{\text{N}} > \cdot \text{C} = \text{N} \cdot \text{H} \\
\text{C}_6\text{H}_4 < \overset{\circ}{\text{N}} > \cdot \text{C} \cdot \text{N} > & \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_4 < \overset{\circ}{\text{N}} > \cdot \text{C} = \text{N} \cdot \text{H} \\
\text{C}_6\text{H}_4 < \overset{\circ}{\text{N}} > \\ \\
\end{align*}
\]

The most convenient method of preparation, however, was from 0-aminophenol and chloroformic ester (Fender, Ber., 1936, 19, 2269).

\[
\begin{align*}
\text{C}_6\text{H}_4 < \overset{\circ}{\text{N}} > \\ \\
\end{align*}
\]

On methylation in alkaline medium it behaved in a similar manner to 1-hydroxybenztiazole (Hunter, J.C.S., 1930, 125; Hunter & Parken, J.C.S., 1935, 1785) and yielded 1-keto-2-methyl 1:2-dihydrobenzoxazole (XX) whose constitution follows from it synthesis from the 1-nitrosoimino-derivative (XX) by Pestham's method (Ber., 1910, 43, 1523).

\[
\begin{align*}
\text{C}_6\text{H}_4 < \overset{\circ}{\text{N}} > \\ \\
\text{C}_6\text{H}_4 < \overset{\circ}{\text{N}} > \\
\text{H}_3 \\ \\
\text{C}_6\text{H}_4 < \overset{\circ}{\text{N}} > \\
\text{CF}_3 \\
\end{align*}
\]
1-Thiobenzoxazole (XXX \(\rightarrow\) XXII) was obtained by the heating of 0-hydroxothiocarbamide and by the action of sodium hydrosulphide on 1-chlorobenzoxazole.

It was also prepared by the action of both thiocarbonyl chloride and carbondisulphide on O-aminophenol.

Methylation of 1-thiobenzoxazole gave an oil which differed from 1-thio-3-methyl-1:2-dihydrobenzoxazole (XXVII), obtained by the action of phosphorous pentasulphide on 1-keto-3-methyl-1:2-dihydrobenzoxazole, which was characterised by the double compound which it formed with mercuric chloride and was evident the 3-methyl ether (XXIV).
Section I.
Tautomeric mobility of the derivatives of 3-substituted benzoxazoles.

Attention was next directed towards the effect of halogen substitution on the tautomericism of the benzoxazoles triad system, the 5-bromo derivatives (XXV  XXVI) being selected for the study.

\[
\begin{align*}
\text{(XXV)} & \\
\text{(XXVI)}
\end{align*}
\]

Tautomeric mobility of 5-bromo-1-hydroxybenzoxazole.

The 5-bromo-1-hydroxybenzoxazole, obtained by direct bromination of 1-hydroxybenzoxazole (compare D. B. Hunter and Khalidi, loc cit) was first shown to be 5-bromo derivative (XXV  XXVI, X:0) by the following synthesis:

5-nitro-1-methylbenzoxazole (G. Newbery & K. A. Phillips, J.C.S., 1928, 121), was hydrolysed and the resulting nitroaminophenol (XXVIII) was condensed with chloroformic ester. The product (XXIX) was converted into 5-nitro-1-hydroxybenzoxazole (XXX), which gave the 5-amino derivative bromate (XXXI) on reduction, which in turn was converted into the 5-bromo derivative by the usual Sandmeyer reaction:

\[
\begin{align*}
\text{(XXXVII)} & \\
\text{(XXXVIII)} & \\
\text{(XXXIX)} & \\
\text{(XXXI)}
\end{align*}
\]
When 5-bromo-1-hydroxybenzoxazole was boiled with concentrated hydrochloric acid, it underwent fission into the hydrochloride of 5-bromo-0-aminophenol.

5-Bromo-1-hydroxybenzoxazole on methylation in alkalimedium behaved similarly to the simple 1-hydroxybenzoxazole already described and yielded the 1-methyl derivative (XXXII) whose constitution follows from the fact that the same product is obtained by the bromination of 1-keto-2-methyl-1:2-dihydrobenzoxazole.

(2). *Parrameric mobility* of 5-bromo-1-thienbenzoxazole.

1-Thienbenzoxazole on bromination in chloroform yielded 5-bromo derivative (compare, Besai, Hunter and Khelidi, loc cit), whose structure has been established by the following synthesis: 5-nitro-1-thienbenzoxazole was prepared by refluxing a mixture of 5 5,5-nitro-0-aminophenol and solid caustic potash. (XXXIII). On reduction it gave 5-amino derivative (XXXIV) which in turn was converted into the 5-Bromo derivative by the usual Sandmeyer reaction:

This on methylation either with dimethyl sulphate or methyl iodide, behaved similarly to the unsubstituted thiol derivativ
already described, gave 5-bromo-1-methylthiobenzoxazole
unaccompanied by the isomeric 5-bromo-1-thio-2-methyl-1:2-
dihydrobenzoxazole which was easily synthesised by the action
of PS on 5-bromo-1-keto-2-methyl-1:2-dihydrobenzoxazole. The
identity of 2-methyl derivative was also established from the
fact that the same product was obtained by the bromination
of 1-methylthiobenzoxazole.

\[
\begin{align*}
\text{Bromination} \\
\text{(3). Tautomeric mobility of 5-bromo-1-aminobenzoxazole.}
\end{align*}
\]

This substance was prepared by the direct bromination
of 1-aminobenzoxazole. When boiled with Conc. HNO₃ the hydrochloric
acid of 5-bromo-o-aminophenol was obtained. This product was
identical with the specimen obtained by the hydrolysis with
Conc. HNO₃ of 5-bromo-1-hydroxybenzoxazole. Hence in this case
also the bromination goes to the 5 position. 5-Bromo-1-amino-
benzoxazole (XXV < XXVI, X = Br) simulated the corresponding
thiazole derivative (Hunter and Jones, loc cit) and yielded
5-bromo-1-imino-2-methyl-1:2-dihydrobenzoxazole (XXXVII)
on methylation, no evidence of the presence of the isomeric
\text{XXXVIII}
\]

5-bromo-1-thiobenzoxazole and mono methylamine, being obtaine
Section II.

Tautomeric mobility of α-Naphthoxazoles.

It appeared of interest to extend the earlier investigations on the behaviour of semicyclic triad systems containing a naphthothiazole complex (Hunter and Jones, J.C.S., 1930, 941; Choudry, Desai and Hunter, J. Ind. Chem. Soc., 1930, 10, 537) to the oxazole analogues, and the α-naphthoxazoles and β-naphthoxazoles \( \text{(XLVI)} \) were therefore studied:

\[
\begin{align*}
& \text{(XLI)} \\
& \text{(XLVI)}
\end{align*}
\]

Tautomeric mobility of 1-Amino-α-Naphthoxazole and 1-Anilino-α-Naphthoxazole.

2-Amino-α-naphthol \( \text{(XLI)} \) was first prepared by reduction of 2-nitro-α-naphthol (Hudgson and Wilson, J.C.S., 1924, 122, 607) and thereafter converted into the 1-hydroxy-2-naphthylthioacetamide \( \text{(XLIII)} \) by treatment of its hydrochloride with potassium thiocyanate.
Treatment of this thiourea-amine in alcoholic solution with mercuric oxide yielded 1-amino-α-naphthoxazole (\(\text{C}_1\))

The yield of 1-amino-α-naphthoxazole was very poor, a large amount of 1-thiol-α-naphthoxazole being formed. This is in marked contrast with the analogous preparation of 1-aminobenzoxazole which is not accompanied even by a trace of the corresponding thiol derivative.

On methylation with methyl iodide, this amine gave a methyl derivative isomeric with 1-methylamino-α-naphthoxazole (\(\text{C}_2\)), synthesised from 1-thiol-α-naphthoxazole and methylamine and which is evidently the 1-imino-2-methyl-1:2-dihydro-α-naphthoxazole (\(\text{C}_3\)). Thus the behaviour of 1-amino-α-naphthoxazole on methylation was exactly similar to that of 1-amino-α-naphthiazole (compare Hunter & Jones, loc cit)

This is evidently due to the effect of aromatic conjugation of the heterocyclic ring on the double bond (1:2) of the amino phase.
It has been shown (compare Desai, Winter and Maleki, loc cit) that the phenyl group of the anilino substituent in 1-anilino benzoxazole competes with the aromatic conjugation of the heterocyclic nucleus for the proximity of the double bond of the triad system during methylation, and an effect similar to this might be anticipated in 1-anilino-α-naphthoxazole.

\[
\begin{align*}
\text{C}_6\text{H}_5\left<^6\right>\text{N}\text{H}_2^+ & \quad \text{C}_6\text{H}_5\left<^6\right>\text{N}^+ \quad e = \nearrow \\
(\text{XLVI}) & \\
(\text{XLVII})
\end{align*}
\]

This is actually the case, and this anilino-α-naphthoxazole on methylation gave rise to a mixture of the 1-phenylmethyl aminonaphthoxazole (XLIX) whose constitution follows from its synthesis from 1-thioc-α-naphthoxazole and mono methyl aniline and the isomeric 1-phenylamino-2-methyl-1:2-dihydro derivative.

\[
\text{(L)}
\]

(2). Tautomer mobility of 1-hydrox-α-naphthoxazole.

