EXPERIMENTAL PART I.
**EXPERIMENTAL PART I.**

General Method for the preparation of Substituted Benzyl chlorides:

In a 500 c.c. r.b. flask, fitted with a reflux condenser and a calcium chloride guard tube, sulphuryl chloride (72.0 gm.) and benzoyl peroxide (0.7 gm.) were placed. Dry substituted toluene (0.64 mol.) was added from above the condenser slowly with shaking and simultaneous cooling. After the addition of substituted toluene was complete the reaction mixture was refluxed on a water-bath for about three hours. The product was washed with water, dried over calcium chloride and distilled under reduced pressure. Yield 75 per cent.

Kiescheimer, Zimmermann, Kummar, Ann., 1925, 446, 225.

Following substituted benzyl chlorides were prepared by the above method in 70 to 75 per cent yield.

<table>
<thead>
<tr>
<th>Name</th>
<th>B.P.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-chloro benzyl chloride</td>
<td>216°</td>
<td>Jackson, Ber., 11, 904.</td>
</tr>
</tbody>
</table>
General Method for the preparation of Substituted Benzyl bromides:-

In a three-necked flask mounted with a mercury sealed stirrer, a dropping funnel and a reflux condenser with a gas-trap, substituted toluene (0.6 mol.) was heated (in an oil-bath) at 120° and exposed to the light of 100 watt lamp. With constant agitation, bromine (0.64 mol.) is added during three hours, and the stirring is continued for another thirty minutes. By this time, the evolution of hydrogen bromide stopped. The product was kept over KOH overnight in a desiccator to absorb hydrogen bromide. The product, if liquid was distilled under reduced pressure or if solid, washed with ethyl alcohol on a suction filter. Yield 65 per cent.


o- and m-bromotoluene were converted to the respective benzyl bromides by the above method except that illumination was not needed.

<table>
<thead>
<tr>
<th>Name</th>
<th>B.P. or M.P.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-bromo benzyl bromide</td>
<td>M.P. 41°;</td>
<td>Weismann, loc. cit.</td>
</tr>
<tr>
<td></td>
<td>B.P. 110-120°/7 mm</td>
<td></td>
</tr>
<tr>
<td>p-iodo benzyl bromide</td>
<td>M.P. 75-78°</td>
<td>Am. C. J., 1, 103; 2, 250.</td>
</tr>
</tbody>
</table>
General Method for the preparation of \( \omega \)-bromo substituted xylene:

In a 500 c.c. three-necked flask, fitted with a reflux condenser, a gas trap and a separatory funnel, xylene (1.41 mol., 150 gm.) is placed and heated to 120°-130° in an oil bath. From the separatory funnel bromine (3.15 mol., 504 gm.) is added slowly through a tube passing below the surface of xylene. After addition of bromine, the reaction mixture is poured into evaporating dish and placed in a vacuum dessicator over KOH till HBr is removed. The product is distilled under reduced pressure. Yield about 80 per cent.


Following xylenes were prepared by this method:

<table>
<thead>
<tr>
<th>Name</th>
<th>B.P. or M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega )-Bromo-o-xylene</td>
<td>B.P. 216°; M.P. 21°.</td>
</tr>
<tr>
<td>( \omega )-Bromo-m-xylene</td>
<td>B.P. 215°.</td>
</tr>
<tr>
<td>( \omega )-Bromo-p-xylene</td>
<td>B.P. 218-220°; M.P. 35°.</td>
</tr>
</tbody>
</table>

General Method for the preparation of Dimethyl benzyl chlorides by Chloromethylation:

A mixture of xylene (1 mol.), conc. HCl (530 gm.) and formaldehyde (106 gm., 37%, 1.27 mol.) is mechanically stirred and held at 60-70° for seven hours,
while a stream of dry hydrogen chloride is introduced into the reaction mixture. The oily layer is separated washed, dried over CaCl₂, and distilled under reduced pressure. Yield 65 to 70 per cent.

(von Braun and Helles, Ber., 1934, 67, 1096.)

<table>
<thead>
<tr>
<th>Name</th>
<th>B.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-Dimethyl benzyl chloride</td>
<td>100-103°/12 mm.</td>
</tr>
<tr>
<td>2,4-Dimethyl benzyl chloride</td>
<td>100-105°/14 mm.</td>
</tr>
<tr>
<td>3,4-Dimethyl benzyl chloride</td>
<td>100-102°/10 mm.</td>
</tr>
</tbody>
</table>

General Method for the preparation of substituted Benzyl chlorides from Aldehydes :-

I. Preparation of substituted Benzyl alcohols by the Cross-Cannizaro reaction of sub. benzaldehyde :-

Aldehyde (1 mol.), methyl alcohol(200 c.c.) and formalin (1.3 mol., 100 c.c.) are heated to 65° and then surrounded by cold water while a solution of NaOH (3 mol., 120 gm. in 120 c.c. water) is added rapidly and the temp. maintained between 65-75°. The mixture is then heated at 70° for 40 mins. and then refluxed for 20 mins. The product is cooled, diluted with water and extracted with benzene and the benzene extract dried with Na₂SO₄. After removing benzene, the alcohol is obtained by distilling under reduced pressure. Yield 85-90 per cent. (Davidson and Bogert, J. Am. Chem. Soc., 1935, 57, 905).

Following benzyl alcohols were prepared by the above method :-
II. Conversion of Benzyl alcohols into Substituted Benzyl chlorides:

Substituted benzyl alcohol (1 mol.) in dry benzene (100 c.c.) is added dropwise during thirty minutes to Thionyl chloride (1.1 mol.) in benzene (50 c.c.), containing a drop of pyridine. After complete addition, the reaction mixture is warmed on a water bath for one hour, and finally treated with ice water. Benzene layer is dried and after removing benzene, the substituted benzyl chloride is purified by distillation under reduced pressure.


Following benzyl chlorides were prepared by this method:-

<table>
<thead>
<tr>
<th>Product</th>
<th>B.P.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Methoxy benzyl chloride</td>
<td>104°/10 mm.</td>
<td>Pechorr, Ann., 373, 76.</td>
</tr>
<tr>
<td>m-Methoxy benzyl chloride</td>
<td>124°/15 mm.</td>
<td>Pechorr, Ann., 391, 45.</td>
</tr>
<tr>
<td>p-Methoxy benzyl chloride</td>
<td>116-120°/</td>
<td>Bennett, loc.cit.</td>
</tr>
</tbody>
</table>
These chlorides were used for the synthesis of malonates described in the second part.

General Method for the preparation of Substituted Benzyl amines :-

(A). From the Halides by the Delépine reaction:

Substituted benzyl halides (1 mol.) dissolved in chloroform was gradually added with constant stirring and cooling to hexamethylene tetramine (1.1 mol.) dissolved in chloroform. After the addition was complete, the mixture was corked and kept overnight. If the complex was not obtained next-day, the mixture was refluxed for 2 to 6 hours and again kept overnight. The solid complex was filtered at the pump and to the nearly dry product dissolved in water ammonia was added in excess. The mixture was refluxed for about one to one and a half hour, poured in excess of cold water and the oily cyclic imine thus obtained was treated with excess of conc. HCl and the mixture evaporated to dryness on a water bath. The amine hydrochloride thus obtained was dissolved in water, a little conc. hydrochloric acid added and the mixture steamed in order to remove volatile impurities. The product was made alkaline by 50 % caustic soda soln., and the oily amine thus obtained was separated or if necessary extracted with ether and the ether solution dried over caustic potash. After removing ether the amine was purified by distillation. Yield 45 to 50 per cent.


