Thioureas have found their way into almost every branch of chemistry. They are used in dyes, photographic films, elastomers, plastics and textiles.

Thioureas show a wide variety of physiological properties. α-Naphthyl thiourea commonly known as 'ANTU' is a well-known rat poison. Its success is based on the fact that it is more toxic to rats than it is to cats, fowls etc. (18). 2-Biphenyl and 4-biphenyl thiourea also show similar activity (104). 'ANTU' and related compounds have a selective effect on capillaries of the lungs of the rats and dogs and cause an increase in permeability with large volumes of fluid collecting in the lungs and pleura (72). Thus rats and dogs tend to die of pulmonary edema (18).

Some thioureas have been found to be useful as insecticides. Thiocarbamido-D.D.T. is more effective than D.D.T. against bed bugs, although its action is of shorter duration (110). Simple compounds such as phenyl and tolyl thioureas are useful in destroying larvae and adults of various strains of Drosophila melanogaster (28). 2-Benzyl-1-(α-Naphthyl) thiourea and its chloro derivatives were found to be effective against Altogenus piccus and Tinia pellionella (79).

Several phenyl, naphthyl and benzyl substituted thioureas
exhibit antiphenoxidase activity (61), probably owing to their ability to form complexes with copper, the essential metal component of the enzymes (69).

Substances having the formula \((ArNHX'NHX''NH)\_2CS\), where \(Ar\) is phenyl or naphthyl and \(X'\) and \(X''\) are heterocyclic nuclei have been claimed to possess anthelmintic properties (38). N-3,4,5-trichloro-N'-3,5-dichloro thiocarbanilide has been found to exhibit anthelmintic activity (14). Shimotani (94) examined eighteen mono-aryl substituted thioureas for anthelmintic properties on earthworms and found that out of these 2-carbethoxy phenyl thiourea showed remarkable vermicidal activity.

1-Naphthyl thiourea has been shown to be effective against parasites in men and dogs while 2-Naphthyl thiourea and 1,5-dinaphthyl thiourea are ineffective (46).

1-Aryl and alkyl-3-aryl thioureas have been shown to possess hypnotic properties (33). Thioureas of the general formula \(R''''C\_6H\_4N(R)CSNR'R''\) have been patented as hypnotics suitable for use as general or local anaesthetics (\(R =\) Alkyl or alkenyl; \(R'\) and \(R''\) = alkyl or alkenyl and \(R'''' =\) alkyl) (20).

Thiourea is the simplest compound showing antithyroid activity. The activity is assigned to the presence of thioureylene grouping \(-\text{NHCOH}-\) (3). Thiourea has approximately one tenth the activity of thiouracil (4, 2). Pseudothioureas are inactive, but incorporation of thiourea moieties into a ring not involving the sulphur seems to increase the potency (109).
Various types of thioureas have been reported to have antibacterial activity. Shimotani (96) reported a high fungicidal action for $2\text{-OH}_2\text{C}_6\text{H}_4\text{NHCSNH}_2$. Guha et al., (50) prepared mercury derivatives of thioureas and found them to be antibacterial. Bendelin and Tuschhoff (9) reported the marked activity of 2-alkyl pseudothiourea hydrohalide derivatives against Staphylococcus aureus and Eberthella typhi. Thiocarbamido derivatives of diaryl sulphones and sulphides, both mono and bis, have shown marked antibacterial properties (60).