1-hydrox-α-naphthoxazole (L \Leftrightarrow \text{LII}) was prepared by the condensation of α-aminonaphthol with either phosgene or chloroformic ester or urethane.
On methylation this behaved similarly to 1-hydroxy-α-naphthiame (Hunter & Jones, loc cit) and also similar to 1-hydroxybenzoxazole (compare, Desai, Hunter & Khaledi, loc cit) and yielded the N-methyl derivative. The constitution of this follows from the fact that 2α-9α-methylamino-α-naphthol was obtained when the methyl derivative was heated in a sealed tube at 100°C for 12 hours. This is in marked contrast with the much greater ease of hydrolysis of 1-keto-9α-methyl-1:8-dihydrobenzoxazole. The resulting basic product melts at and is different from 1-hydroxy-α-naphthylamine and is 9α-methylamino-α-naphthol. I am busy preparing sufficient amount for further investigation.

\[
\begin{align*}
\text{H}_{\text{N}}\text{O} & \overset{\text{CH}_3}{\longrightarrow} \\
\text{H}_{\text{N}}\text{O} & \overset{\text{CH}_3}{\longrightarrow}
\end{align*}
\]

(3). Tautomeric mobility of 1-thiol-α-naphthoxazole.

It was prepared by the action of CS on 2-amino-α-naphthol in presence of alkali. It was also obtained as a principal by-product during the preparation of 1-amino-α-napht oxazole by the action of yellow mercuric oxide on 1-hydroxy-2-naphthylthiourea. This has been methylated by either methyl
iodide or dimethylsulphate under three different conditions an interesting result was obtained.

On methylation with methyl iodide in presence of methoxide this behaved similarly to \(1\)-thio- benzoxazole (compare Desai, Hunter and Khidri, loc cit) and also similar to \(1\)-thio-

- naphthiazole (compare Hunter and Jones, loc cit) and yielded only 3-methyl derivative. The methylation with dimethyl-
sulphate in presence of methyl alcohol, gave primarily 3-methyl derivative, and also a very small quantity of an acidic product

It contained 2 and 3 and gave C, 71.91% and H, 5.77%. From this data it is not possible to come to any conclusion regarding its constitution, and we hope to investigate it further when more of it is available. But the methylation with methyl sulphonate in alkaline medium gave rise to a mixture of isomeric methyl derivatives, due to the simultaneous attachment of the alkyl group to 3 as well as to 5. The proportion of 1-methylthio-

- naphthoxazole (\(1\)) to 1-thio-3-methyl-1:2-dihydro-a-naphth oxazole (\(\nu\)) was 8:1. Thus the result of the methylation of 1-thiol-a-naphthoxazole is quite different from those of \(X\)

- 1-thio- benzoxazole, 1-thienobenzthiazole and 1-thio-a-naphthiazole. A similar type of results have also been obtained by Chirag, Hasan and Hunter (unpublished work) in the methylation of 5-bromo-1-thiobenzthiazole, with the production of 5-bromo-1-

- thio-3-methyl-1:2-dihydrobenzthiazole (\(\nu\)) and 5-bromo-1-

- methylthienobenzthiazole (\(\nu\)).

\[
\begin{align*}
\text{iodide or dimethylsulphate under three different conditions an} \\
\text{interesting result was obtained.}
\end{align*}
\]

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- thio-3-methyl-1:2-dihydrobenzthiazole (\(\nu\)) and 5-bromo-1-

- methylthienobenzthiazole (\(\nu\)).

\[
\begin{align*}
\text{iodide or dimethylsulphate under three different conditions an} \\
\text{interesting result was obtained.}
\end{align*}
\]
Section III.

Tautomeric mobility of 1-Naphthoxazoles.

Tautomeric mobility of 1-Amino-b-naphthoxazole.

At first 1-amino-2-naphthol was prepared by the reduction of Orange II, which was then converted into 2-hydrox-1-naphthy1 thiocarbonamide by the action of potassium or ammonium sulphocyanide.

Treatment of this thiocarbonamide in alcoholic solution with freshly precipitated yellow mercuric oxide gave 1-Amino-b-Naphthoxazole accompanied by a large amount of 1-mercapto-b-naphthoxazole.
This sort of behaviour of 2-hydroxy-1-naphthylthio carbamate is very much similar to that of 1-hydroxy-2-naphthyl thiocarbamate but presents a striking contrast to the analogous preparation of 1-aminobenzoxazole from 2-hydroxyphenylthiocarbamide. The presence of the amino group was proved by coupling the diazotized product with β-naphthol. But the methylation with methyl iodide yielded the methyl derivative of the tautomeric form (LXII) giving rise to 1-amino-2-methyl-1:2-dihydro-β-naphthoxazole and unaccompanied by the isomeric 1-methylamino-β-naphthoxazole synthesised from 1-mercapto-β-naphthoxazole and mono methylamine. Thus its behaviour is analogous to the 1-amino-α-naphthoxazole.

\[ \text{Teatomeric mobility of } 1\text{-Anilino-β-Naphthoxazole.} \]

The preparation of this substance by the action of aniline on 1-mercapto-β-naphthoxazole with the elimination of H₂S supports the (LXVI) formula.
Methylation with methyl iodide, however, gave rise to a mixture of 1-phenylamino-1-naphthothiazole \((LXVI)\) and 1-phenylamino-2-methyl-1:2-dihydro-1-naphthothiazole \((LXIX)\). The identity of \((LXVI)\) was established by its synthesis from 1-mercapto-1-naphthothiazole and mono methyl aniline. The formation of \((LXIX)\) shows that its progenitor must have the constitution represented by the tautomeric formula \((LXVII)\).

**Tautomeric mobility of 1-Hydrox-1-naphthothiazole.**

1-hydrox-1-naphthothiazole was prepared by the action of either carbon1 chloride or urethane or chlorformic ester on 1-amino-2-naphthol. The solubility of this substance in alkali supports the presence of the hydroxyl group, showing that it has the structure represented by \((LXX)\) but the methylation by dimethylsulphate in presence of alkali yielded 1-halo-1-methyl-1:2-dihydro-1-naphthothiazole \((LXXI)\), showing that the parent substance had formula \((LXXI)\).
The constitution of the \( \text{R}-\text{methyl} \) derivative follows from the fact that \( \text{R}-\text{methyl} \text{-anilino-1-naphthol} \) is obtained, when the methylation product is heated in a sealed tube with 50 per cent sulphuric acid for 14 hours.

**Teutonemic mobility of 1-mercapto-1-naphthoxazol.**

The preparation of the mercapto derivative from 1-amino-2-naphthol, alcohol and CS could be best be represented by formula (LXXVIII).

\[
\text{C}_{12} \text{H}_{10} \text{N}_{2} \text{O}_{4} \rightarrow \text{C}_{12} \text{H}_{10} \text{N}_{2} \text{O}_{4} \text{S} \quad \text{CS} \quad \text{H}_{2} \text{O} \quad \text{C}_{12} \text{H}_{10} \text{N}_{2} \text{O}_{4} \text{S} \quad \text{H}_{2} \text{O}
\]

while the teutonemic formula (LXXIX) was supported by the formation of this substance from \( \text{R}-\text{methyl} \text{-naphthylthiocarbamide} \) and yellow mercuric oxide. The marked acidic character of this substance was in conformity with formula (LXXIV).

Methylation with methyl sulphate in alkali medium gives both \( \text{CS} \) (LXXX), and \( \text{N} \) (LXXIX) methyl derivatives. The \( \text{R}-\text{methyl} \) derivative was synthesised by the action of \( \text{PS} \) on 1-ketp-3-
methyl-1:2-dihydro-b-naphthoxazole. With methyl iodide in methoxide it gave only the S-methyl derivative identical with the S-methyl derivative obtained from above. But when this was methylated by methyl sulphate in methyl alcohol, it not only gave both the S and R-methyl derivatives, but also a very small quantity of an acidic product. This acidic product contains N, S, and gave C, 70.9% and H, 3.6%. From this data it was not possible to assign any constitution to this. We hope to investigate this further in the near future.

Thus it resembles the a-analogues in its behaviour.
Experimental

Section I
Preparation of 5-Nitro-α-Aminophenol.