Following amines were prepared by the above process:

<table>
<thead>
<tr>
<th>Amine</th>
<th>B.P.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-chloro benzyl amine</td>
<td>103°/11</td>
<td>Prenzen, Ber., 38, 1417.</td>
</tr>
<tr>
<td>p-chloro benzyl amine</td>
<td>109°/14</td>
<td>Shoppee, ibid, 1931, 1235.</td>
</tr>
<tr>
<td>o-bromo benzyl amine</td>
<td>118°/9</td>
<td>--do--</td>
</tr>
<tr>
<td>n-bromo</td>
<td>126°/16</td>
<td>--do--</td>
</tr>
<tr>
<td>p-bromo</td>
<td>103°/12</td>
<td>--do--</td>
</tr>
<tr>
<td>n-iodo</td>
<td>132°/6</td>
<td>Shoppee, loc. cit.</td>
</tr>
<tr>
<td>o-methyl</td>
<td>199-205°</td>
<td>Krober, Ber., 23, 1026</td>
</tr>
<tr>
<td>n-methyl</td>
<td>196-99°</td>
<td>Graymore, loc. cit.</td>
</tr>
<tr>
<td>p-methyl</td>
<td>105°/22</td>
<td>Shoppee, loc. cit.</td>
</tr>
<tr>
<td>3,4-Dimethyl</td>
<td>220-220</td>
<td>new.</td>
</tr>
<tr>
<td>2,4-Dimethyl</td>
<td>218-190</td>
<td>Hünrichsen, Ber., 21, 3083.</td>
</tr>
<tr>
<td>2,5-Dimethyl</td>
<td>220-220</td>
<td>new.</td>
</tr>
</tbody>
</table>

(B). From the aldehydes by Leuckart reaction:

Substituted benzaldehyde (0.1 mol.) was added dropwise with constant shaking to ammonium formate (0.8 mol.) at 165°. The reaction mixture which was taken in a distilling flask fitted with a water condenser at the side, was heated at 165-190° for four hours. A small amount of the aldehyde recovered with the distillate was returned to the reaction mixture from time to time. Finally, the reaction mixture was cooled, transformed to a round bottom flask, hydrochloric acid (100 c.c., 12 to 15 per cent) added and refluxed.
for four hours. It was made strongly alkaline by 50% NaOH solution and the amine liberated was isolated and purified as usual. Yields vary according to the nature of aldehyde as shown in the table.


Following amines were prepared by the above method :-

<table>
<thead>
<tr>
<th>Amine</th>
<th>Yield %</th>
<th>B.P.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Methoxy benzyl amine</td>
<td>30</td>
<td>114°/14</td>
<td>Lewis, loc.cit.</td>
</tr>
<tr>
<td>p-Methoxy benzyl amine</td>
<td>23</td>
<td>115°/12</td>
<td>Lewis, loc.cit.</td>
</tr>
</tbody>
</table>

(C). From Ketones by Leuckart reaction :

In a 500 c.c. r.b. flask (Claisen) are placed Ammonium formate (4 mol.; 250 gm.), the ketone (1.25 mol.) and a few chips of porous pâte.

The flask is fitted with a cork carrying a thermometer nearly to the bottom, and the side-arm is connected to a small condenser set for distillation. On heating the flask with a small flame the mixture first melts to two layers and distillation occurs; at 150-55° it becomes homogeneous and reaction takes place with foaming. Heating is continued until temperature reaches 185-90°. During
this process water, ketone and ammonium carbonate distil,
The temperature is maintained at 155° for three hours
and distilled ketone is added back to the reaction
mixture.

The reaction mixture is then cooled,
conc. HCl (150 c.c.) is added and refluxed for one hour.
The mixture is cooled and made alkaline by 50 % NaOH
solution, when the amine separates out as an oil. It is
isolated and purified as usual. Yield 60 to 70 per cent.
(Ingerson et al., loc. cit.; Org. Synthesis, Coll. Vol. II,
p. 504).

The following amines were prepared by

this method :-

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Product</th>
<th>B.P.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone</td>
<td>Phenyethylamine</td>
<td>184-85°</td>
<td>Ingersoll, loc. cit.</td>
</tr>
<tr>
<td>Propiophenone</td>
<td>Phenyl propylamine</td>
<td>107°/16 mm.</td>
<td>Busch, Ber., 1905, 37, 1765</td>
</tr>
<tr>
<td>Butyrophenone</td>
<td>Phenyl butylamine</td>
<td>99°/16 mm.</td>
<td>J. Am. Chem. Soc., 1931, 53, 1876</td>
</tr>
</tbody>
</table>

(D). Alkylation of Hydroxy aldehydes:

p-Hydroxybenzaldehyde (0.1 mol.;
12.2 gm.), anhydrous \( \text{K}_2\text{CO}_3 \) (0.4 mol.; 60 gm.), ethyl
methyl ketone (80 c.c.) and \( n \)-alkyl halide (0.16 mol.)
were refluxed and agitated vigorously for three hours.
The solvent was then decanted from \( \text{K}_2\text{CO}_3 \), which was
washed with ether, ether washings were added to ethyl methyl ketone extract and both solvents distilled off. Residual p-n-alkoxy benzaldehydes were purified by distilling under reduced pressure. Yield 65 to 75 per cent. (Gray and Jones, J. Chem. Soc., 1954, 1469.)

These aldehydes were converted into the corresponding oximes by hydroxyl amine hydrochloride, sodium acetate and alcohol by the usual method.

p-n-alkoxybenzaldehydes were reduced by sodium and alcohol according to Org. Synthesis Coll. Vol. II, p. 318.

Following amines were prepared:

<table>
<thead>
<tr>
<th>Yield 45 to 50 per cent.</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Oxime M.P.</th>
<th>Benzyl amine</th>
<th>Reference</th>
</tr>
</thead>
</table>

General Method for the preparation of Substituted alkoxy Phenyl amines i.e. p-Amino phenyl alkyl ethers:

(A) p-Nitro phenyl alkyl ether:

p-Nitrophenol (0.1 ml., 14 gm.).
anhydrous \( \text{K}_2\text{CO}_3 \) (0.4 mol., 60 gm.), ethyl methyl ketone (80 c.c.) and n-alkyl halide (0.16 mol.) were refluxed and agitated vigorously for three hours. The solvent was then decanted and \( \text{K}_2\text{CO}_3 \) residue washed with ether. Ether washings were added to the solvent extract and both solvents distilled off. The residual p-Nitro phenyl ether purified by distilling under reduced pressure. Yield 50 to 60 per cent.

(Weygand and Gabler, J.prakt.chem. 1940, 155, 332 ;

Following p-Nitrophenyl ethers were prepared by the above method:

<table>
<thead>
<tr>
<th>p-Nitrophenyl alkyl ether</th>
<th>B.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl</td>
<td>285\degree M.P. 56\degree</td>
</tr>
<tr>
<td>n-Proplyl</td>
<td>285\degree 89\degree</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>160\degree 7 mm.</td>
</tr>
<tr>
<td>n-Amyl</td>
<td>M.P. 32\degree</td>
</tr>
<tr>
<td>n-Hexyl</td>
<td>165\degree 5 mm.</td>
</tr>
<tr>
<td></td>
<td>172-74\degree 5 mm., M.P. 26\degree</td>
</tr>
</tbody>
</table>

(B). p-Amino phenyl alkyl ethers:

Stannous chloride (4 parts) is dissolved in conc. HCl (5 parts) and solution heated to 85\degree and p-Nitro phenyl ether (1 part) was added in small portions with constant stirring. Temperature rose to 105\degree. The reaction mixture was then boiled for a few minutes and allowed to cool. It was made alkaline by NaOH and extracted with ether. The ether extract was dried over
caustic potash after removal of ether, the residual oil was distilled under reduced pressure. Yield 80 to 85 per cent.

(Gutekunst and Gray, J. Am. Chem. Soc., 1922, 44, 1742.)

Following ethers were prepared:

<table>
<thead>
<tr>
<th>p-Aminophenyl alkyl ether B.P.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl 254° 135°/10</td>
<td>Spiegel, Ber., 1901, 54, 1938.</td>
</tr>
<tr>
<td>n-Propyl 136°/10</td>
<td>--do--</td>
</tr>
<tr>
<td>n-Butyl 144°/12</td>
<td>J. Am. Chem. Soc., 44, 1742.</td>
</tr>
<tr>
<td>n-Amyl 275°</td>
<td>Spiegel, loc. cit.</td>
</tr>
</tbody>
</table>

General Method for the preparation of Isothiocyanate:

In a three-necked r.b. flask, surrounded by ice bath fitted with a mechanical stirrer and a reflux condenser, thermometer and a 250 c.c. dropping funnel, are placed carbon disulphide (1.0 mol., 76 gm.) and a cold solution of caustic soda (1 mol., 76 gm.) in water (160 c.c.). To this mixture, cooled to 10-15° is added, with stirring, the appropriate substituted amine (1 mol.). Stirring is continued and the mixture is warmed gently over steam-bath for one to two hours to complete the reaction. The bright red solution is cooled to 35-40° and to it is added over a period of one hour, with stirring ethyl chlorocarbonate (1 mol., 108.5 gm.). After all the ethyl chlorocarbonate was added the mixture was allowed to stand for thirty minutes when the temperature should fall to 30° to 40°.
The isothiocyanate which usually separates out as an oil is removed from the reaction mixture and dried over CaCl₂. Sometimes it is extracted with ether, ethereal extract dried over CaCl₂ and after removal of ether an oil is obtained. It is purified by distilling under reduced pressure. Yield 60 to 70 per cent. (Kaluza, Monatsh, 1912, 33, 363; Moore and Crossley, Org. synthesis, 21, 81-82.)