Massie (78) suggested long chain alkyl thioureas which are lipoid soluble as therapeutic agent for tubercle bacillus which contains large amount of lipoidal tissue. A variety of ureas and thioureas have been tested for tuberculostatic and bacteriostatic activity. Huebner et al., (55) and Mayer et al., (80) reported the high tuberculostatic activity of 4-4'-diethoxy thiocarbanilide in mice infected with Bacillus tubercle H37Rv. The existence of a specific relation between the structure and the pharmacological activity in this series is as follows:

For the basic structure, $(p\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4\text{NH})_2\text{CS}$, the following variations result in the total loss of activity: (1) Shortening the alkoxy group to methoxyl or lengthening it to octyloxyl; (2) replacement of the alkoxy groups with an alkyl group which is branched at the carbon adjacent to the benzene ring; (3) replacement of both alkoxy groups with halogens or dialkyl-amino groups; (4) replacement of one of the alkoxy groups with
hydrogen; (5) shifting the alkoxy groups to the 2- or 3-positions; (6) placement of a second substituent (methyl, halogen, or amino) on the benzene ring; (7) replacement of the thiocarbanilide moiety with the corresponding carbanilide, guanidine, guanylthiourea, dithiobiuret, or cyclohexyl substituted thiourea groups.

Several similar compounds were examined. 4-Ethoxy-4'-isobutoxy thiocarbanilide and 4-n-butoxy-4'-dimethylamino thiocarbanilide (44) and derivatives of N-ethoxy phenyl thiourea (54) exceeded the activities of PAS and Streptomycin and approached that of Isoniazid. Unsaturated ether derivatives of 4,4'-dihydroxy thiocarbanilide (25), 4-ethoxy-4'-diethylaminoethoxy diphenyl thiourea (103) and 4,4'-diisoamyloxy thiocarbanilide (77) have been reported to possess high tuberculostatic activity. N- (p-Alkoxy phenyl)-N'-quinolyl thioureas (45), N-4-alkoxy phenyl-N'-4- (α-pyridyl) phenyl thioureas (99) and N- (p-n-butoxy phenyl ) N'- (p-2-pyridyl phenyl) thiourea (74) have been found to exhibit tuberculostatic activity. Tuberculostatic activity has also been observed in compounds of the type \((p-\text{ClC}_6\text{H}_4)_2-\text{CNHCSNHNCH-(C}_6\text{H}_4\text{Cl-p})_2\) (105), and \(p-\text{C}_6\text{H}_5\text{C}_6\text{H}_4-\text{NHCSNHC}_6\text{H}_4\text{C}_6\text{H}_9-p\) (56), 1-p-acyl phenyl-3-alkyl thioureas (37) and \(N,N''\)-disubstituted thioureas (24). Thiourea derivatives of PAS were found to be equal or more active than the acid itself (6, 64, 91).

A series of substituted 2-pyridyl and 4- (1-phenyl-2,3-dimethyl)-5-pyrazolyl thioureas have been synthesised and tested
for their antitubercular activity against Mycobacterium tuberculosis in Dubos medium. The minimum inhibitory concentrations of the compounds studied ranged from 10 mg. per 100 ml. to 0.16 mg. per 100 ml. (47, 48).

Beaver et al., (8) found substituted phenyl ureas to be bacteriostatic. 2-Thenyl thioureas have been shown to be useful as antibacterial drugs (100). Thiourea derivatives have also been shown to exhibit activity against human leprosy (44, 22) and against several species of actinomyces and fungi. 3,5-(CF3)2-thiocarbonilide has been claimed to protect natural fibres against harmful fungi and bacteria (26). Buu-Hoi et al., (21) found certain diaryl thioureas to be active against influenza virus infection in mice.

Aryloxyalkyl group has been found to impart a wide variety of physiological activities. Basic phenol ethers (27), derivatives of phenoxy acetic acid and phenoxy propionic acid (81), alkylamino phenoxy-2-propanols (43), 2-phenoxyethyl amine derivatives (13), aryloxyalkyl ethers (111), local anaesthetics containing arylether group (106), and aryloxyalkane hydroxamic acids (98), have been shown to exhibit fungistatic activity. 3,4-Dichlorophenoxy alkanols (29) have been reported to be useful as germicides and enzyme inhibitors. N-Substituted aryloxyalkyl amines (12) have been shown to exhibit potential antispasmodic activity. N,N-Diaryloxyalkyl guinidine hydrochloride (84), and N-substituted-2 (alkoxy phenoxy) ethyl amines (5)
have been reported to be antihypertensive agents. Phenox-
ethylamine and some of its derivatives were found to be
sympatholytic (15). Phenoxalkyl piperazines have been found
to exhibit hypotensive and adrenolytic effects (88).