The preparation of this compound can be divided into the following:

(1). The preparation of 1-methylbenzoxazole and

(2). The nitration of the methylbenzoxazole and its hydrolysis.

(1). The preparation of 1-methylbenzoxazole.

This was prepared in a much better yield by a slight modification of Ladenburg's method (Ber., 2, 1624).

A mixture of α-aminophenol (20 gr.), glacial acetic acid (20 cc) and acetic anhydride (30 cc) is refluxed on sand bath for 6 hours. Excess of glacial acetic acid (b.p. 113°) and acetic anhydride (b.p. 130°) are removed completely. Phosphorous pentoxide (15 gr.) is added, the remaining liquid is gently distilled and the fraction between b.p. 190°-210° collected. This is pure methylbenzoxazole. Yield 92% of theoretical.

(2). Nitration of 1-methylbenzoxazole.

This was prepared by the method of Hewson & Phillip (J.C.S., 1928, 121).

1-Methylbenzoxazole (25 g) is added to sulphuric acid (125 cc., d.1.84), the temperature being allowed to rise to 60°-70°. The cooled mixture is then nitrated at 10° by the slow addition of nitric acid (15 cc., d.1.42) and sulphuric acid (150 cc., d.1.84) with mechanical stirring (3 hrs). Completion of nitration is shown by the absence of the characteristic smell of the unchanged material on dilution with water. The bulk is poured on ice, washed free from acid, and dried. This crude product is a mixture of 5-nitro and 4-nitro-1-methylbenzoxazole.
Yield, 27 gr. 90\% of the theoretical. M.P. 146°-147°. This is very susceptible to hydrolytic agents.

The crude nitrate product is boiled with 100 cc of Conc. HCl (c. 1.16) for nearly 2 hours, cooled, excess of sodium acetate is then added. The precipitate thus formed is washed thoroughly with cold water which removes the bulk of 4-nitro-2-aminophenol. The residue of 5-nitro-2-aminophenol is recrystallised from boiling water, when light coloured needles are obtained, m.p. 202°. Yield, 15 gr.

**Synthesis of 5-Nitro-1-Hydroxybenzoxazole.**

5-Nitro-2-aminophenol (10 g) is added to sodium ethoxide (1.5 g Na in 30 cc absolute alcohol), and chlorformic ester (2.2 g) is then gently added. Cooled, when the mixture became hot. The mixture refluxed on water bath for 5 hours. Alcohol removed. to solid residue water is added to remove sodium chloride and filtered. The intermediate product, when recrystallised from boiling water, shining needles melting at 174° are obtained (Found C, 47.7\%; H, 4.3\%; C H O N requires C, 47.8\% and H, 4.4\%). The ester is dry distilled. It explodes if over heated. Recrystallised from boiling water containing little alcohol in small lustrous needles m.p. 244°-246°.

(Found C, 46.95\%, H, 2.8\%; C H O N requires C, 46.86\% and H, 2.7\%)

Cyclisation can also be brought about within half an hour, when the 150 cc round bottomed flask containing the addiit: product is heated in paraffin bath, kept at 180°. The product is extracted by 1\% NaOH solution., filtered and acidified by
dilute HCl. The crude stuff is recrystallised from dilute alcohol.

**Synthesis of 5-Amino-1-Hydroxybenzoxazole.**

The 5-nitro-1-hydroxybenzoxazole is dissolved in rather more than one equivalent of dilute caustic soda (nearly 10%) and the solution heated to boiling. Filtered to remove suspended impurities. Dry sodium hydrosulphite powder is then added little by little until the red colour of the solution disappears. On cooling, the amino-1-hydroxybenzoxazole separates out as a mass of colourless crystals, which are filtered off, and washed with cold water. Recrystallised from dilute alcohol m.p. 204°C (Found C, 56.1%; H, 3.05%; C_HO requires C, 56.00% and H, 4.00%).

**Preparation of 5-Acetylamine-1-hydroxybenzoxazole.**

The acetyl derivative has been prepared by heating the substance with acetic anhydride on a free flame for 5 minutes, and pouring the mixture into water, crystallised from dilute alcohol in small needles m.p. 204°C (Found C, 56.32%; H, 4.05%; C_HO requires C, 56.29% and H, 4.10%).

**Synthesis of 5-Chloro-1-hydroxybenzoxazole.**

A mixture of crystallised copper sulphate (1.5g), sodium bromide (3g), and copper turnings (1g) is boiled under reflux condenser with 40cc of water and 4 gm of Conc. H SO until almost decolourised. 5-Amino-1-hydroxybenzoxazole (1.5g) is then added and the whole allowed to cool. Ice is added until the temperature falls to 0°C, and then a cold aqueous solution of 1g sodium nitrite gently run in. During the addition
the temperature should not exceed 50, more ice being added from time to time when necessary. When all the nitrite has been added and the whole is allowed to stand over night at room temperature, the precipitated 5-bromo-1-hydroxybenzoxazol is collected, washed with water and recrystallised from dilute alcohol. It forms needles m.p. 108°-109°. Yield, 1.3 g (Found: N, 8.35%; C, H, O, F requires N, 8.4%)

Mono brominated 1-hydroxybenzoxazole has been identified as 5-bromo-1-hydroxybenzoxazole by m.p. and mixed m.p. with the genuine specimen synthesised above.

Unsuccessful attempt was made to hydrolyse the 5-bromo-1-hydroxybenzoxazole with 25% NaOH solution. However, on refluxing it with Conc. HCl on sand bath for 14 hours, the oxazole ring was opened up. The acid solution was cooled and made alkaline with dilute NaOH and filtered. The alkaline solution on acidification with dil HCl, gave the hydrochloride of 5-bromo-α-aminophenol. Recrystallised from dil alcohol in small needles m.p. 290° sharp. The 5-bromo-α-aminophenol has a great tendency to form hydrochloride in presence of dil HCl.

**Methylation of 5-Bromo-1-Hydroxybenzoxazole.**

The bromo hydroxy compound (1g) is dissolved in chloroform (15cc) and KOH solution (12cc, 30%) added to it. Dimethylsulphate (5cc) is gradually added and the mixture vigorously shaken. It gets warm, cooled in cold water. Kept at room temperature for 4 hours, warmed on water bath gently for 30 minutes and left overnight. Excess of methylsulphate is destroyed by adding KOH solution (20cc, 5%) and the product extracted with chloroform, dried and the solvent
recovered. Recrystallised from dilute alcohol, long needles m.p.
150° are obtained. (Found Br. 35.12%; C 66 O 2 H 29 requires
Br. 35.08%). This is ß-Promo-1-keto-3-methyl-1:2-dihydrobenzoxazole.

Promotion of 1-Keto-3-methyl-1:2-dihydrobenxoxazole.

1-Keto-3-methyl-1:2-dihydrobenzoxazole (1g)
in chloroform (250cc) and bromine (1g) in
chloroform (500c) is then added gradually. The mixture is
warmed after keeping it at room temperature for 4 hours.
The chloroform is evaporated off and the residue treated
with sulphur dioxide water. The crude product, on
crystallisation from alcohol, is obtained in needles
m.p. 149°-153°. This melting point is not depressed by
admixture with the product obtained by methylating the
ß-Bromo-1-hydroxybenzoxazole.
**Synthesis of 5-Nitro-1-Mercaptobenzoxazole.**

A mixture of 5-nitro-O-aminophenol (10g), carbon disulphide (30cc), solid KOH (10g) and alcohol (40cc) is refluxed on a water bath for 10 hours. The excess of carbon disulphide and alcohol are removed, and the residue dissolved in water, filtered and acidified with dilute HCl, when 5-nitro-1-mercaptobenzoxazole is precipitated. Then recrystallised from dilute alcohol, short needles m.p. 210c-213c are obtained. (Found S, 16.25%; C H O N S requires S, 16.32%).

**Synthesis of 5-Amino-1-Mercaptobenzoxazole.**

5-Nitro-1-mercaptobenzoxazole (2g) is dissolved in NaOH solution by warming (1g NaOH in 50cc water). The solution is slightly cooled and dry sodium hydrosulphite powder (3g) is added by shaking till red colour has been completely destroyed. On cooling, straw coloured needles separated out, filtered and recrystallised from dilute alcohol, when grey coloured small needles m.p. 290c are deposited. (Found S, 19.7%; C H O N S requires S, 19.87%).

5-Amino-1-mercaptobenzoxazole (1g) is dissolved in alkali solution, and acidified by means of dil HCl, more Conc. HCl is added. Calculated quantity of sodium nitrite is then added to the ice cooled solution by stirring. When all the nitrite has been run in the solution should cease show a faint reaction to starch iodide paper.