For convenience, isothiocyanates are divided into three parts viz. (A) substituted benzyl isothiocyanates, (B) α-Phenyl alkyl isothiocyanates and (C) substituted alkoxy phenyl isothiocyanates.

(A) Substituted benzyl isothiocyanates:

o-Chlorobenzyl Isothiocyanate:

It was obtained in 62 per cent yield from o-Chlorobenzyl amine (14.2 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 138⁰/7 mm.; D₂₇: 1.203; N₂₇: 1.5788.

Found S, 17.4 per cent; Cl, 19.3 per cent.
C₆H₅NC1S requires S, 17.5 per cent; Cl, 19.3 per cent.

m-Chlorobenzyl Isothiocyanate:

It was obtained in 60 per cent yield from m-Chlorobenzyl amine (14.2 gm.), Carbon disulphide
(7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 142-46°/6 mm.; D₂₇: 1.201; N₂₇: 1.5784.

Found S, 17.4 per cent; Cl, 19.3 per cent.

C₆H₅NCIS requires S, 17.5 per cent; Cl, 19.3 per cent.

p-Chlorobenzyl Isothiocyanate:

It was obtained in 65 per cent yield from p-Chlorobenzyl amine (14.2 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 130-35°/4 mm.; D₂₇: 1.206; N₂₇: 1.5698.

Found S, 17.4 per cent; Cl, 19.2 per cent.

C₆H₅NCIS requires S, 17.5 per cent; Cl, 19.3 per cent.

p-Bromobenzyl Isothiocyanate:

It was obtained in 60 per cent yield from p-Bromobenzyl amine (18.6 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 130-34°/5 mm.; D₂₇: 1.403; N₂₇: 1.5048.

Found S, 14.0 per cent; Br, 35.0 per cent.

C₆H₅NBrS requires S, 14.1 per cent; Br, 35.0 per cent.

m-Bromobenzyl Isothiocyanate:

It was obtained in 62 per cent yield from m-Bromobenzyl amine (18.6 gm.), Carbon disulphide
(7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 147°/5 mm.; D_27^27 : 1.503; N_D^27 : 1.6384.

Found S, 14.0 per cent; Br, 35.0 per cent.

C_8H_6NBrS requires S, 14.1 per cent; Br, 35.0 per cent.

d-Bromobenzyl Isothiocyanate:

It was obtained in 68 per cent yield from d-Bromobenzyl amine (15.6 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and the ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 140-44°/5-7 mm.; D_27 : 1.381; N_D^27 : 1.6057.

Found S, 13.9 per cent; Br, 34.9 per cent.

C_8H_6NBrS requires S, 14.1 per cent; Br, 35.0 per cent.

m-Iodobenzyl Isothiocyanate:

It was prepared in 58 per cent yield from m-Iodobenzyl amine (33.3 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 162°/3-4 mm.; D_27 : 1.667; N_D : 1.6170.

Found S, 11.6 per cent; I, 46.0 per cent.

C_8H_6NIS requires S, 11.6 per cent; I, 46.1 per cent.

p-Iodobenzyl Isothiocyanate:

It was prepared in 64 per cent yield
from p-Iodobenzyl amine (33.3 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.
B.P. 167°/3-4 mm.; $D_{27}$: 1.521; $N_D^{27}$: 1.6086.

Found S, 11.7 per cent; I, 46.1 per cent.

C$_8$H$_6$NIS requires S, 11.6 per cent; I, 46.1 per cent.

p-Ethoxybenzyl Isothiocyanate:

It was prepared in 60 per cent yield from p-Ethoxybenzyl amine (15.1 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.
B.P. 98°/5 mm.

Found S, 16.46 per cent.

C$_{10}$H$_{11}$NOS requires S, 16.58 per cent.

p-Butoxybenzyl Isothiocyanate:

It was obtained in 60 per cent yield from p-Butoxybenzyl amine (17.9 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the process described above.
B.P. 142-45°/8-10 mm.

Found S, 14.20 per cent.

C$_{18}$H$_{15}$NOS requires S, 14.47 per cent.
o-Methylbenzyl Isothiocyanate:

It was prepared in 60 per cent yield from o-Methylbenzyl amine (12.1 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 120°/7 mm.; \( \frac{N}{D}^{27} \): 1.5874.

Found S, 19.50 per cent.

\( \text{C}_9\text{H}_9\text{NS} \) requires S, 19.63 per cent.

m-Methylbenzyl Isothiocyanate:

It was prepared in 60 per cent yield from m-Methylbenzyl amine (12.1 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 148°/15 mm.; \( \frac{N}{D}^{27} \): 1.5632.

Found S, 19.58 per cent.

\( \text{C}_9\text{H}_9\text{NS} \) requires S, 19.63 per cent.

p-Methylbenzyl Isothiocyanate:

It was prepared in 65 per cent yield from p-Methylbenzyl amine (12.1 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 155°/17 mm.; \( \frac{N}{D}^{38.5} \): 1.5486.

Found S, 19.60 per cent.

\( \text{C}_9\text{H}_9\text{NS} \) requires S, 19.63 per cent.
o-Methoxybenzyl Isothiocyanate:

It was prepared in 68 per cent yield from o-Methoxybenzyl amine (13.7 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 132°/5-7 mm.

Found S, 17.80 per cent.

C₉H₉NSO requires S, 17.87 per cent.

m-Methoxybenzyl Isothiocyanate:

It was prepared in 65 per cent yield from m-Methoxybenzyl amine (13.7 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 128°/3 mm.; N²⁷: 1.5912.

Found S, 17.82 per cent.

C₉H₉NSO requires S, 17.87 per cent.

p-Methoxybenzyl Isothiocyanate:

It was prepared in 70 per cent yield from p-Methoxybenzyl amine (13.7 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 125°/7 mm.; N²⁷: 1.5935.

Braun and Deutsch, Ber., 1912, 45, 2191-96 notes B.P. 170°/16 mm.
3,4-Dimethylbenzyl Isothiocyanate:

It was prepared in 70 per cent yield from
3,4-Dimethylbenzyl amine (13.5 gm.), Carbon disulphide
(7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate
(10.9 gm.) by the procedure described above.
B.P. 170°/12 mm.

Found S, 18.00 per cent.

C_{10}H_{11}NS requires S, 18.07 per cent.

2,4-Dimethylbenzyl Isothiocyanate:

It was prepared in 70 per cent yield
from 2,4-Dimethylbenzyl amine (13.5 gm.), Carbon disulphide
(7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate
(10.9 gm.) by the procedure described above.
B.P. 120°/50 mm.

Found S, 17.98 per cent.

C_{10}H_{11}NS requires S, 18.07 per cent.

2,5-Dimethylbenzyl Isothiocyanate:

It was prepared in 70 per cent yield
from 2,5-Dimethylbenzyl amine (13.5 gm.), Carbon disulphide
(7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate
(10.9 gm.) by the procedure described above.
B.P. 160°/9 mm.; \( \nu_{D}^{58.5} \): 1.5608.

Found S, 18.10 per cent.

C_{10}H_{11}NS requires S, 18.07 per cent.
(B) \( \alpha \)-Phenyl alkyl isothiocyanates:

\( \alpha \)-Phenyl ethyl isothiocyanate:

It was prepared in 62 per cent yield from \( \alpha \)-Phenyl ethyl amine (12.1 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 140°/5 mm.; \( \bar{N} \) \( \text{D} \): 1.5253.

Found S, 19.58 per cent.

C\(_9\)H\(_9\)NS requires S, 19.63 per cent.

\( \alpha \)-Phenyl n-propyl isothiocyanate:

It was prepared in 60 per cent yield from \( \alpha \)-Phenyl n-propyl amine (13.5 gm.), ethyl chloro carbonate (10.9 gm.), NaOH (4.0 gm.) and Carbon disulphide (7.6 gm.) by the procedure described above.

B.P. 160°/3 mm.; \( \bar{N} \) \( \text{D} \): 1.5482.

Found S, 18.00 per cent.

C\(_{10}\)H\(_{11}\)NS requires S, 18.07 per cent.

\( \alpha \)-Phenyl n-butyl isothiocyanate:

It was prepared in 62 per cent yield from \( \alpha \)-Phenyl n-butyl amine (14.9 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 130°/10 mm.

Found S, 16.70 per cent.

C\(_{11}\)H\(_{13}\)NS requires S, 16.75 per cent.
(C) Substituted alkoxy phenyl isothiocyanates:

p-n-Propoxy phenyl Isothiocyanate:

It was prepared in 60 per cent yield from p-n-Propoxy aniline (p-Amino phenyl n-propyl ether) (15.1 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 160°/12 mm., \( \frac{N_D^{35.5}}{D} = 1.5855 \).