It was therefore of interest to prepare thioureas containing
aryloxyalkyl group. Several 1-aryloxyethyl-2-thioureas and
symmetrical 1,3-diaryloxyethyl-2-thioureas have been prepared by
the condensation of aryloxyethyl isothiocyanates with ammonia
and appropriate aryloxyethyl amines respectively.

(I) \[
\begin{align*}
\text{OCH}_2\text{CH}_2\text{NCS} + \text{NH}_3 & \rightarrow \text{OCH}_2\text{CH}_2\text{NHCSNH}_2 \\
\text{X} & \text{X}
\end{align*}
\]

(II) \[
\begin{align*}
\text{OCH}_2\text{CH}_2\text{NCS} + \text{H}_2\text{NCH}_2\text{CH}_2\text{O} & \rightarrow \text{OCH}_2\text{CH}_2\text{NHCSNHCH}_2\text{CH}_2\text{O} \\
\text{X} & \text{X}
\end{align*}
\]

where,
\[
X = \text{H; } o-/p-\text{Cl; } o-/p-\text{CH}_3; \ 2,4-/2,5-(\text{Cl})_2; \\
2,4-(\text{CH}_3)_2; \ 2-\text{CH}_3-4-\text{Cl}
\]
PART II

THEORETICAL
and pyridine (85) and ethyl potassium xanthate (87) have been successfully employed to accelerate this reaction.

(3) Thiophosgene and an Amine:

Primary amines react with thiophosgene to give isothiocyanates or 1,3-disubstituted thioureas depending upon the ratio of the reactants (86, 63).

$$\begin{align*}
\text{CSSCl}_2 + \text{RNH}_2 & \rightarrow \text{RNCS} + 2\text{HCl} \\
\text{CSSCl}_2 + 2\text{RNH}_2 & \rightarrow \text{RNHCSNHR} + 2\text{HCl}
\end{align*}$$

The mechanism of this reaction has been explained in the following manner (40):

$$\begin{align*}
\text{RR'NH} + \text{CSSCl}_2 & \rightarrow (\text{RR'NHClCSSCl}) \rightarrow \text{RR'NCSCl} + \text{HCl} \\
\text{I} & \\
\text{(a) When R'} & \text{ is not H or if R'} = \text{ H and I is stable :} \\
\text{I} + \text{RR'NH} & \rightarrow \text{RR'NCSNRR'} + \text{HCl} \\
\text{(b) When R'} & = \text{ H and I is unstable :} \\
\text{RNHCSCl} & \rightarrow \text{RNCS} + \text{HCl} \\
\text{RNCS} + \text{H}_2\text{NR} & \rightarrow \text{RNHCSNHR}
\end{align*}$$

Preparation of thioureas by this method is best carried out by refluxing one mole of thiophosgene with two moles of the amine in aqueous (41), chloroform-aqueous (83, 41), or acetone-aqueous (83) medium. When thiophosgene has completely reacted, a mole of potassium carbonate is added and the heating continued for several hours.
(C) **Organic Isothiocyanate and an Amine**:

\[
\text{RNCs} + \text{R'R''NH} \rightarrow \text{RNCSNR'R''}
\]

The addition of ammonia, primary and secondary amines to isothiocyanates takes place readily with the formation of \(\text{N,N'}\)-disubstituted thiourea (53). The addition of amine to isothiocyanate is usually carried out in presence of solvents like alcohol, benzene, toluene, acetone, chloroform, pyridine or ether (66, 23). \(\text{R, R', R''}\) may be aromatic, aliphatic, alicyclic or heterocyclic. In this way 1-mono, 1,1- or 1,3-disubstituted or 1,1,3-trisubstituted thioureas have been synthesised. The method is simple and yields are good.