1-Naphthol is dissolved in sodium hydroxide solution by warming, cooled to 15c, and the suspension of the diazotize salt, obtained as above, run in slowly with continual stirring. A brown coloured ppt. filtered and recrystallised from dilute
alcohol, small needles, m.p. 110° (Found S, 10.00%; C H O N S
requires S, 9.96%).

5-Promo-1-Mercaptobenzoxazole.

A mixture of crystallised copper sulphate (1.5g),

1144219 n

sodium bromide (3g), copper turnings (1g), water (35cc) and Conc

1144219 n

sulphuric acid (3cc) is boiled under a reflux condenser until

1144219 n

almost decolorised. 5-amino-1-mercaptobenzoxazole (1.8g) is

then added and the whole allowed to cool. Ice is added until

1144219 n

the temperature falls to 30°, and then a cold, aqueous solution

1144219 n

of sodium nitrite (0.9g) slowly run in. During the addition

1144219 n

the temperature should not exceed 30°, more ice being added

1144219 n

from time to time if necessary. Then all the nitrite has been

1144219 n

added the whole is allowed to stand overnight at the room

temperature. The precipitated 5-Promo-1-mercaptobenzoxazole

then collected, washed with cold water, and recrystallised

from dilute alcohol. It forms long needles melting at 198°-200°.

This melting point was not depressed by admixture with

the specimen prepared by brominating 1-mercaptobenzoxazole.

Yield 1.8g. (Found Br, 34.7%; C H O N S Br. requires Br, 34.3%)

Methylation of 5-Promo-1-Mercaptobenzoxazole.

Method I. By means of methyl iodide and methoxide.

5-Promo-1-mercaptobenzoxazole (1.8g) is dissolved in

sodium methoxide (0.2g Na in 30cc absolute methanol), methyl

iodide (1cc) is added gently and shaken. The mixture is kept

at room temperature for 3 hours, warmed on water bath for 45

minutes and left overnight. It is then evaporated to dryness

the residue treated with water and filtered. The insoluble

solid crystallised from dilute methyl alcohol, and long needle

m.p. 148° are obtained. (Found Br, 32.62%; C H O N S Br.,
Method II. By means of dimethyl sulphate in alkali medium.

The bromo-mercaptan (1g) is dissolved in chloroform (10cc) and 30% KOH solution (12cc) is added to it. Dimethylsulphate (3cc) is next added gradually, and the mixture after keeping at ordinary temperature for 1 hour, is warmed on water bath for 20 minutes. Excess of dimethylsulphate is destroyed by adding 30% KOH solution (20cc) and the product extracted with chloroform, dried and the chloroform recovered. The crude product crystallised from dilute methanol in long needle m.p. 148°c and was found to be identical with that obtained by method I. This is 5-bromo-1-thiomethylbenzoxazole.

synthesis of 5-bromo-1-thio-2-methyl-1:2-dihydrobenzoxazole.

5-Bromo-1-keto-2-methyl-1:2-dihydrobenzoxazole (1g) is intimately mixed with phosphorous pentasulphide (1.2g) and heated in a hard glass test tube with an air condenser in a paraffin bath, kept at 120°c-125°c, for 1 hour. A crystalline substance sublimed on the cooler parts of the test tube. The melt is extracted with benzene, the solution on concentration deposited long white needles m.p. 110°c. (Found: C, 32.8%. S, 13. C H O N S Br. requires C, 32.2% and S, 13.1%).
Formation of 1-thiomethylbenzoxazole.

A chloroform solution (20cc) of 1-methylthiobenzoxazole (1g) was gradually treated with bromine (1g in 50cc chloroform) at room temperature. After standing for some time, the mixture was slightly warmed. The chloroform was evaporated off and the substance was reduced with 50 water, then crystallised from alcohol. Long needles m.p. 148o were obtained. This m.p. was not depressed by admixture with the specimen prepared by metilating 5-bromo-1-mercaptobenzoxazole.
Preparation of 5-bromo-1-aminobenzoxazole.

This substance was prepared by the direct bromination of 1-aminobenzoxazole in chloroform. (compare Bessai, Hunter and Khalidi, J.C.S., 1934, 1186). When boiled with Conc. HCL, the hydrochloride of 5-bromo-O-aminophenol, m.p. 299°, was obtained. This melting point was not depressed by admixture with the specimen prepared by the hydrolysis of 5-bromo-1-hydrobenzoxazole. Hence in this case also the bromination goes to the 5 position.

Methylation of 5-bromo-1-aminobenzoxazole.

A mixture of 5-bromo-1-aminobenzoxazole (1g) and methyl iodide (i.1cc) was heated in a sealed tube, at 100°, for 18 hours. There was no pressure when the tube opened. The mixture was warmed up with 10% caustic soda solution and the substance extracted with chloroform, dried and the solvent recovered on water bath. The crude solid crystallised from methylalcohol, long needles m.p. 105°-106° (along the sides of the conical flask) were deposited accompanied by a resinous deposit. (Found Fr. 35.3%; C₂H₂O₂N₂ requires Fr., 35.4%)

The resinous mass was divided into two parts. One portion on treatment with petrol ether gave long needles m.p. 105° identical with that obtained above. The other portion was converted into picrate by heating equimolecular quantities of methylated base (gun) and picric acid in benzene. Crystallised from benzene needles m.p. 210° (Found Fr., 17.43%; C₁₄H₇O₃N₃S₂ requires Fr. 17.52%). Picrate of the crystallised methylated base (needles m.p. 210°) was precipitated readily. When recrystallised from benzene gave needles m.p. 210°. This was found to be identical with the above specimen.
The picrate of 5-bromo-1-aminobenzoxazole was prepared by heating the base and picric acid, in molecular proportions in benzene for 30 minutes on water bath. Crystallised from benzene small needles m.p. 210c are obtained. Mixed m.p. with the picrate of the methylated base was 190c. (Found Br. 17.71%; C H O N Br. requires Br. 17.62%).

Synthesis of 5-bromo-1-methylaminobenzoxazole.

A mixture of 5-bromo-1-mercaptobenzoxazole (1g) and mono methylamine in equimolecular proportion was heated in a sealed tube, at 100c, for 12 hours. Excess of methylamine was removed by warming the tube and the mixture taken in ether, washed completely with 10% NaOH solution to remove unreacted bromo mercaptae. The solution dried and the ether recovered. When crystallised from methanol, needles m.p. 170c-172c were deposited. This compound depresed the m.p. of its isomer to 80c. (Found Br. 35.52%; C H O N Br. requires Br., 35.24%).
Section II
Synthesis of 2-Amino-1-Naphthol.

The preparation of this compound has been divided into the following:

(1). Preparation of 2-Nitro and 4-Nitro-1-Naphthols
and
(2). Reduction of 2-Nitro-1-Naphthol to 2-Amino-1-Naphthol

(1). 2-Nitro-1-Naphthol was prepared by nitration of a-Naphthylamine and treating the 2-nitro-1-naphthylamine with alkali according to the method of Hodgson & Kilner (J.C.S., 1924, 125, 307).

1-Naphthylamine (35g) is boiled for 20 minutes with glacial acetic acid (200cc) and acetic anhydride (27cc) (Hodgson & Kilner, J.C.S., 1924, 125, 307), and nitric acid (d,1.5; 12.5cc) added to the suspension resulting on cooling to 10c-15c. After 48 hours, the solid,30gms, ('yield 75%') is filtered off, washed twice with glacial acetic acid and dried. The nitrated product is hydrolysed with caustic potash, 60cc of 30% and water 150cc in presence of alcohol 500cc. At first alcohol is distilled off very slowly on water bath, when 700cc alcohol had distilled off, (1hour), more water (200cc) is added and the distillation continued on a sand bath until the distillate is free from ammonia---- total time nearly 4hrs.

The potassium salt of 2-nitro-1-naphthol separates out on cooling. Filtered and washed at least twice with 5% KOH solution 50cc. The filtrate and washings are warmed and acidified with glacial acetic acid, 4-nitro-1-naphthol is collected, yield 15 gms.
The insoluble potassium salt of 2-nitro-1-naphthol acidified in boiling aqueous solution, with acetic acid gives free 2-nitro-1-naphthol. For getting pure 2-nitro-1-naphthol it is imperative that the acidified stuff must be filtered off while hot. M.P. 129c, yield 10 gms.

(2). Reduction——. The method for reducing 2-nitro-1-naphthol recommended by Fisher & Hamner (J.C.S., 1934, 965) did not work satisfactorily in our hands, hence we used the hydrosulphite method.