Found S, 16.5 per cent.

\( C_{10}H_{11}ONS \) requires S, 16.5 per cent.

p-n-Butoxy phenyl Isothiocyanate:

It was prepared in 65 per cent yield from p-Amino phenyl n-butyl ether (16.5 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate by the procedure described above.

B.P. 170°/15 mm.; \( \frac{N_D^{38.5}}{D} = 1.5830 \).

Found S, 15.08 per cent.

\( C_{11}H_{13}ONS \) requires S, 15.45 per cent.

p-n-Amyloxy phenyl Isothiocyanate:

It was prepared in 60 per cent yield from p-Amin0 phenyl n-Amy1 ether (17.9 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.
Found S, 14.10 per cent.

\[ \text{C}_{12}\text{H}_{15}\text{ONS} \quad \text{requires} \quad \text{S, 14.47 per cent.} \]

**p-n-Hexyloxy phenyl Isothiocyanate:**

It was prepared in 68 per cent yield from p-Amino phenyl hexyl ether (13.9 gm.), Carbon disulphide (7.6 gm.), NaOH (4.0 gm.) and ethyl chloro carbonate (10.9 gm.) by the procedure described above.

B.P. 180°/7 mm.; \( \delta \)\text{D} : 1.5626.

Found S, 13.13 per cent.

\[ \text{C}_{13}\text{H}_{17}\text{ONS} \quad \text{requires} \quad \text{S, 13.61 per cent.} \]

**General Method for the preparation of N: monosubstituted Thioureas:**

In a 500 c.c. three necked flask, equipped with a mechanical stirrer, a reflux condenser and a dropping funnel, is placed conc. ammonia solution (2 mol.) and appropriate isothiocyanate (1.3 mol.) is added with stirring over a period of one hour. After the addition is complete, the condenser is removed and the solution is heated on a water bath for thirty minutes to remove excess ammonia. Solution is then boiled and filtered, the filtrate chilled in an ice-bath. Substituted thiourea crystallises out as colourless solid mass which is collected on a filter and washed with ice water. Yield about 60 to 65 per cent.
The following method gives better yields and requires less time:

A freshly distilled isothiocyanate is slowly added to an alcoholic ammonia solution and the mixture heated just to boiling. The reaction mixture is then stirred vigorously, corked and put in an ice bath. In most cases, within an hour, thiourea separated out. It is filtered, washed with ice water and dried. The mother liquor on dilution gave more thiourea. Yield 70 to 80 per cent.

For convenience, \( N \) : monosubstituted thioureas are divided into three parts viz.

(A) \( N \) : monosubstituted benzyl thioureas (B) \( \alpha \)-Phenyl alkyl thioureas and (C) monosubstituted alkoxy phenyl thioureas.

(A) \( N \) : monosubstituted benzyl thioureas:

**o-Chlorobenzyl Thiourea:**

It was prepared in 80 per cent yield from \( o \)-Chlorobenzyl isothiocyanate (6.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 126\(^\circ\).

\[
\text{Found S, 16.0 per cent; Cl, 17.6 per cent.}
\]

\[
\text{C}_8\text{H}_9\text{N}_2\text{ClS} \quad \text{requires S, 15.9 per cent; Cl, 17.7 per cent.}
\]
m-Chlorobenzyl Thiourea:

It was prepared in 66 per cent yield from m-Chlorobenzyl isothiocyanate (6 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 133°.

Found S, 15.9 per cent.; Cl, 17.6 per cent.

C₈H₇N₂ClS requires S, 15.9 per cent.; Cl, 17.7 per cent.

p-Chlorobenzyl Thiourea:

It was prepared in 80 per cent yield from p-Chlorobenzyl isothiocyanate (6 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 141°.

Found S, 15.9 per cent.; Cl, 17.6 per cent.

C₈H₇N₂ClS requires S, 15.9 per cent.; Cl, 17.7 per cent.

o-Bromobenzyl Thiourea:

It was prepared in 75 per cent yield from o-Bromobenzyl isothiocyanate (10 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 127°.

Found S, 13.0 per cent.; Br, 32.6 per cent.

C₈H₇N₂BrS requires S, 13.1 per cent.; Br, 32.6 per cent.
m-Bromobenzyl Thiourea:

It was prepared in 70 per cent yield from m-Bromobenzyl isothiocyanate (10 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 151°.

Found S, 13.1 per cent.; Br, 32.6 per cent.

C₈H₉N₂BrS requires S, 13.1 per cent.; Br, 32.6 per cent.

p-Bromobenzyl Thiourea:

It was prepared in 80 per cent yield from p-Bromobenzyl isothiocyanate (10 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 157°.

Found S, 13.1 per cent.; Br, 32.6 per cent.

C₈H₉N₂BrS requires S, 13.1 per cent.; Br, 32.6 per cent.

m-Iodobenzyl Thiourea:

It was prepared in 68 per cent yield from m-Iodobenzyl isothiocyanate (18 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless platelets, m.p. 151°.

Found S, 10.9 per cent.; I, 43.4 per cent.

C₈H₉N₂Iₛ requires S, 10.9 per cent.; I, 43.4 per cent.
p-Iodobenzyl Thiourea:
It was prepared in 72 per cent yield from p-Iodobenzyl isothiocyanate (18 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 162-64°.

Found S, 11.0 per cent.; I, 43.4 per cent.
C₈H₉N₂IS requires S, 10.9 per cent.; I, 43.4 per cent.

p-Methylbenzyl Thiourea:
It was prepared in 70 per cent yield from p-Methylbenzyl isothiocyanate (7 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water incolorless platelets, m.p. 106°.

Found S, 17.36 per cent.
C₉H₁₂N₂S requires S, 17.77 per cent.

o-Methoxybenzyl Thiourea:
It was prepared in 70 per cent yield from o-Methoxybenzyl isothiocyanate (9.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 145°.

Found. S, 16.08 per cent.
C₉H₁₂N₂OS requires S, 16.32 per cent.
m-Methoxybenzyl Thiourea:

It was prepared in 70 per cent yield from m-Methoxybenzyl isothiocyanate (9.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 102°.

Found S, 16.26 per cent.

C₉H₁₂N₂OS requires S, 16.32 per cent.

3,4-Dimethylbenzyl Thiourea:

It was prepared in 65 per cent yield from 3,4-Dimethylbenzyl isothiocyanate (9.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 120°.

Found S, 16.28 per cent.

C₁₀H₁₄N₂S requires S, 16.49 per cent.

2,4-Dimethylbenzyl Thiourea:

It was prepared in 65 per cent yield from 2,4-Dimethylbenzyl isothiocyanate (9.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 84°.

Found S, 16.38 per cent.

C₁₀H₁₄N₂S requires S, 16.49 per cent.
2,5-Dimethylbenzyl Thiourea:

It was prepared in 70 per cent yield from 2,5-Dimethylbenzyl isothiocyanate (9.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in colourless needles, m.p. 110°.

Found S, 16.41 per cent.

C_{10}H_{14}N_{2}S requires S, 16.49 per cent.

(B) Monosubstituted α-Phenyl alkyl thioureas:

α-Phenyl ethyl Thiourea:

It was prepared in 65 per cent yield from α-Phenyl ethyl isothiocyanate (7 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from alcohol in brown needles, m.p. 147°.

Found S, 17.70 per cent.

C_{9}H_{12}N_{2}S requires S, 17.77 per cent.

α-Phenyl propyl Thiourea:

It was prepared in 68 per cent yield from α-Phenyl propyl isothiocyanate (6 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from dil. alcohol in colourless platelets, m.p. 135°.

Found S, 16.28 per cent.

C_{10}H_{14}N_{2}S requires S, 16.49 per cent.
α-Phenyl n-butyl Thiourea:

It was prepared in 70 per cent yield from α-Phenyl n-butyl isothiocyanate (9.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from dil. alcohol in yellowish platelets, m.p. 98°.

Found S, 15.18 per cent.

C₁₁H₁₆N₂S requires S, 15.38 per cent.

(C) Monosubstituted alkoxy phenyl Thioureas:

p-n-Propoxy phenyl Thiourea:

It was prepared in 80 per cent yield from p-n-propoxy phenyl isothiocyanate (8.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in yellowish needles, m.p. 160°. Spiegel, Ber., 1901, 34, 1935-47 notes its m.p. 158°.

p-n-Butoxy phenyl Thiourea:

It was prepared in 75 per cent yield from p-n-Butoxy phenyl isothiocyanate (10.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in brownish needles, m.p. 158°.