(D) **Alkali Thiocyanate and Amine Hydrochloride**:

Heating ammonium thiocyanate at 160\(^\circ\) for several hours causes it to rearrange to thiourea (59). Use is made of this rearrangement in preparing 1-monosubstituted (71, 90, 95), and 1,1-disubstituted thioureas (68).

\[
\text{R'NH} + \text{HCl} + \text{NH}_4\text{SCN} \rightarrow \text{NH}_4\text{Cl} + \text{R'NH}_2\text{SCN} \rightarrow \text{R'RNCSNH}_2
\]

The reaction can be carried out in an inert solvent (92) or in an aqueous medium (70). 1,3-Disubstituted thioureas cannot be prepared by this method.

(E) **Thioureas and Organic Halides**:

Thioureas react with acyl, alkyl, aralkyl and heterocyclic
halides to give thiourea derivatives. Monoaryl thioureas upon treatment with an acyl halide give first the S-acyl-N-aryl compound which on heating is converted first into the 1-aryl-1-acyl and finally to the 1-aryl-3-acyl thiourea (35, 36). This is the most common method for preparing pseudothioureas.

The most suitable method for the preparation of 1-3-disubstituted (dissimilar substituents) thioureas is (C) viz. the reaction between isothiocyanates and amines. This method was used for the preparation of thioureas described in the present work. Kaye and Parris, and Buu-Hoi (66, 23) have used similar method for the preparation of thiourea derivatives.

The necessary isothiocyanates may be prepared in a number of ways described in the following pages:

1. **Thiophosgene and a Primary Amine**:

   When one mole of a primary amine is permitted to react with one mole of thiophosgene, an isothiocyanate is formed (86, 30). Certain substituents like cyano, bromo, iodo and nitro groups in aromatic amines were found to retard the reaction or prevent it from taking the desired course (39). Chloro substituents in the meta or para positions do not affect the reaction but one o-chloro group hinders it and two o-chloro groups stop it entirely.

   The isothiocyanate can best be prepared by slowly adding with agitation one mole of the amine, either pure or in an
aqueous solution, to one mole of thiophosgene in an aqueous or chloroform solution. The mixture is heated to reflux. Upon completion of reaction the product is steam-distilled or extracted with suitable solvent (42, 40).

2. **Decomposition of Substituted Thiourea**

\[ \text{RHNCSNHR} \rightarrow \text{RH}_2 + \text{RNCS} \]

1,3-Disubstituted thioureas in presence of acid decompose to yield isothiocyanates. The liberated amine is fixed by the acid. Acetic anhydride (31, 89, 23), phosphoric acid (97), concentrated hydrochloric acid (73), and 30-50 per cent sulphuric acid (103) are frequently employed. The product is usually obtained by steam-distillation. Yields of isothiocyanates are quite satisfactory in this method. Isothiocyanates have also been prepared by heating 1,3-disubstituted thioureas in chlorobenzene (11).

3. **Decomposition of Ammonium Dithiocarbamates**

\[ \text{RNHCSSNH}_4 + MX_2 \rightarrow \text{RNCS} + \text{NH}_4X + \text{MS} + \text{HX} \]

An aromatic amine with carbon disulphide and ammonia yields the ammonium salt \( \text{RNHCSSNH}_4 \). This, in turn, gives the isothiocyanate by the removal of \( \text{NH}_4\text{SH} \). Many reagents such as ethyl chloroformate (1, 65, 7, 52), cupric sulphate (75), lead carbonate (51), lead nitrate (32), and chloroacetic acid (19) have been utilised for the decomposition of ammonium dithio-
carbamates. Decomposition of ammonium dithiocarbamate by ethyl chloroformate is often called Andreevsky-Kaluza Synthesis for isothiocyanates.