2-Nitro-1-Naphthol (10gm) is dissolved in rather more than equivalent of very dilute caustic soda (4 gr NaOH in nearly 300cc water) and the solution heated to boiling. Filtered to remove suspended impurities. Dry sodium hydrosulphite powder (50 gr) is then added little by little until the red colour of the solution disappears. On cooling 2-Amino-1-Naphthol separates out as a mass of colourless crystals, which are filtered off and dried. The amino compound does not decolorise immediately when exposed to air. The crystals darken at 100c but finally melt at 150c.

The amino compound is more stable as a hydrochlorid which has been prepared as follows: The aminonaphthol (obtained above) is dissolved in 250cc of 10% HCl by warming. Filtered hot to remove resinous mass. The filtrate is collected in a conical flask containing 150cc HCl. Allowed to stand for 1/2 an hour, filtered and dried in vacuo. Light purple coloured needles m.p. 260c. Yield is almost theoretical. This compound
has been preserved in rubber corked bottle (light red colour for at least 3 months without decomposition.

**Preparation of 1-Hydroxy-2-Naphthylthiourea.**

A solution of 2-amino-1-naphthol hydrochloride (10 gr) potassium sulphocyanide (10 gr) and Conc. HCl 20c in water 100cc is heated on water bath for 10 hours, with occasional addition of water, till the contents become solid. After the removal of potassium chloride and potassium sulphocyanide with water, the residue is dried. On treatment with ethylacetate most of the impurities removed and a crystalline substance, small needles melting at 228c-246c-248c are obtained. The m.p. is raised to 252c by further crystallisation from alcohol. Yield. 10 gr. nearly 77% of the theoretical. (Found 3, 14.7% C H O N S requires S, 14.8%).

The thiourea is very sensitive to air. At first the effect is on the surface, but on long standing, it as a whole gets coloured black, but the melting point remains unaffected.

**Preparation of 1-Amino-2-Naphthoxazole.**

A solution of 1-hydroxy-2-naphthylthiourea (10 gr) in alcohol (100cc) is treated with freshly precipitated yellow mercuric oxide (25 gr) and heated under reflux on water bath for 18-20 hours. Ammonia is evolved. The filtrate, after the removal of mercuric sulphide, is evaporated to dryness. The residue treated with 1% alkali solution (NaOH) and filtered. The alkali insoluble product is warmed with benzene and filtered. There is nearly 0.5 gr solid which is insoluble in f it and that this is mercuric mercaptide, decomp near 300c.
The benzene on concentration deposits needles m.p. 194-195°. On recrystallisation from alcohol long needles melting at 195° are obtained. Yield is from 1.5 to 2 gr. This is the desired 1-aminoc-naphthoxazole. (Found C, 71.7%; H, 4.35%; C_8 H_5 O N requires C, 71.73% and H, 4.34%). The presence of the amino group has been ascertained by coupling the diazotised product with p-naphthol.

The alkali solution is acidified with dilute HCl and the precipitate collected. The precipitate is further boiled with water and filtered, residue crystallised from dilute alcohol, long shining needles melting at 202° are obtained. This compound has been identified as 1-mercapto-naphthoxazole by melting point and mixed melting point with the authentic specimen. Yield 3.5 gm.

**1-Acetyl-1-amino-naphthoxazole.**

The acetyl derivative is prepared by heating the substance with acetic anhydride on free flame for 5 minutes, and pouring the mixture into cold water. The crude product is recrystallised from dilute alcohol, needles m.p. 210°. (Found C, 69.1% and H, 4.8%; C_8 H_5 O N requires C, 69.32% and H, 4.42%).

**Methylation of 1-Amino-naphthoxazole.**

A mixture of 1-aminoc-naphthoxazole (1.5 gr) and methyliodide (3.2cc) is heated in a sealed tube at 100° for 18 hours. After cooling, the mixture is slightly warmed with dilute NaOH solution, and extracted with chloroform, dried and
the chloroform recovered. On cooling, the substance, slightly sticky, is obtained. The sticky matter is removed when treated with small quantity of methyl alcohol (50c) leaving the methylated product almost pure. Recrystallised from alcohol small needles - light red colour- melting at 154°C are obtained. Mixed melting points with the parent substance and 1-methyl-amino-α-naphthoxazole are 140c and 132c respectively. Hence the crystals are of 1-imino-2-methyl-1:2-dihydro-α-naphthoxazo (Found C, 72.8%; H, 5.1%; C H O N requires C, 72.72% and H, 5.05%).

The acet1 derivative prepared by heating the substance with acetic anhydride on a free flame for ten minutes, and pouring the mixture into cold water, crystallised from dil alcohol in needles m.p. 139°C (Found C, 73.1%; H, 4.9%; C H O N requires C, 70.00% and H, 5.00%).

Synthesis of 1-methylamino-α-naphthoxazole.

A mixture of 1-mercapto-α-naphthoxazole (1g) and mono methylamine (1g, 4cc of 30% solution) is heated in a sealed tube at 180°C for 12 hours. There was no pressure when the tube is opened. The mixture is taken up in ether and washed thoroughly with 10% NaOH solution to remove the unchanged mercaptan. The solution dried and the solvent recovered on water bath. The solid residue crystallised from dilute methyl alcohol in needles m.p. 130°C. Its melting point is depressed by its isomer to 126°C. (Found C, 72.7%; H, 4.9%; C H O N requires C, 72.7% and H, 5.0%).

The acet1 derivative has been prepared by the usual method.
It is boiled with excess of acetic anhydride on a free flame for
5 minutes and poured into cold water, crude product collected.
Recrystallized from 0.l% alcohol in needles m.p. 130°. (Found
C, 70.2%; H, 5.0%. $C\text{H}_2\text{O}_2$ requires C, 70.96%; H, 5.03%).

**Synthesis of 1-Anilino-2-Naphthoxazole.**

A mixture of 1-mercapto-2-naphthoxazole (2g) and
aniline (1.25g) is heated in a hard glass tube in paraffin
bath, kept at 200°, until the evolution of $H_2S$ is over (time
taken is nearly 3 hours). On cooling, small needles m.p. 220° are
obtained. The m.p. is raised to 225° when recrystallized
through benzene. This compound can best be purified through its
picrate, which is prepared easily. The free base is liberated
when the picrate is warmed with dilute caustic soda solution.
Free base when recrystallized either from alcohol or benzene
melts at 230° sharp. (Found C, 76.5%; H, 4.65%. $C\text{H}_2\text{O}_2$ require
C, 76.46% and H, 4.61%). (Compare P. Jacobson, J.r., 21, 2, 3942)
Yield, 2.2 g. --- 95% of the theoretical.

1-Anilino-2-Naphthoxazole gave a picrate when it was
refluxed on water bath for 30 minutes in benzene solution
with equimolecular amount of picric acid. Recrystallized from
benzene small needles m.p. 215°-220° are deposited. (Found
C, 56.6%; H, 3.0%. $C\text{H}_2\text{O}_2$ requires C, 56.44% and H, 3.06%)
(P. Jacobson, J.r., 21, 2, 3942).
Methylation of 1-Aniline-e-Naphthoazole.

A mixture of 1-aniline-e-naphthoazole (2g) and methyl iodide (3cc) was heated in a sealed tube at 100°C for 16 hours. The mixture was worked up with alkali, and the substance extracted with chloroform, dried and recovered. As the resulting gas did not show any sign of solidification, it was dissolved in benzene, and a solution of picric acid (1.5g) in the same solvent added, and the mixture refluxed on water bath for nearly 1 hour. Even after long standing, the benzene solution deposited sticky needles, hence the benzene was evaporated off to dryness. To the dry residue ethyl acetate 10cc was added and filtered on a Buchner funnel. The ethyl acetate mother liquor deposited shining yellow small needles melting at 168°C. The melting point was not altered by further crystallisation.

Yield nearly 7%. This was the picrate of 1-phenylamino-2-methyl-1:2-dihydro-e-naphthoazole, as it was different from the picrate of 1-methylphenylamino-e-naphthoazole prepared synthetically. (Found C, 57.37%; H, 3.57%; C, 4.01. Requires C, 57.35% and H, 3.37%). The residue (insoluble in ethyl acetate) crystallised from benzene when needles m.p. 200°C were deposited. Yield nearly 25%. This picrate was identified as the that of 1-methylphenylamino-e-naphthoazole by melting point and mixed m.p. with the authentic specimen. (Found C, 57.08%; H, 3.26%; C, N, O, K. Requires C, 57.05% and H, 3.37%).


A mixture of 1-anisylcarboxy-e-naphthoazole (1g) and mono methyl aniline (1g) was heated in a hard glass tube, in
paraffin bath, kept at 180°-190° for nearly 8 hours, when the
evolution of the H₂S was over. The cooled mixture was alternately
warmed with dil HCl (1:1) and dilute caustic soda solution
(nearly 10%) till antipyriniline and unreacted mercaptan were
completely removed. The residual gum did not show signs of
solidification, it was treated with calculated quantity of
picric acid in benzene and refluxed for nearly 30 minutes.
The picrate crystallised from the same solvent, when needles
m.p. 237°-238° were obtained.