Found S, 14.13 per cent.

C₁₁H₁₆N₂O₅S requires S, 14.28 per cent.
p-n-Amyloxy phenyl Thiourea:

It was prepared in 70 per cent yield from p-n-Amyloxy phenyl isothiocyanate (10.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in brownish needles, m.p. 154°. Spiegel, Ber., 1901, 34, 1935-47 notes its m.p. 157°.

p-n-Hexyloxy phenyl Thiourea:

It was prepared in 80 per cent yield from p-n-Hexyloxy phenyl isothiocyanate (13.0 gm.) and alcoholic ammonia solution, by the procedure described above. It crystallised from hot water in brownish needles, m.p. 112°.

Found S, 12.58 per cent.

C\textsubscript{13}H\textsubscript{20}N\textsubscript{2}OS requires S, 12.69 per cent.

General Method for the preparation of N:N'-disubstituted Thioureas:

The amine (0.1 mol.) was dissolved in ether (15 c.c.) and solution of substituted isothiocyanate (0.1 mol.) in ether (25 c.c.) was added to it. The mixture was gently refluxed on a water bath for one to two hours. The ether was removed by distillation and the solid obtained was crystallised from dilute alcohol usually in needles. Yield above 60 per cent.

(Kaye and Parris, J. Org. Chem., 1951, 16, 1862.)
Procedure (B).

The solution of appropriate aryl amine (0.1 mol.) and aryl isothiocyanate (0.1 mol.) in a few c.c.s. of alcohol (2 to 5 c.c.) was heated to boiling for few minutes and kept overnight. In most cases thiourea was obtained as a crystalline solid. It was recrystallised from alcohol. Yield about 60-70 per cent. (Buu-Hoi et al., J. Chem. Soc., 1955, 1573.)

For convenience, N: N'-disubstituted thioureas are divided into three parts viz.,

(A) Thioureas having general formula \( XC_6H_4CH_2NHCSNHR \)

(B) Thioureas having general formula \( XC_6H_4CH_2NHCSNHC_6H_4OR \)

(C) Thioureas having general formula \( XC_6H_4CH_2NHCSNHC_6H_4N(CH_3)_2 \)

(A) Thiourea of the type \( XC_6H_4CH_2NHCSNHR \):  

1-(Benzyl)-3-(o-Chlorobenzyl)-Thiourea:

It was prepared in 60 per cent yield from Benzylamine (10.7 gm.) and o-Chlorobenzyl isothiocyanate (18.35 gm.) by the procedure (A) described before. It crystallised from alcohol in colourless needles, m.p. 165°.

Found S, 11.0 per cent.; Cl, 12.2 per cent.

\( C_{15}H_{15}N_2ClS \) requires S, 11.0 per cent.; Cl, 12.2 per cent.

1-(Benzyl)-3-(m-Chlorobenzyl)-Thiourea:

It was prepared in 62 per cent yield from
Benzylamine (10.7 gm.) and m-Chlorobenzyl isothiocyanate (18.35 gm.) by the procedure (A) described above. It crystallised from dil. alcohol in colourless needles, m.p. 84°.

Found S, 11.1 per cent.; Cl, 12.2 per cent.

\[ C_{15}H_{15}N_2ClS \] requires S, 11.0 per cent.; Cl, 12.2 per cent.

1-[(Benzyl)-3-(p-Chlorophenyl)] Thiourea:

It was prepared in 70 per cent yield from Benzylamine (10.7 gm.) and p-Chlorobenzyl isothiocyanate (18.35 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 140°.

Found S, 11.0 per cent.; Cl, 12.2 per cent.

\[ C_{15}H_{15}N_2ClS \] requires S, 11.0 per cent.; Cl, 12.2 per cent.

1-[(Benzyl)-3-(o-Bromophenyl)] Thiourea:

It was prepared in 65 per cent yield from Benzylamine (10.7 gm.) and o-Bromobenzyl isothiocyanate (22.8 gm.) by the procedure (A) described previously. It crystallised from alcohol in colourless needles, m.p. 100°.

Found S, 9.5 per cent.; Br, 23.8 per cent.

\[ C_{15}H_{15}N_2BrS \] requires S, 9.6 per cent.; Br, 23.8 per cent.

1-[(Benzyl)-3-(m-Bromobenzyl)] Thiourea:

It was prepared in 60 per cent yield from
Benzylamine (10.7 gm.) and m-Bromobenzyl isothiocyanate (22.8 gm.) by the procedure (A) described previously. It crystallised from alcohol in colourless needles, m.p. 90°.

\[ \text{Found S, 9.5 per cent.; Br, 23.6 per cent.} \]
\[ \text{C}_{15}\text{H}_{16}\text{N}_{2}\text{BrS requires S, 9.6 per cent.; Br, 23.8 per cent.} \]

1-(Benzyl)-3-(p-Bromobenzyl)-Thiourea:

It was prepared in 65 per cent yield from Benzylamine (10.7 gm.) and p-Bromobenzyl isothiocyanate (22.8 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 139°.

\[ \text{Found S, 9.6 per cent.; Br, 23.8 per cent.} \]
\[ \text{C}_{15}\text{H}_{16}\text{N}_{2}\text{BrS requires S, 9.6 per cent.; Br, 23.8 per cent.} \]

1-(Benzyl)-3-(p-Iodobenzyl)-Thiourea :

It was prepared in 55 per cent yield from Benzylamine (10.7 gm.) and p-Iodobenzyl isothiocyanate (27.5 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in yellowish needles, m.p. 103°.

\[ \text{Found S, 8.4 per cent.; I, 33.2 per cent.} \]
\[ \text{C}_{15}\text{H}_{15}\text{N}_{2}\text{IS requires S, 8.4 per cent.; I, 33.2 per cent.} \]
1-(β-Naphthyl)-3-(o-Chlorobenzyl)-Thiourea:

It was prepared in 60 per cent yield from β-Naphthylamine (14.3 gm.) and o-Chlorobenzyl isothiocyanate (18.35 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 157°.

Found S, 9.8 per cent.; Cl, 10.8 per cent.

C_{18}H_{15}N_{2}ClS requires S, 9.8 per cent.; Cl, 10.9 per cent.

1-(β-Naphthyl)-3-(m-Chlorobenzyl)-Thiourea:

It was prepared in 60 per cent yield from β-Naphthylamine (14.3 gm.) and m-Chlorobenzyl isothiocyanate (18.35 gm.) by the procedure (A) described previously. It crystallised from alcohol in colourless needles, m.p. 124°.

Found S, 9.8 per cent.; Cl, 10.8 per cent.

C_{18}H_{15}N_{2}ClS requires S, 9.8 per cent.; Cl, 10.9 per cent.

1-(β-Naphthyl)-3-(p-Chlorobenzyl)-Thiourea:

It was prepared in 60 per cent yield from β-Naphthylamine (14.3 gm.) and p-Chlorobenzyl isothiocyanate (18.35 gm.) by the procedure (A) described previously. It crystallised from alcohol in colourless needles, m.p. 143°.

Found S, 9.8 per cent.; Cl, 10.8 per cent.

C_{18}H_{15}N_{2}ClS requires S, 9.8 per cent.; Cl, 10.9 per cent.
1-(o-Naphthyl)-3-(o-Bromobenzyl)-Thiourea:

It was prepared in 60 per cent yield from o-Naphthylamine (14.3 gm.) and o-Bromobenzyl isothiocyanate (22.6 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 163°.

Found S, 8.6 per cent.; Br, 21.5 per cent.

C_{18}H_{15}N_{2}BrS requires S, 8.6 per cent.; Br, 21.5 per cent.

1-(o-Naphthyl)-3-(m-Bromobenzyl)-Thiourea:

It was prepared in 58 per cent yield from o-Naphthylamine (14.3 gm.) and m-Bromobenzyl isothiocyanate (22.8 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 129°.

Found S, 8.7 per cent.; Br, 21.5 per cent.

C_{18}H_{15}N_{2}BrS requires S, 8.6 per cent.; Br, 21.5 per cent.

1-(o-Naphthyl)-3-(p-Bromobenzyl)-Thiourea:

It was prepared in 60 per cent yield from o-Naphthylamine (14.3 gm.) and p-Bromobenzyl isothiocyanate (22.8 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 157°.

Found S, 8.6 per cent.; Br, 21.5 per cent.

C_{18}H_{15}N_{2}BrS requires S, 8.6 per cent.; Br, 21.5 per cent.
1-(\(\alpha\)-Naphthyl)-3-(p-Iodobenzyl)-Thiourea:

This was prepared in 52 per cent yield from \(\alpha\)-Naphthylamine (14.3 gm.) and p-Iodobenzyl isothiocyanate (27.5 gm.) by the procedure (A) described previously. It crystallised from alcohol in brownish needles, m.p. 166°.