\[
\begin{align*}
R-\text{NH}_2 + \text{CS}_2 + \text{NaOH} & \longrightarrow R-\text{NHCS}_2\text{Na} + \text{H}_2\text{O} \\
R-\text{NHCS}_2\text{Na} + \text{ClCOOC}_2\text{H}_5 & \longrightarrow R-\text{NHCS}_2\text{COOC}_2\text{H}_5 + \text{NaCl} \\
R-\text{NHCS}_2\text{COOC}_2\text{H}_5 & \longrightarrow R-\text{NCS} + \text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH}
\end{align*}
\]

A similar method for the preparation of aralkyl mustard oils involves the treatment of amine and carbon disulphide in alcoholic solution with iodine and sodium (17). The reaction proceeds in the following manner:

\[
\begin{align*}
4\text{RNH}_2 + 2\text{CS}_2 & \longrightarrow 2\text{RNHCS}^-(\text{NH}_3\text{R})^+ & \text{SC}(-\text{S})\text{NHR} + 2\text{RNH}_3^{-}\text{I} \\
2\text{S} + 2\text{NaI} + 2\text{RNCS} & \xrightarrow{I_2} & \text{SC}(-\text{NR})\text{SNa} \\
\text{SC}(-\text{NR})\text{SNa} & \longrightarrow \text{SC}(-\text{NR})\text{SNa}
\end{align*}
\]

4. Alkali Thiocyanate and Organic Halide:

Sodium, potassium or ammonium thiocyanate reacts with an organic halide to give an organic thiocyanate which, upon heating is converted into the isothiocyanate.

\[
\text{RCI} + \text{KSCN} \longrightarrow \text{RSCN} \xrightarrow{\text{heat}} \text{RNCS}
\]

The reaction is usually carried out by heating the reactants in 1:1 ratio in an inert solvent like benzene (62). This method is suitable for the preparation of acyl, alkyl and aralkyl isothiocyanates (102, 67). Tarlton and McKay (101) carried out
this reaction in presence of an iodide or bromide in dimethyl formamide or dialkyl sulphoxide and obtained excellent yield of bis isothiocyanates.

5. Sandmeyer Reaction:

\[
\text{Aromatic} + \text{HNCO} \rightarrow \text{Diazocomp.} \rightarrow \text{Thiocyanate} \rightarrow \text{Isothiocyanate}
\]

This is a well-known adaptation of Sandmeyer reaction and has been used quite successfully in preparing various aromatic isothiocyanates (34). The major restriction is that the initial amine must be able to withstand diazotisation without injury to other functional groups which may be present.

6. Addition of Sulphur to Cyanides and Cyanates:

In a recent patent (93) organic isothiocyanates have been prepared by heating an organic halide, an alkali metal cyanide and sulphur in the presence of an oxygenated solvent such as an aliphatic aldehyde or ketone.

\[
\text{RCI} + \text{S} + \text{NaCN} \rightarrow \text{RNCS} + \text{NaCl}
\]

The addition of sulphur to benzonitrile to give the corresponding isothiocyanate was reported by Weith (107).

We have followed the method (3) in which sodium dithiocarbamate formed by the action of carbon disulphide and sodium hydroxide on an amine was decomposed by ethyl chloroformate (Andreasch-Kaluza Synthesis).
Aryloxyethyl amines required for the preparation of isothiocyanates were prepared from the corresponding aryloxyethyl bromides by the method of Graymore (49, 82).

**TABLE B-I**

1-ARYLOXYETHYL-2-TILOUREAS

These were prepared by the action of alcoholic ammonia on aryloxyethyl isothiocyanates in alcoholic solution.

\[
\begin{align*}
\text{OCH}_2\text{CH}_2\text{NHCSNH}_2
\end{align*}
\]