Synthesis of 1-Hydroxy-1-Naphthoxazol.
The hydroxy compound was has been prepared by three
methods which are described hereunder.
Method I. From chlorformic ester and 2-amino-1-naphthol.
2-Amino-1-Naphthol hydrochloride (2.34g) is dissolve
in alcoholic sodium ethoxide (0.7g Na in 45cc of absolute alcohol
the mixture cooled in ice, the chlorformic ester (2g) is
gradually added. After heating the mixture under reflux on
water bath for 3 hours, the alcohol is removed. The best way of
obtaining the hydroxy compound is to heat the warm residue
in the round bottomed flask, for three hours, in paraffin bath
kept at 180°-190°. Cyclisation takes place smoothly. The
hydroxy naphthoxazol is recovered by means of 10% NaOH solution
the solution acidified filtered and the crude product washed
with cold water. Recrystallised from alcohol, needles m.p. 218°
-220° are obtained. The melting point is not raised by further
crystallising it through benzene. (Found C, 71.40% and H, 3.87%;
C₇H₇N₂ requires C, 71.39% and H, 3.76%). Yield 3.3 gr.

Method II. From carbonyl chloride and 2-Amino-1-Naphthol.

A mixture of 2-amino-1-naphthol hydrochloride (2g)
carbonyl chloride (1.2 gr. ---10cc of 12% soln in toluene),
and pyridine 30cc is vigorously shaken for three hours in a
separating funnel. After 24 hours, toluene and pyridine
removed on water bath and the residue treated with 10% NaOH
solution, filtered, and the filtrate acidified. Light brown
substance of m.p. 300°C is obtained. Recrystallised from
alcohol in small needles, m.p. 290°C. Its melting point is not
depressed by the product obtained by method I. Yield 1.5g.

A black residue nearly 1g, insoluble in hot NaOH
solution, is obtained. This has been found to be insoluble in
alcohol and acetone. Crystallises from glacial acetic acid
on long standing, in black coloured needles m.p. 285°C. This
is under investigation.

Method III. From Urethane and 2-Amino-1-Naphthol.

2-amino-1-naphthol (3.0g) is intimately mixed with
urethane (2g) and heated in a hard glass tube for nearly 4 hrs.
in Griffin bath, kept at 160°C, until the evolution of ammonia
is complete. The melt cooled and treated with 10% NaOH solution.
The filtered alkali solution is acidified with dilute HCl, when
slightly coloured substance m.p. 314°C-side is obtained. The
m.p. is raised to 320°C by crystallising it from alcohol and
benzene. This is has been identified to be 1-hydroxy-1-naphth
oxazole by taking mixed m.p. with genuine specimen obtained
by methods I & II. Yield nearly 3 gr.
Methylation of 1-Hydroxy-a-Naphthoxagol.

The hydroxy compound (1g) is dissolved in chloroform by warming, cooled, and 10cc KOH solution (30%) is added to it. Dimethyl sulphate (5cc) is added gradually and vigorously shaken. The mixture after keeping at room temperature for 2 hr is heated on an electric water bath for 1 hr cooled and left overnight. The excess of dimethyl sulphate is destroyed by adding 20cc of 30% KOH solution, and the methylated product extracted with chloroform, dried and the chloroform recovered on water bath. The crude product is crystallised from dil methanol, when small needles m.p. 1636 are obtained.

(Found C, 72.77; H, 4.50; C, N & H requires C, 72.3; H, 4.05). 12.4.2

Unsuccessful attempts were made to hydrolyse the methylated product by boiling with Conc. HCl and also by heating it with Conc. HCl in a sealed tube at 160°. However, when heated with 50 per cent sulphuric acid in a sealed tube at 160° for 12 hours under gases fission into 22-methylamino-a-naphthol. The 22-methylamino-a-naphthol was obtained on basification with Conc. ammonia.

continued
1-Mercapto-a-Naphthoxazole.

(1). From 2-Amino-1-Naphthol and Carbodisulphide,
(F. Jacobson, P. 234-234.)

A mixture of 2-amino-1-naphthol hydrochloride (10g) carbodisulphide (20cc), solid KOH (5g) and alcohol 75cc is refluxed for 3 hours. The excess of carbodisulphide and alcohol is removed and the residue dissolved in water and filtered. The filtrate acidified by dilute HCl, when the mercapto naphthoxazole is precipitated. Recrystallised from alcohol, small shining needles melting at 1620c are deposited. Yield, 8 gr. —— 80% of the theoretical. This is the best way of obtaining the mercaptonaphthoxazole.

(2). It is also obtained as a principal by-product during the preparation of 1-amino-a-naphthoxazole from 1-hydroxy-a-naphthylthiourea by the action of yellow mercuric oxide.

Methylation of 1-Mercapto-a-Naphthoxazole.

Method I. By means of methyl iodide and sodium methoxide.

1-Mercapto-a-naphthoxazole (1g) is dissolved in sodium methoxide (0.115g Na in 30cc absolute methanol), methyl iodide (1.5cc) is added gently and vigorously shaken. Kept at room temperature for nearly for 4 hours, warmed on water bath for nearly 30 minutes and left overnight. The mixture is evaporated to dryness and the residue treated with water to remove sodium iodide. The insoluble solid crystallised from methyl alcohol, when long shining needles of m.p. 730-350c are deposited. (Found C, 67.6%; H, 4.01%; and S, 14.7%; C H O N S requires C, 67.30%, H, 4.2% and S, 14.9%).
This is 1-methylthio-α-naphthoxazole.

**Method II. By means of dimethylsulphate in alkali medium.**

1-Mercapto-α-naphthoxazole (1g) is dissolved in chloroform (20cc) and 15cc KOH solution (30%) added. Dimethylsulphate (5cc) is gently added, slight rise of temperature is observed, hence cooled. Kept at room temperature for 30 minutes and then warmed gently on water bath for 1 hour, cooled and left over night. Extracted with chloroform, dried and the solvent recovered. The residue solidified after 3 hours.

Crystallised from methylalcohol, long needles m.p. 190c-192c are deposited first. Yield nearly 70%. This is 1-thio-2-methyl-1,2-dihydro-α-naphthoxazole. Found S = 14.85% C12H9NOS requires S = 14.9%

The mother liquor is slightly diluted, another crop of crystals m.p. 78c-80c are deposited. This methylation product has been identified as 1-methylthio-α-naphthoxazole by m.p. and mixed m.p. with that obtained by method I. Yield nearly 80%.

**Method III. By means of dimethylsulphate in methylalcohol.**

A mixture of 1-mercapto-α-naphthoxazole (1g), methylalcohol (20cc) and dimethylsulphate (5cc) is refluxed on water bath for an hour. During heating bad smelling gas is evolved. The mixture is allowed to cool and methyl alcohol removed. Excess of methylsulphate is decomposed by Conc. ammonia. Filtered, the neutral solid residue, black in colour, dried and crystallised from hexane.

It deposits needles m.p. 78c-80c. This is 1-methylthio-α-naphthoxazole as identified by taking mixed m.p. with the genuine specimen obtained from method I and II.
The ammoniacal solution is acidified and the ppt. crystallised from methyl alcohol, when long needles melting at 232° are deposited. Yield nearly 0.2 gr. This compound contains N, S, and gave C, 71.01% and H, 3.77%. We hope to investigate it further when more of it is available.

**Synthesis of 1-thio-2-methyl-1,2-dihydro-naphthoxazole**

An intimate mixture of 1-buto-2-methyl-1,2-dihydro-α-naphthoxazole (2.8g) and ZnS (0.3g) is heated for nearly 3 hours in paraffin bath kept at 170°. Needle shaped crystalline substance sublimes on the cooler parts of the tube. The substance is taken in benzene and crystallised in long needles m.p. 139°. This compound does not depress the m.p. of the product (18°) obtained by nitricating the α-mercaptan-naphthoxazole by means of methyl sulphate in alkali medium.
Section III
Synthesis of 1-Amino-2-Naphthol.

The preparation of this compound has been divided into two parts, which are described hereunder.

(1). The preparation of Orange II, and

(2). The reduction of Orange II to 1-Amino-2-Naphthol

(1). Sulphanilic acid (17.5 gr) is dissolved in water containing little caustic soda. Ice is added until the temperature is below 5°C. Hydrochloric acid (30cc) is then added, and 17% sodium nitrite (27 gr) solution gradually run in until diazotization is complete. The diazo compound usually separates out as fine needles, but these are not isolated.