Found S, 7.6 per cent.; I, 30.3 per cent.
C\(_{18}\)H\(_{15}\)N\(_2\)IS requires S, 7.7 per cent.; I, 30.3 per cent.

1-(\(\alpha\)-Naphthyl)-3-(m-Iodobenzyl)-Thiourea:

It was prepared in 55 per cent yield from \(\alpha\)-Naphthylamine (14.3 gm.) and m-Iodobenzyl isothiocyanate (27.5 gm.) by the procedure (A) described previously. It crystallised from alcohol in brownish needles, m.p. 156°.

Found S, 7.6 per cent.; I, 30.3 per cent.
C\(_{18}\)H\(_{15}\)N\(_2\)IS requires S, 7.7 per cent.; I, 30.3 per cent.

1-(/\(\beta\)-Naphthyl)-3-(o-Chlorobenzyl)-Thiourea:

It was prepared in 60 per cent yield from \(\beta\)-Naphthylamine (14.3 gm.) and o-Chlorobenzyl isothiocyanate (18.35 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 160°.

Found S, 9.8 per cent.; Cl, 10.8 per cent.
C\(_{18}\)H\(_{15}\)N\(_2\)ClS requires S, 9.8 per cent.; Cl, 10.9 per cent.
1-(3-Naphthyl)-3-(m-Chlorobenzyl)-Thiourea:

It was prepared in 55 per cent yield from \( \beta \)-Naphthylamine (14.3 gm.) and m-Chlorobenzyl isothiocyanate (18.35 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 153\(^\circ\).

Found S, 9.8 per cent.; Cl,10.8 per cent.

\[ C_{18}H_{15}N_2ClS \] requires S, 9.8 per cent.; Cl,10.9 per cent.

1-(\( \beta \)-Naphthyl)-3-(p-Chlorobenzyl)-Thiourea:

It was prepared in 60 per cent yield from \( \beta \)-Naphthylamine (14.3 gm.) and p-Chlorobenzyl isothiocyanate (18.35 gm.) by the procedure (A) described previously. It crystallised from alcohol in colourless needles, m.p. 169\(^\circ\).

Found S, 9.7 per cent.; Cl,10.8 per cent.

\[ C_{18}H_{15}N_2ClS \] requires S, 9.8 per cent.; Cl,10.9 per cent.

1-(\( \beta \)-Naphthyl)-3-(o-Bromobenzyl)-Thiourea:

It was prepared in 55 per cent yield from \( \beta \)-Naphthylamine (14.3 gm.) and o-Bromobenzyl isothiocyanate (22.8 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 161\(^\circ\).

Found S, 8.6 per cent.; Br,21.5 per cent.

\[ C_{18}H_{15}N_2BrS \] requires S, 8.6 per cent.; Br,21.5 per cent.
1-($\beta$-Naphtyl)-3-(m-Bromobenzyl)-Thiourea:

It was prepared in 50 per cent yield from $\beta$-Naphthylamine (14.3 gm.) and m-Bromobenzyl isothiocyanate (22.8 gm.) by the procedure (A) described previously. It crystallised from alcohol in colourless needles, m.p. 153°.

Found S, 8.6 per cent.; Br, 21.5 per cent.

$C_{18}H_{15}N_{2}BrS$ requires S, 8.6 per cent.; Br, 21.5 per cent.

1-($\beta$-Naphtyl)-3-(p-Bromobenzyl)-Thiourea:

It was prepared in 60 per cent yield from $\beta$-Naphthylamine (14.3 gm.) and p-Bromobenzyl isothiocyanate (22.8 gm.) by the procedure (A) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 173°.

Found S, 8.6 per cent.; Br, 21.5 per cent.

$C_{18}H_{15}N_{2}BrS$ requires S, 8.6 per cent.; Br, 21.5 per cent.

1-($\beta$-Naphtyl)-3-(p-Iodobenzyl)-Thiourea:

It was prepared in 60 per cent yield from $\beta$-Naphthylamine (14.3 gm.) and p-Iodobenzyl isothiocyanate (22.8 gm.) by the procedure (A) described previously. It crystallised from alcohol in brown needles, m.p. 180°.

Found S, 7.6 per cent.; I, 30.3 per cent.

$C_{18}H_{15}N_{2}IS$ requires S, 7.7 per cent.; I, 30.3 per cent.
1-(β-Naphthyl)-3-(m-Iodobenzyl)-Thiourea:

It was prepared in 52 per cent yield from β-Naphthylamine (14.3 gm.) and m-Iodobenzyl isothiocyanate (27.5 gm.) by the procedure (A) described before. It crystallised from dil. alcohol in brownish needles, m.p. 172°.

Found S, 7.6 per cent.; I, 30.2 per cent.
C₁₈H₁₅N₂IS requires S, 7.7 per cent.; I, 30.3 per cent.

(B) Thioureas of the type XCH₂CH₂NHCSNHC₆H₄OR:

1-(p-Chlorobenzyl)-3-(p-methoxyphenyl)-Thiourea:

It was prepared in 70 per cent yield from p-Anisidine (1.3 gm.) and p-Chlorobenzyl isothiocyanate (1.84 gm.) by the procedure (B) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 132°.

Found S, 10.38 per cent.; Cl, 11.42 per cent.
C₁₈H₁₅N₂Cl₂S requires S, 10.44 per cent.; Cl, 11.58 per cent.

1-(p-Chlorobenzyl)-3-(p-ethoxyphenyl)-Thiourea:

It was prepared in 68 per cent yield from p-Phenetidine (1.4 gm.) and p-Chlorobenzyl isothiocyanate (1.84 gm.) by the procedure (B) described above. It crystallised from dil. alcohol in colourless needles, m.p. 148°.
Found S, 9.94 per cent.; Cl, 11.0 per cent.

C_{16}H_{17}NOClS requires S, 9.98 per cent.; Cl, 11.07 per cent.

1-(p-Chlorobenzyl)-3-(p-n-propoxyphenyl)-Thiourea:

It was prepared in 60 per cent yield from p-Aminophenyl n-propyl ether (1.5 gm.) and p-Chloro benzyl isothiocyanate (1.84 gm.) by the procedure (B) described previously. It crystallised from dil. alcohol in colourless needles; m.p. 120°.

Found S, 9.48 per cent.; Cl, 10.48 per cent.

C_{17}H_{19}N_{2}OClS requires S, 9.56 per cent.; Cl, 10.61 per cent.

1-(p-Chlorobenzyl)-3-(p-n-butoxyphenyl)-Thiourea:

It was prepared in 60 per cent yield from p-Amino phenyl n-butyl ether (1.65 gm.) and p-Chloro benzyl isothiocyanate (1.84 gm.) by the procedure (B) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 110°.

Found S, 8.98 per cent.; Cl, 9.93 per cent.

C_{18}H_{21}N_{2}OClS requires S, 9.18 per cent.; Cl, 10.18 per cent.

1-(p-Chlorobenzyl)-3-(p-n-amlyoxyphenyl)-Thiourea:

It was prepared in 60 per cent yield from p-Aminophenyl n-amyl ether (1.8 gm.) and p-Chloro benzyl isothio-cyanate (1.84 gm.) by procedure (B) described previously. It crystallised from dil. alcohol
in colourless needles, m.p. 86°.

Found S, 8.78 per cent.; Cl, 9.72 per cent.

\( \text{C}_{19}\text{H}_{23}\text{N}_{2}\text{OClS} \) requires S, 8.82 per cent.; Cl, 9.79 per cent.

1-(p-Chlorobenzyl)-3-(p-n-hexyloxyphenyl)-Thiourea:

It was prepared in 62 per cent yield
from p-Aminophenyl n-hexyl ether (2.0 gm.) and p-Chlorobenzyl isothiocyanate (1.84 gm.) by the procedure (B) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 92°.

Found S, 8.42 per cent.; Cl, 9.20 per cent.

\( \text{C}_{20}\text{H}_{25}\text{N}_{2}\text{OClS} \) requires S, 8.49 per cent.; Cl, 9.42 per cent.

1-(p-Bromobenzyl)-3-(p-methoxyphenyl)-Thiourea:

It was prepared in 60 per cent yield
from p-Anisidine (1.2 gm.) and p-Bromobenzyl isothiocyanate (2.3 gm.) by the procedure (B) described previously. It crystallised from dil. alcohol in colourless platelets, m.p. 147°.

Found S, 9.00 per cent.; Br, 22.72 per cent.