<table>
<thead>
<tr>
<th>No.</th>
<th>X</th>
<th>M.P. degree C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>H</td>
<td>141</td>
</tr>
<tr>
<td>2.</td>
<td>o-Cl</td>
<td>140-141</td>
</tr>
<tr>
<td>3.</td>
<td>p-Cl</td>
<td>160-161</td>
</tr>
<tr>
<td>4.</td>
<td>o-CH₃</td>
<td>134</td>
</tr>
<tr>
<td>5.</td>
<td>p-CH₃</td>
<td>134</td>
</tr>
<tr>
<td>6.</td>
<td>2,4-(Cl)₂</td>
<td>141</td>
</tr>
<tr>
<td>7.</td>
<td>2,5-(Cl)₂</td>
<td>123</td>
</tr>
<tr>
<td>8.</td>
<td>2,4-(CH₃)₂</td>
<td>140</td>
</tr>
<tr>
<td>9.</td>
<td>2-CH₃-4-Cl</td>
<td>152</td>
</tr>
</tbody>
</table>
TABLE B-II

SYMMENTRICAL 1,3-DIARYLOXYETHYL-2-ThIOUREAS:

These were prepared by the action of appropriate aryloxyethyl amines on aryloxyethyl isothiocyanates in alcoholic solution.

\[
\begin{array}{c}
\text{No.} & X & \text{M.P. degree C} \\
1. & H & 110 \\
2. & o-Cl & 93 \\
3. & p-Cl & 143-144 \\
4. & o-CH_3 & 117-118 \\
5. & p-CH_3 & 131 \\
6. & 2,4-(Cl)_2 & 105 \\
7. & 2,5-(Cl)_2 & 113 \\
8. & 2,4-(CH_3)_2 & 134 \\
9. & 2-CH_3-4-Cl & 152 \\
\end{array}
\]
PART II

EXPERIMENTAL
Aryloxyethyl amines required for the preparation of aryl­
oxyl ethyl isothiocyanates were prepared as described in Experimental Part I.

**GENERAL METHOD**

**FOR**

**THE PREPARATION OF ARYLOXYETHYL ISOThIOCYANATES :**

In a three-necked round bottomed flask, surrounded by ice-
bath, and fitted with a mechanical stirrer, a reflux condenser,
a thermometer and a dropping funnel, were placed carbon disulphide
(1.0 mole.) and an ice cold aqueous solution of caustic soda
(1.0 mole. in 169 ml. of water). To this mixture was added with
stirring, substituted aryloxyethyl amine (1.0 mole.) and the
mixture was warmed gently on a water bath for one to two hours
to complete the reaction. The bright red solution was cooled
to 35-40°C; and it was added over a period of one hour, with
stirring, ethylchloroformate (1.0 mole.). After the addition
of ethylchloroformate was complete, the mixture was allowed to
stand for thirty minutes while the temperature was maintained
between 30-40°C. The isothiocyanate, which separated as an oil,
was extracted with ether and the ethereal extract was dried over
anhydrous calcium chloride. After the removal of ether, the
isothiocyanate was purified by distillation under reduced
pressure (Kaluza, Monatsh, 1912, 33, 363; Moore and Crossley, Org. Synthesis 1941, 21, 81).

Following isothiocyanates were prepared by this method:

**ARYLOXYETHYL ISOTHIOCYANATES**:

```
\[
\begin{array}{c}
\text{OCH}_2\text{CH}_2\text{NCS} \\
X
\end{array}
\]
```

<table>
<thead>
<tr>
<th>No.</th>
<th>X</th>
<th>B.P.</th>
<th>Molecular Formula</th>
<th>Per cent Sulphur</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>degree</td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>1</td>
<td>H</td>
<td>148°/6 mm.</td>
<td>C₉H₉ONS</td>
<td>17.7</td>
</tr>
<tr>
<td>2</td>
<td>o-Cl</td>
<td>170-172°/9 mm.</td>
<td>C₉H₈ONS Cl</td>
<td>14.9</td>
</tr>
<tr>
<td>3</td>
<td>p-Cl</td>
<td>155-156°/3 mm.</td>
<td>C₉H₈ONS Cl</td>
<td>14.8</td>
</tr>
<tr>
<td>4</td>
<td>o-CH₃</td>
<td>145-147°/5 mm.</td>
<td>C₁₀H₁₀ONS</td>
<td>16.6</td>
</tr>
<tr>
<td>5</td>
<td>p-CH₃</td>
<td>157°/6 mm.</td>
<td>C₁₀H₁₁ONS</td>
<td>16.8</td>
</tr>
<tr>
<td>6</td>
<td>2,4-(Cl)₂</td>
<td>173°/6 mm.</td>
<td>C₉H₇ONS Cl₂</td>
<td>12.8</td>
</tr>
<tr>
<td>7</td>
<td>2,5-(Cl)₂</td>
<td>168°/6 mm.</td>
<td>C₉H₇ONS Cl₂</td>
<td>12.7</td>
</tr>
<tr>
<td>8</td>
<td>2,4-(CH₃)₂</td>
<td>167°/8 mm.</td>
<td>C₁₁H₁₃ONS</td>
<td>15.6</td>
</tr>
<tr>
<td>9</td>
<td>2-CH₃-4-Cl</td>
<td>193°/11 mm.</td>
<td>C₁₀H₁₀ONS Cl</td>
<td>14.1</td>
</tr>
</tbody>
</table>
GENERAL METHOD FOR THE PREPARATION OF

1-ARYLOXYETHYL-2-THOUREAS :

Freshly distilled aryloxyethyl isothiocyanate was slowly added to an excess of alcoholic ammonia solution. The mixture was heated just to boiling, stirred for about ten minutes, corked and cooled in ice. The thiourea separated immediately on dilution with water. These were filtered, washed with cold water and recrystallised either from absolute or aqueous alcohol.

The compounds prepared are shown in the following table:
TABLE B-III

1-ARYLOXYETHYL-2-THIOUREAS

\[
\begin{tikzpicture}
  \draw[thick] (0,0) -- (1,0) -- (1.5,0.5) -- (0.5,1) -- (0,1) -- (-0.5,0.5) -- cycle;
  \draw[thick] (0.5,0.5) -- (1,1);
  \node at (0.75,0.25) {X};
  \node at (-0.25,0.75) {OCH\textsubscript{2}CH\textsubscript{2}NHCSNH\textsubscript{2}};
\end{tikzpicture}
\]

<table>
<thead>
<tr>
<th>No.</th>
<th>X</th>
<th>M.P. degree C</th>
<th>Molecular Formula</th>
<th>Per cent Sulphur Found</th>
<th>Per cent Sulphur Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>H</td>
<td>141</td>
<td>C\textsubscript{9}H\textsubscript{12}ON\textsubscript{2}S</td>
<td>16.2</td>
<td>16.3</td>
</tr>
<tr>
<td>2.</td>
<td>o-Cl</td>
<td>140-141</td>
<td>C\textsubscript{9}H\textsubscript{11}ON\textsubscript{2}SCl</td>
<td>14.0</td>
<td>13.9</td>
</tr>
<tr>
<td>3.</td>
<td>p-Cl</td>
<td>160-161</td>
<td>C\textsubscript{9}H\textsubscript{11}ON\textsubscript{2}SCl</td>
<td>13.9</td>
<td>13.9</td>
</tr>
<tr>
<td>4.</td>
<td>o-CH\textsubscript{3}</td>
<td>134</td>
<td>C\textsubscript{10}H\textsubscript{14}ON\textsubscript{2}S</td>
<td>15.0</td>
<td>15.2</td>
</tr>
<tr>
<td>5.</td>
<td>p-CH\textsubscript{3}</td>
<td>134</td>
<td>C\textsubscript{10}H\textsubscript{14}ON\textsubscript{2}S</td>
<td>15.1</td>
<td>15.2</td>
</tr>
<tr>
<td>6.</td>
<td>2,4-(Cl)\textsubscript{2}</td>
<td>141</td>
<td>C\textsubscript{9}H\textsubscript{10}ON\textsubscript{2}SCl\textsubscript{2}</td>
<td>12.1</td>
<td>12.1</td>
</tr>
<tr>
<td>7.</td>
<td>2,5-(Cl)\textsubscript{2}</td>
<td>123</td>
<td>C\textsubscript{9}H\textsubscript{10}ON\textsubscript{2}SCl\textsubscript{2}</td>
<td>12.2</td>
<td>12.1</td>
</tr>
<tr>
<td>8.</td>
<td>2,4-(CH\textsubscript{3})\textsubscript{2}</td>
<td>140</td>
<td>C\textsubscript{11}H\textsubscript{16}ON\textsubscript{2}S</td>
<td>14.2</td>
<td>14.3</td>
</tr>
<tr>
<td>9.</td>
<td>2-CH\textsubscript{3}-4-Cl</td>
<td>152</td>
<td>C\textsubscript{10}H\textsubscript{13}ON\textsubscript{2}SCl</td>
<td>13.0</td>
<td>13.1</td>
</tr>
</tbody>
</table>
GENERAL METHOD FOR THE PREPARATION OF