1-Naphthol (14.4 gr) is dissolved in 150 cc water, to which NaOH (4.5 g) has been added. This solution is made up to about 180 cc by adding more water. It is then cooled. The diazonium solution is carefully added, with stirring, until coupling is complete, the temperature not being allowed to rise above 5°C. The mass gives a slight alkaline reaction. After half an hour the dye separates out, a little salt being added to complete the precipitation. The whole filtered off and dried. The yield is 34 gr.

(2). Reduction of Orange II to 1-Amino-2-Naphthol.

The reduction of Orange II to 1-Amino-2-naphthol by tin and hydrochloric acid proved somewhat tedious operation hence sodium hydrosulphite in alkali was employed. With this reagent the reduction went more smoothly and gave a much better yield.

Orange II (50 gr) is dissolved in boiling water
(500cc) and to this is added tin (65 gr) dissolved in Conc. HCl (375cc). When the decolorisation is complete, the solution is filtered quickly and on cooling the hydrochloride of aminonaphthol separates out as a mass of colourless crystals. Fine needles, soluble in alcohol and dilute dilute HCl. Yield, 20 gr. (Ber., 25, 880). M.P. 2500-2550c.

(ii). Orange II (50 gr) is dissolved in 10cN NaOH solution heated to boiling and filtered. The solution cooled to 60c, dry sodium hyposulphite powder added gradually with stirring until decolorisation is complete. On cooling, the mass of colourless crystals separates out. Collected and dried. The crystals are dissolved in 13 per cent HCl and warmed. Filtered, and the filtrate collected in a conical flask containing Conc. HCl. Amino naphthol separates out as hydrochloride in long needles, m.p. 2500-2550c. Yield, 26 gr.

Preparation of 2-hydroxy-1-naphthylthiourea.

A solution of 1-amino-2-naphthol hydrochloride (15g) ammonium sulphocyanide (10gr), and Conc. HCl (200cc) in water (1000cc) is heated on water bath for 12 hours, with stirring. Water, (500cc, each time) is added four times and the solution evaporated to dryness. On treatment with water, ammonium chloride and ammonium sulphocyanide are dissolved, thiourea is left out as a residue. It is further purified through ethyl-acetate, when small needles decomp near 300c, are obtained, (S, 14.9%; C H O N S requires S, 14.67%). The thiourea gets black when exposed to air, but no change in m.p. has been observed.
Preparation of 1-Amino-b-Naphthoxazole.

A solution of 2-hydroxy-1-naphthylthiourea, 10 gr., in alcohol, 800 cc., is treated with freshly precipitated yellow mercuric oxide 20 gr.-25 gr., and heated on water bath under reflux for at least 24-28 hours, until the evolution of NH₃ is complete. The filtrate, after the removal of HgS, is evaporated to dryness. The solid warmed with dilute caustic soda solution and filtered. The residual solid dried and treated with warm benzene and filtered. The benzene solution on standing deposits pates m.p. 1760. It has also been recrystallised from alcohol. This is 1-amino-b-naphthoxazole. Yield, 1.5 gr. to 2 gr. (Found C, 71.80%; H, 4.44%; C₉H₈O₂ requires C, 71.73%; H, 4.45%). The benzene insoluble product is mercuric mercaptide m.p. 2760-2780.

The alkal solution is acidified with dilute HCl and the precipitate washed with water, crystallised from alcohol deposits needles m.p. 2560-2580. This has been identified as 1-mercapto-1-naphthoxazole by m.p. and mixed m.p. with the authentic specimen.

1-Acetylarnino-1-Naphthoxazole.

The acetyl derivative is prepared by heating the amino compound with acetic anhydride on flame for 5 minutes and pouring the mixture into cold water. The crude product is recrystallised from dilute alcohol in small needles m.p. 2120. (Found C, 69.28% and H, 4.92%; C₉H₈O₂ requires C, 69.02% and H, 4.4%).
Methylation of 1-Amino-1-Naphthoxazole.

A mixture of 1-amino-1-naphthoxazole (1.5g) and methyl iodide (3.2cc), is heated in a sealed tube at 100°C for 20 hours. When the tube opened, there was no pressure. The mixture is warmed with dilute caustic soda and extracted with chloroform, dried and the solvent recovered. The solid residue is crystallised from dilute methyl alcohol in small needles m.p. 1430-1500°C. This is different from 1-methylamino-1-naphthoxazole, as ascertained by mixed melting point. Hence the crystals are of 1-imino-2-methyl-1:2-dihydro-b-naphthoxazol (Found C, 72.32%; H, 5.00%; C H O N requires C, 72.72% and H, 5.05%).

The acetyl derivative of 1-imino-2-methyl-1:2-dihydro-b-naphthoxazol has been prepared by heating it with acetic anhydride on a free flame for 10 minutes, and pouring the mixture into cold water, crystallised from dilute alcohol in needles m.p. 130°C. (Found C, 73.1%; H, 5.00%; C H O N requires C, 72%, H, 5.00%).

Synthesis of 1-Methylamino-1-Naphthoxazole.

A mixture of 1-mercapto-1-naphthoxazole (1g) and mono methyl amine (1 eq, 4cc of 30% solution) was heated in a sealed tube at 100°C for 14 hours. There was no pressure when the tube was opened. The mixture was taken up in ether and washed thoroughly with 10 per cent NaCl solution to remove the unreacted mercaptan. The solution dried and the solvent removed on water bath. The solid residue recrystallised from dilute methyl alcohol in long needles m.p. 130°C. (Found C, 72.0%; H, 5.1%; C H O N requires C, 72.72% and H, 5.05%).
The acet-1 derivative of 1-methylamino-b-naphthoxazole is obtained by heating the compound with acetic anhydride in a test tube on a flame for 3 minutes. After cooling, the mixture is poured into cold water, a solid separates out. The solid collected and recrystallised from dilute alcohol in small needles m.p. 140c. (Found C, 69.3%; H, 5.0%; C, H, O, N, requires C, 70.0% and H, 5.0%).

Preparation of 1-Aniline-b-Naphthoxazole.

An intimate mixture of 1-mercapto-b-naphthoxazole (2g) and aniline (1.25g) is heated in a hard glass tube for 8-10 hours in paraffin bath, kept at 160c-185c. On cooling the mixture is first washed with warm dilute HCl (1:1) to remove unreacted aniline, the residue refluxed on water bath with 10 per cent NaOH solution to remove unused mercaptan. The residual solid crystallised from dil alcohol in small needles m.p. 172c. Yield, 2.2 gr. (Found C, 78.6%; H, 4.8%; C, H, O, N, requires C, 78.46% and H, 4.61%). (P, Jacobson, F. 21, 417)

1-Aniline-b-Naphthoxazole gives picrate when the molecular proportion of the base and picric acid in benzene solution is refluxed on water bath for nearly 30 minutes. The residual solid crystallised from the same solvent deposited small needles m.p. 210c-212c.

The picrate is also obtained immediately when the alcoholic solution of the aniline compound and picric acid, in molecular proportions, are mixed and warmed. The picrate
crystallised in fine needles from benzene. (Found C, 56.44% and 
H, 3.15%; C₂₃H₂₂N₂O₂ requires C, 56.44% and H, 3.06%). (J. Jacobsen
Ber., 21, 1, 417).

**Methylation of 1-anilino-b-naphthoxazole.**

A mixture of 1-anilino-b-naphthoxazole (2 gr) and methyl iodide (3 ml) is heated in a sealed tube at 100°C for
nearly 24 hours. There was no pressure when the tube was opened. The mixture is warmed up with dilute caustic soda
solution and the product extracted with chloroform, dried and
recovered. As the resulting gum did not easily solidify,
it is taken in acetone and a solution of picric acid (1.5g) in
the same solvent added and the mixture refluxed on water bath
for nearly 2 hours. On concentration, the acetone solution
deposited small needles which gave a very ragged melting point.
The acetone was evaporated to dryness. The solid residue
treated with a small quantity of ethyl acetate, well shaken and
filtered on the Buchner funnel. The ethyl acetate solution on
standing deposits small shining yellow needles m.p. 174°C-176°C.
The m.p. is not altered by further crystallisation from the
same solvent. This picrate constituted about 75% of the total
picrate obtained from the methylation product. This is the
picrate of 1-phenyl-imino-2-methyl-1:2-dihydro-b-naphthoxazole,
as it is different from the picrate of 1-methylphenylamino-b-
naphthoxazole prepared synthetically. (Found C, 57.2% and H, 3.4%
C₂₃H₂₂N₂O₂ requires C, 57.25%, H, 3.37%). The residue (insoluble
in ethyl acetate) is crystallised from benzene when small needles
m.p. 194°C-196°C are deposited. This is identified as that of
1-methylphenylamino-b-naphthoxazole by melting point and
mixed melting point with the genuine specimen. (Found C, 57.35%; H, 3.3%; C H O N requires C, 57.28% and
H, 3.27%).