\( \text{C}_{15}\text{H}_{15}\text{N}_{2}\text{OBrS} \) requires S, 9.11 per cent.; Br, 22.79 per cent.

1-(p-Bromobenzyl)-3-(p-ethoxyphenyl)-Thiourea:

It was prepared in 60 per cent yield
from p-Phenetidine (1.4 gm.) and p-Bromobenzyl isothiocyanate (2.3 gm.) by the procedure (B) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 135°.
Found S, 8.71 per cent.; Br, 21.66 per cent.
\[ \text{C}_{16}\text{H}_{17}\text{N}_{2}\text{OBrS} \text{ requires } S, 8.76 \text{ per cent.}; \text{Br}, 21.91 \text{ per cent.} \]

**1-(p-Bromobenzyl)-3-(p-n-propoxyphenyl)-Thiourea:**

It was prepared in 58 per cent yield from p-Aminophenyl n-propyl ether (1.5 gm.) and p-Bromo benzyl isothiocyanate (2.3 gm.) by the procedure (B) described previously. It crystallised from alcohol in colourless granules, m.p. 120°.

Found S, 8.39 per cent.; Br, 20.93 per cent.
\[ \text{C}_{17}\text{H}_{19}\text{N}_{2}\text{OBrS} \text{ requires } S, 8.44 \text{ per cent.}; \text{Br}, 22.10 \text{ per cent.} \]

**1-(p-Bromobenzyl)-3-(p-n-butoxyphenyl)-Thiourea:**

It was prepared in 60 per cent yield from p-Aminophenyl n-butyl ether (1.65 gm.) and p-Bromo benzyl isothiocyanate (2.3 gm.) by the procedure (B) described previously. It crystallised from alcohol in colourless needles, m.p. 154°.

Found S, 8.11 per cent.; Br, 20.08 per cent.
\[ \text{C}_{18}\text{H}_{21}\text{N}_{2}\text{OBrS} \text{ requires } S, 8.14 \text{ per cent.}; \text{Br}, 20.35 \text{ per cent.} \]

**1-(p-Bromobenzyl)-3-(p-n-amlyoxyphenyl)-Thiourea:**

It was prepared in 60 per cent yield from p-Aminophenyl n-amyl ether (1.8 gm.) and p-Bromo benzyl isothiocyanate (2.3 gm.) by the procedure (B) described previously. It crystallised from alcohol in
colourless needles, m.p. 93°.

Found S, 7.81 per cent.;Br, 19.59 per cent.

C₁₈H₂₅N₂OBrS requires S, 7.86 per cent.;Br, 19.65 per cent.

1-(p-Bromobenzyl)-3-(p-n-hexyloxyphenyl)-Thiourea:

It was prepared in 55 per cent yield from p-Aminophenyl n-hexyl ether (2.0 gm.) and p-Bromo benzyl isothiocyanate (2.3 gm.) by the procedure (B) described previously. It crystallised from alcohol in colourless needles, m.p. 96°.

Found S, 7.53 per cent.;Br, 18.86 per cent.

C₂₀H₂₆N₂OBrS requires S, 7.60 per cent.;Br, 19.00 per cent.

1-(p-Ethoxybenzyl)-3-(p-methoxyphenyl)-Thiourea:

It was prepared in 56 per cent yield from p-Anilidin (1.2 gm.) and p-Ethoxybenzyl isothiocyanate (2.0 gm.) by the procedure (B) described previously. It crystallised from alcohol in colourless needles, m.p. 113°.

Found S, 10.03 per cent.;

C₁₇H₂₀N₂O₂S requires S, 10.12 per cent.

1-(p-Ethoxybenzyl)-3-(p-ethoxyphenyl)-Thiourea:

It was prepared in 58 per cent yield from p-Phenetidine (1.4 gm.) and p-ethoxybenzyl isothio cyanate (2.0 gm.) by the procedure (B) described
previously. It crystallised from alcohol in colourless needles, m.p. 98°.

\[ \text{Found S, 9.62 per cent.} \]

\[ \text{C}_{16}\text{H}_{22}\text{N}_{2}\text{O}_{2}\text{S} \text{ requires S, 9.69 per cent.} \]

\(1-(p\text{-Ethoxybenzyl})-3-(p\text{-n-propoxyphenyl})\text{-Thiourea} :\)

It was prepared in 60 per cent yield from \(p\text{-Aminophenyl n-propyl ether (1.5 gm.) and}\n\(p\text{-Ethoxybenzyl isothiocyanate (2.0 gm.) by the procedure (B) described previously. It crystallised from alcohol in colourless needles, m.p. 78°.}\n
\[ \text{Found S, 9.18 per cent.} \]

\[ \text{C}_{19}\text{H}_{24}\text{N}_{2}\text{O}_{2}\text{S} \text{ requires S, 9.30 per cent.} \]

\(1-(p\text{-Ethoxybenzyl})-3-(p\text{-n-butoxyphenyl})\text{-Thiourea} :\)

It was prepared in 60 per cent yield from \(p\text{-Aminophenyl n-butyl ether (1.65 gm.) and}\n\(p\text{-Ethoxybenzyl isothiocyanate (2.0 gm.) by the procedure (B) described previously. It crystallised from alcohol in colourless needles, m.p. 85°.}\n
\[ \text{Found S, 8.88 per cent.} \]

\[ \text{C}_{20}\text{H}_{26}\text{N}_{2}\text{O}_{2}\text{S} \text{ requires S, 8.93 per cent.} \]

\(1-(p\text{-Ethoxybenzyl})-3-(p\text{-n-amlyoxyphenyl})\text{-Thiourea} :\)

It was prepared in 58 per cent yield from \(p\text{-Aminophenyl n-amyl ether (1.8 gm.) and p-Ethoxy benzyl isothiocyanate (2.0 gm.) by the procedure (B)\)
described previously. It crystallised from alcohol in needles, m.p. 61°.

Found S, 8.58 per cent.

C_{21}H_{28}N_{2}O_{2}S requires S, 8.60 per cent.

1-(p-Ethoxybenzyl)-3-(p-n-hexyloxyphenyl)-Thiourea:

It was prepared in 60 per cent yield from p-Aminophenyl n-hexyl ether (2.0 gm.) and p-Ethoxy benzyl isothiocyanate (2.0 gm.) by the procedure (B) described previously. It crystallised from alcohol in colourless flakes, m.p. 56°.

Found S, 8.22 per cent.

C_{22}H_{30}N_{2}O_{2}S requires S, 8.29 per cent.

1-(p-Butoxybenzyl)-3-(p-methoxyphenyl)-Thiourea:

It was prepared in 56 per cent yield from p-Anisidine (1.2 gm.) and p-Butoxybenzyl isothio cyanate (2.2 gm.) by the procedure (B) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 175°.

Found S, 9.23 per cent.

C_{19}H_{24}N_{2}O_{2}S requires S, 9.30 per cent.

1-(p-Butoxybenzyl)-3-(p-ethoxyphenyl)-Thiourea:

It was prepared in 55 per cent yield from p-Phenylidine (1.4 gm.) and p-n-Butoxybenzyl isothio cyanate (2.2 gm.) by the procedure (B) described
previously. It crystallised from dil. alcohol in colourless needles, m.p. 96°.

Found S, 8.87 per cent.

\[ \text{C}_{20} \text{H}_{26} \text{N}_{2} \text{O}_{2} \text{S} \text{ requires S, 8.93 per cent.} \]

1-(p-Butoxybenzyl)-3-(p-n-propoxyphenyl)-Thiourea:

It was prepared in 60 per cent yield from p-Aminophenyl n-propyl ether (1.5 gm.) and p-Butoxy benzyl isothiocyanate (2.2 gm.) by the procedure (B) described previously. It crystallised from alcohol in colourless needles, m.p. 85°.

Found S, 8.57 per cent.

\[ \text{C}_{21} \text{H}_{28} \text{N}_{2} \text{O}_{2} \text{S} \text{ requires S, 8.60 per cent.} \]

1-(p-Butoxybenzyl)-3-(p-n-butoxyphenyl)-Thiourea:

It was prepared in 60 per cent yield from p-Aminophenyl n-butyl ether (1.65 gm.) and p-Butoxy benzyl isothiocyanate (2.2 gm.) by the procedure (B) described previously. It crystallised from dil. alcohol in colourless needles, m.p. 71°.