SYMМETRICAL 1,3-DIARYLOXYETHYL-2-THIOUREAS:

A mixture of aryloxyethyl isothiocyanate (0.01 mole) and appropriate aryloxyethyl amine (0.01 mole) in absolute alcohol (25-40 ml.) was heated to boiling for a few minutes and kept overnight. In most cases thiourea was obtained as a crystalline solid. It was recrystallised from ethyl alcohol (Buu-Hoi et al., J. Chem. Soc., 1955, 1573).

The compounds prepared are shown in the following table:
## TABLE B-IV

**SYMметRICAL 1,3-DiarylOxyethyl-2-ThioureAs**

![Diagram of the compound](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>X</th>
<th>M.P. degree C</th>
<th>Molecular Formula</th>
<th>Per cent Sulphur Found</th>
<th>Per cent Sulphur Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>H</td>
<td>110</td>
<td>C_{17}H_{20}O_{2}N_{2}S</td>
<td>10.1</td>
<td>10.1</td>
</tr>
<tr>
<td>2.</td>
<td>o-Cl</td>
<td>93</td>
<td>C_{17}H_{18}O_{2}N_{2}SCl_{2}</td>
<td>9.0</td>
<td>9.1</td>
</tr>
<tr>
<td>3.</td>
<td>p-Cl</td>
<td>143-144</td>
<td>C_{17}H_{18}O_{2}N_{2}SCl_{2}</td>
<td>8.9</td>
<td>9.1</td>
</tr>
<tr>
<td>4.</td>
<td>o-CH₃</td>
<td>117-118</td>
<td>C_{19}H_{24}O_{2}N_{2}S</td>
<td>9.8</td>
<td>9.7</td>
</tr>
<tr>
<td>5.</td>
<td>p-CH₃</td>
<td>131</td>
<td>C_{19}H_{24}O_{2}N_{2}S</td>
<td>9.7</td>
<td>9.7</td>
</tr>
<tr>
<td>6.</td>
<td>2,4-(Cl)₂</td>
<td>105</td>
<td>C_{17}H_{16}O_{2}N_{2}SCl_{4}</td>
<td>8.3</td>
<td>8.3</td>
</tr>
<tr>
<td>7.</td>
<td>2,5-(Cl)₂</td>
<td>113</td>
<td>C_{17}H_{16}O_{2}N_{2}SCl_{4}</td>
<td>8.2</td>
<td>8.3</td>
</tr>
<tr>
<td>8.</td>
<td>2,4-(CH₃)₂</td>
<td>134</td>
<td>C_{21}H_{28}O_{2}N_{2}S</td>
<td>9.4</td>
<td>9.3</td>
</tr>
<tr>
<td>9.</td>
<td>2-CH₃-4-Cl</td>
<td>152</td>
<td>C_{19}H_{22}O_{2}N_{2}SCl_{2}</td>
<td>8.8</td>
<td>8.8</td>
</tr>
</tbody>
</table>
PART II

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PART II

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