Synthesis of 1-methylphenylethyno-d-naphthoxazole.

A mixture of 1-mercapto-d-naphthoxazole (1g) and mono methylaniline (1g) is heated in a hard glass test tube, in
a paraffin bath, kept at 100°C for nearly 6 hours when the
evolution of H S is complete. The cooled residue is alternately
warmed with dilute HCl (11) and 10 per cent NaOH solution
till monomethylaniline and unreacted mercaptan are completely
eliminated. The residual gummy product is treated with the
calculated quantity of picric acid in benzene and refluxed
on water bath for nearly 30 minutes. The picrate crystallised
from the same solvent when needles m.p. 195°C are obtained.
Synthesis of 1-Hydroxy-2-Naphthoxazole.

The hydroxy compound has been prepared by three methods of which the first two give very satisfactory yields.

Method I. From 1-Amino-2-Naphthol and chlorformic ester.

1-Amino-2-naphthol hydrochloride (2.94g) is added to alcoholic solution of sodium ethoxide (0.7g, 7a in 25cc abs. alcohol), chlorformic ester (2g) is added gently by shaking, cooling when necessary. The mixture is refluxed on water bath for 8 hours. Alcohol is removed completely and to the resinous mass residue, water added to remove NaCl and the water decanted off. The round bottomed flask containing the addition product is heated for nearly 4 hours in paraffin bath, kept at 150o-190o. The required hydroxy compound is extracted by 10% NaOH solution. The alkali solution acidified, the precipitate on crystallisation from dilute alcohol deposits small needles melting at 203o. The hydroxy compound is also sparingly soluble in water, from which it separates out as shining plates m.p. 149o. This product when heated on sand bath sublimes in plates m.p. 255o. Yield, 2.4 cr. 80% of the theoretical (Found C, 71.39%; H, 3.56%; C H O N requires C, 71.35%; H, 3.78%).

Method II. From urethane and 1-Amino-2-Naphthol.

An intimate mixture of 1-amino-2-naphthol hydrochloride (5g) and urethane (3g) is heated in a hard glass test tube in paraffin bath kept at 190o for 8 hours. The cooled residue is treated with excess of 10% NaOH solution and filtered. The filtrate acidified and the crude solid crystallised from dil. alcohol when small plates melting at 230o are deposited.
Yield, 4.5 gr.

Method III. From carbonyl chloride and 1-Amino-2-Naphthol.

Carbonyl chloride (1.2g in 100cc of 12% solution in toluene) is gently added to 1-amino-2-naphthol hydrochloride (2g) in pyridine (20cc). The mixture vigorously shaken in a separating funnel for nearly 4 hours, and then allowed to stand for 16 hours. The reaction is completed by gently refluxing on water bath for 3 hours. After cooling, toluene and pyridine are removed, and the blackish residue taken with dilute alkali solution. Filtered and the filtrate acidified. Light black coloured precipitate m.p. 200c is obtained. When recrystallised from dilute alcohol plates m.p. 207c-208c are obtained. Yield, 1g is nearly 80% of the theoretical. This hydroxy compound is identical with that obtained by methods I and II.

There is nearly 0.8 gr substance m.p. 250c insoluble in NaOH solution. This is under investigation.

Methylation of 1-Hydroxy-b-Naphthoxasole.

The hydroxy compound (1g) is dissolved in chloroform (50cc) by warming, cooled, 10cc alkali (KOH 30%) added to it. Dimethyl sulphate (5cc) is next added by gently shaking. Heat is produced during the addition, hence cooled. A white spongy layer is obtained when kept for 3 hours at room temperature. This disappears on warming on water bath for 30 minutes, cooled and left over night. The excess of dimethylsulphate is destroyed by adding 20cc of KOH (30%) solution, and the product is extracted.
and the product is extracted with chloroform, dried and the solvent recovered. The crude product is recrystallised from dilute methyl alcohol. Shining long needles melting at 188° are obtained. (Found C, 72.36% and H, 4.85%; C H O N requires C, 72.36% and H, 4.85%).

When the methylated product m.p. 189° is heated in a sealed tube at 170° with 50% sulphuric acid for 12 hours 1-methylamino-2-naphthol m.p. 176° is obtained on basification with Conc. ammonia.

1-Mercapto-b-Naphthoxazole.

From 1-Amino-2-Naphthol and carbon disulphide. (P. Jacobson, J. 21, 417.)

A mixture of 1-amino-2-naphthol hydrochloride (10g), carbon disulphide (200c.c.), solid KOH (5g) and alcohol (100cc.) is refluxed on water bath for 12 hours. The excess of carbon disulphide and alcohol is removed on water bath and to the residue water is added. Filtered, filterate acidified by Conc. HCl, when the mercapto-b-naphthoxazole is precipitated, recrystallised from dilute alcohol, in long shining needles m.p. 252° are obtained. Yield is 80% of the theoretical. This is the most convenient mode of preparing the mercaptan in very satisfactory yield.

(2). It is also obtained as a principal by-product during the preparation of 1-amino-b-naphthoxazole from 2-dicyano-2-hydroxy-1-naphthylthiocourea by the action of yellow mercuric oxide.
Methylation of 1-Mercapto-b-Naphthoxazole.

The mercapto derivative has been methylated under three different conditions by two methylating agents.

Method I. By means of methyl iodide in presence of methoxide.

1-Mercapto-b-naphthoxazole (1g) is dissolved in methyl alcohol solution of methoxide (0.115g Na in 30cc abs. methanol), methyl iodide (1cc) is gently added. The solution, very well shaken for some time, is left for 3 hours at room temperature. Gently warmed on water bath for 30 minutes and allowed to stand over night. Excess of methyl alcohol and methyl iodide evaporated off, and the solid residue treated with water to remove sodium iodide. The insoluble product crystallised from methyl alcohol in heavy long needles m.p. 514.72°C. (Found C, 66.6%, H, 4.0% ; C H O N S requires C, 67.1% H, 4.2% and S, 14.8%). This is 1-methyl-thio-b-naphthoxazole.

Method II. By means of dimethyl sulphate in alkali medium.

1-Mercapto-b-Naphthoxazole (1g) is dissolved in chloroform (30cc) and 30 per cent caustic soda potash soln (10cc) is added. Dimethyl sulphate (5cc) is next added by shaking. The mixture gets warm, cooled, kept at room temperature for 45 minutes, gently warmed for 20 minutes on water bath, then left over night. Excess of dimethyl sulphate is destroyed by adding more of KOH solution (30cc), and the methylated product extracted with chloroform, dried and the solvent recovered. The solid residue solidifies immediately, which on re-crystallisation from small quantity of methanol (15cc), deposits the first crop of long needles m.p. 1800-1820°C. This
product is 1-thio-2-methyl-1:2-dihydro-b-naphthoxazole as identified by genuine specimen. found S = 14.9; C, H, O, S; required S = 14.95.

The mother liquor, on dilution, again deposits light needles m.p. 660-665. This product is identical with that obtained from methylation method I. (Found C, 66.6% H, 4.07%, S, 15.10%; C, H, O, S requires C, 67.00%; H, 4.2% and S, 14.9.

Method III. By dimethyl sulphate in presence of methanol.

A mixture of 1-mercapto-b-naphthoxazole (1g.), methanol (15cc) and dimethyl sulphate (2cc) was refluxed on water bath for 1½ hour. After about 20 minutes, a bad smelling gas was liberated. The mixture was allowed to cool, and the methyl alcohol was evaporated off. The excess of dimethyl sulphate was decomposed by conc. ammonia. The methylated product being neutral was extracted with ether. The ether dried and recovered. The residue solidified after nearly 30 minutes. Crystallised from methyl alcohol only, needles m.p. 1650 were deposited. This melt melting point was not depressed by admixture with the specimen obtained from method II.

On diluting the mother liquor, a second crop of low melting substance was obtained m.p. 660-665. This was identified as C-methyl derivative by taking the mixed m.p. with a known specimen.

The ammoniacal solution was acidified with dil HCl the precipitate so obtained crystallised from alcohol in shining needles m.p. 214° sharp. It contains H,S, and gave C, 70.9% and H, 3.8%.
Synthesis of 1-thio-2-methyl-1:2-dihydro-b-naphthoxazole.

An intimate mixture of 1-thio-2-methyl-1:2-dihydro-b-naphthoxazole (0.5g) and P_2S_5 (0.3g) was heated in a glass tube with an air condenser for nearly 8 hours in paraffin bath kept at 170°c. A crystalline substance sublimes on the cooler parts of the test tube. The product is extracted by means of benzene, which on concentration deposits long needles m.p. 180°c sharp. This melting point was not depressed by admixture with the methylated product melting at 180°-182°c obtained by methods II and III.