Found S, 8.13 per cent.

\[ \text{C}_{22} \text{H}_{30} \text{N}_{2} \text{O}_{2} \text{S} \text{ requires S, 8.29 per cent.} \]

1-(p-Butoxybenzyl)-3-(p-n-amylxoxphenyl)-Thiourea:

It was prepared in 58 per cent yield from p-Aminophenyl n-amyl ether (1.8 gm.) and p-Butoxy
benzyl isothiocyanate (2.2 gm.) by the method (B) described previously. It crystallised from alcohol in colourless needles, m.p. 135°.

Found S, 7.92 per cent.

C_{23}H_{32}N_{2}O_{2}S requires S, 8.00 per cent.

1-(p-Butoxybenzyl)-3-(p-n-hexyloxyphenyl)-Thiourea:

It was prepared in 60 per cent yield from p-Aminophenyl n-hexyl ether (2.0 gm.) and p-Butoxy benzyl isothiocyanate (2.2 gm) by the procedure (B) described previously. It crystallised from alcohol in colourless needles, m.p. 73°.

Found S, 7.62 per cent.

C_{24}H_{34}N_{2}O_{2}S requires S, 7.72 per cent.

(C) Thioureas of the type \( XC_6H_4CH_2NHCSNHCH_3C_6H_4N(CH_3)_2 \):

1-(p-Chlorobenzyl)-3-(p-Dimethylanilinophenyl)-Thiourea:

It was prepared in 60 per cent yield from p-Amino dimethyl aniline (1.4 gm.) and p-Chloro benzyl isothiocyanate (1.84 gm.) by the procedure (B) described previously. It crystallised from dil. alcohol in brownish needles, m.p. 138-39°.

Found S, 9.97 per cent; Cl, 11.0 per cent.

C_{16}H_{19}N_{3}ClS requires S, 10.01 percent; Cl, 11.11 per cent.
1-(p-Bromobenzyl)-3-(p-Dimethylaminophenyl)-Thiourea:

It was prepared in 60 per cent yield from p-Amino dimethyl aniline (1.4 gm.) and p-Bromo-
benzyl isothiocyanate (2.28 gm.) by the procedure (B) described previously. It crystallised from alcohol in
brownish needles, m.p. 148°C.

Found S, 8.73 per cent.; Br, 21.91 per cent.

C_{16}H_{18}N_{3}BrS requires S, 8.79 per cent.; Br, 21.97 per cent.

1-(p-Methoxybenzyl)-3-(p-Dimethylaminophenyl)-Thiourea:

It was prepared in 63 per cent.
yield from p-Amino dimethyl aniline (1.4 gm.) and
p-Methoxybenzyl isothiocyanate (1.8 gm.) by the procedure
(B) described previously. It crystallised from alcohol
in colourless needles, m.p. 108°C.

Found S, 10.00 per cent.

C_{17}H_{21}N_{3}OS requires S, 10.15 per cent.

1-(p-Ethoxybenzyl)-3-(p-Dimethylaminophenyl)-Thiourea:

It was prepared in 60 per cent yield
from p-Amino dimethyl aniline (1.4 gm.) and p-Ethoxy-
benzyl isothiocyanate (1.93 gm.) by the procedure (B)
previously. It crystallised from dil. alcohol in colour-
less needles, m.p. 68-69°C.

Found S, 9.68 per cent.

C_{18}H_{23}N_{3}OS requires S, 9.72 per cent.
1-(p-Butoxybenzyl)-S-(p-Dimethylaminophenyl)-Thiourea:

It was prepared in 62 per cent yield from p-Amino dimethyl aniline (1.4 gm.) and p-Butoxybenzyl isothiocyanate (2.21 gm.) by the procedure (B) described previously. It crystallised from dil. Alcohol in colourless needles, m.p. 120°.

Found S, 6.92 per cent.

C_{20}H_{27}N_3OS requires S, 8.96 per cent.
"Physiological Activity of some of the Benzyl Thioureas."
"Physiological Activity of Some of the Benzyl-Thioureas."

Some of the thioureas were tested for their physiological activity.

For studying antibacterial properties the organisms used were *Staphylococcus aureus* and *Salmonella typhosa*. In addition micro-organisms of dysentary and colon typhoid group were also used. Method used was serial broth dilution method.

For testing antitubercular activity the organism used was *Mycobacterium tuberculosis* (Bovine strain). Method used was serial broth dilution method using Yeoman's medium.

Similarly antifungal activity was tested against *Aspergillus niger*, *Trichophyton Rubrum*, *Trichophyton Glabrum* and *Epidermophyton Floccosum*, using the Agar streak method. The results are recorded in Table I,II and III respectively.
### TABLE I.

**BACTERIAL SPECTRUM OF BENZYL THIOUREA DERIVATIVES.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>St. Au</th>
<th>Para A</th>
<th>Para B</th>
<th>Shigga</th>
<th>Sonne</th>
<th>Flexner</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. o-Chlorobenzyl thiourea</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2. m-Chlorobenzyl thiourea</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3. p-Chlorobenzyl thiourea</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>4. o-Bromobenzyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>5. m-Bromobenzyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>6. p-Bromobenzyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>7. m-Chlorobenzyl-α-naphthyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>8. m-Chlorobenzyl-β-naphthyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>9. p-Chlorobenzyl-α-naphthyl thiourea</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>10. p-Chlorobenzyl-β-naphthyl thiourea</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>11. p-Chlorobenzyl-benzyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>12. p-Chlorobenzyl-β-benzyl thiourea</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>13. m-Iodobenzyl-α-naphthyl thiourea</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>14. Benzyl thiourea</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figures indicate activity in micrograms per ml.

*St. Au.* = *Staphylococcus Aureus*, *Para A* and *Para B* are strains of *Salmonella typhosus*; *Shigga, Sonne* and *Flexner* are the strains of bacillary *Dysentery*.

*Above results indicate that introduction of Bromine increases the Antibacterial activity.*
**TABLE II.**

**ANTITUBERCULAR ACTIVITY OF BENZYL THIOUREA DERIVATIVES.**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(Bovine Strain)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. o-Chlorobenzyl thiourea</td>
<td>100 m/ml.</td>
</tr>
<tr>
<td>2. m-Chlorobenzyl</td>
<td>100 m/ml.</td>
</tr>
<tr>
<td>3. p-Chlorobenzyl</td>
<td>100 m/ml.</td>
</tr>
<tr>
<td>4. o-Bromobenzyl</td>
<td>50 m/ml.</td>
</tr>
<tr>
<td>5. m-Bromobenzyl</td>
<td>50 m/ml.</td>
</tr>
<tr>
<td>6. p-Bromobenzyl</td>
<td>50 m/ml.</td>
</tr>
<tr>
<td>7. m-Chlorobenzyl α-naphthyl thiourea</td>
<td>100 m/ml.</td>
</tr>
<tr>
<td>8. m-Bromobenzyl</td>
<td>50 m/ml.</td>
</tr>
<tr>
<td>9. m-Chlorobenzyl β-naphthyl thiourea</td>
<td>50 m/ml.</td>
</tr>
<tr>
<td>10. p-Chlorobenzyl</td>
<td>50 m/ml.</td>
</tr>
<tr>
<td>11. p-Chlorobenzyl benzyl thiourea</td>
<td>50 m/ml.</td>
</tr>
<tr>
<td>12. p-Bromobenzyl benzyl thiourea</td>
<td>50 m/ml.</td>
</tr>
<tr>
<td>13. m-Iodobenzyl α-naphthyl thiourea</td>
<td>100 m/ml.</td>
</tr>
<tr>
<td>14. Benzyl thiourea</td>
<td>100 m/ml.</td>
</tr>
</tbody>
</table>

Above indicates that introduction of bromine enhances the activity.
### TABLE III.

**ANTIFUNGAL ACTIVITY.**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>A</th>
<th>T.R.</th>
<th>T.G.</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. o-Chlorobenzyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>2. m-Chlorobenzyl thiourea</td>
<td>*</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>3. p-Chlorobenzyl thiourea</td>
<td>*</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>4. o-Bromobenzyl thiourea</td>
<td>*</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>5. m-Bromobenzyl thiourea</td>
<td>*</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>6. p-Bromobenzyl thiourea</td>
<td>*</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>7. m-Chlorobenzyl α-naphthyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>8. m-Bromobenzyl α-naphthyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>9. m-Chlorobenzyl β-naphthyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>10. p-Chlorobenzyl thiourea</td>
<td>*</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>11. p-Chlorobenzyl benzyl thiourea</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>12. p-Bromobenzyl benzyl thiourea</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>13. m-Iodobenzyl α-naphthyl thiourea</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>14. Benzyl thiourea</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figures indicate activity in micrograms per ml.


T.G. = *Trichophyton glabrum*, E = *Epidermophyton floccosum*.

Here also halogens enhance the antifungal properties. Bromine has the best effect.