Preparation of Substituted Benzyl Halides:

Benzyl Bromide:

a) Photobromination of substituted Toluenes: In a three-necked round-bottom flask mounted with a mercury sealed stirrer, a dropping funnel and reflux condenser with a gas trap, dry substituted toluene (0.6 mole) was heated in an oil bath at 120°C and irradiated with light of 200 watt lamp. With constant agitation, bromine (102 g.; 0.64 mole) was added during two hours and stirring and heating was continued for another two hours. By this time, the evolution of hydrogen bromide ceased. The product was kept in a desiccator over caustic potash to absorb hydrogen bromide. The product if liquid was distilled under reduced pressure, and if solid was washed with ethyl alcohol on a suction filter. Yield 65-98%.

b) General Method for the Preparation of -Bromoxylenes:

In a three-necked round bottom flask fitted with a reflux condenser a gas trap and a separating funnel, was placed the appropriate xylene (150 g.; 0.40 mole) which was then heated to 120 to 130°C in an oil bath. From the separating funnel dry bromine (252.0 g.; 1.58 mole) was added slowly through a tube passing below the surface of xylene. When all the bromine had been added the product was transferred to an evaporating dish and kept in a desiccator over potash till free from hydrogen bromide. It is then distilled...
at the ordinary pressure (96).

ω-Bromo-p-xylene B.P. 218-20°C m.p. 35°C was prepared by this method.

Synthesis of p-Chloro-benzylamine:

a) By Delepine Reaction: p-chlorobenzylbromide (1.0 mole) dissolved in chloroform was gradually added with constant shaking and cooling to hexamethylene tetramine (1.1 mole) in chloroform. The reaction is very exothermic so it requires constant cooling in a water bath. After the addition was complete the flask was kept at room temperature overnight. If a solid complex was not obtained, the reaction mixture was refluxed for two to six hours, and kept overnight. The solid complex, thus obtained was filtered and air dried.

The solid hexamine complex was dissolved in minimum amount of water, ammonia was added and the mixture, was refluxed for about one and a half hour. The reaction product was poured in excess of water and the oily cyclic imine thus obtained separated and treated with excess of concentrated hydrochloric acid. The mixture was evaporated to dryness on a water bath. The amine hydrochloride thus obtained was dissolved in water and the solution was steamed to remove volatile impurities. The solution was made alkaline and the liberated amine was dried over caustic potash. After removing the ether the amine was purified by distillation under reduced pressure (97).

The amines described in Table I were prepared by this method:
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<tr>
<th>Name</th>
<th>B.P. in degree</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>2. p-methyl-benzyl amine</td>
<td>105°/22 mm</td>
<td>-do-</td>
</tr>
<tr>
<td>3. p-bromobenzyl amine</td>
<td>102°/12 mm</td>
<td>-do-</td>
</tr>
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</table>
Preparation of p-Methoxy benzyl amine using Leuckart Reaction:

Ammonium carbonate (2.0 moles; 108 g.) was placed in a three necked 500 ml. flask, fitted with a separating funnel, a thermometer which extended nearly to the bottom of the flask and a distilling bend carrying a condenser for distillation. 98% formic acid (108-15 g.; 2.05 mole) was added slowly through the separating funnel. When the reaction became moderate the mixture was heated continuously and then slowly distilled until the temperature was about 165° during which considerable frothing took place.

To the ammonium formate thus obtained, the ketone (0.5 mole) was added and heating was continued. The distillate was collected in a separating funnel. The recovered ketone, if any, was separated from time to time and returned to the reaction mixture. When the distillation of water practically ceased, the temperature was maintained in this range for further three to four hours.

The end of the reaction was clearly marked when the decomposition of ammonium carbonate in the condenser nearly ceased. The crude formyl derivative of amine was refluxed with about 100 ml. of concentrated hydrochloric acid, for each mole of ketone used. Hydrolysis was complete in three to four hours, as shown by the solution of all but a small amount of inert material consisting of unchanged ketone and condensation products. The amine hydrochloride was separated from the unchanged ketone and the condensation products by a separating funnel. The amine was liberated from the solution by the addition of alkali and it was extracted with ether.
and dried over caustic potash. After the removal of ether the amine was purified by distillation under reduced pressure.
General Method for the Preparation of Isothiocyanates:

In a three-necked round bottom flask, fitted with a mechanical stirrer, a reflux condenser, a thermometer and a dropping funnel, were placed carbon disulfide (1.1 mole) and ice cold aqueous solution of caustic soda (1.0 mole in 160 ml. water). To this mixture was added with stirring, 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 to this solution ethyl chloroformate (1.0 mole) was added with stirring over a period of one hour. The addition should be carried out in a hood due to the formation of COS which is poisonous. After the addition of the ethyl chloroformate 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 the ether, the isothiocyanate was purified by distillation under reduced pressure.

Alternatively to a mixture of 43.0 ml. carbon disulfide and 9.0 ml. of ammonia (0.88 d.) kept in an ice-salt bath was added with stirring amine (0.6 mole) through the separating funnel over a period of thirty minutes. After the addition of the amine was complete the reaction mixture was stirred for further one hour. The solid ammonium dithiocarbamate was filtered, washed with ether and dissolved in a minimum quantity of distilled water. To this
lead nitrate (200 gm. in minimum quantity of distilled water) was added with stirring. This was then further stirred for one hour.

Isothiocyanate was steam-distilled in a receiver containing dilute sulfuric acid. The isothiocyanate was separated by a separating funnel and dried over anhydrous calcium chloride. The isothiocyanate(10) obtained by this method is pure enough for further use.

With solid amines like 4-chloro-aniline, the following procedure was used.

To a mixture of carbon disulfide (6.0 g.; 0.75 mole) amine (0.5 mole) and ethanol (90.0 mole; 95%) kept in an ice-salt bath was added with stirring ammonia (81.6 ml.; 63 mole; 0.88 d.) through the separating funnel over a period of thirty minutes. The ammonium dithiocarbamate formed is then treated as in the previous method(10).

The isothiocyanates prepared are described in Table II.
TABLE II

Synthesis of Aryl and Aralkyl Isothiocyanates

<table>
<thead>
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<th>Reference</th>
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<td>4-Bromophenyl isothiocyanate</td>
<td>63°C m.p.</td>
<td>Dains, Brewster and Olander, ibid., 448, 963</td>
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<td>3</td>
<td>2-Methyl phenyl isothiocyanate</td>
<td>238</td>
<td>Dains, Brewster and Olander, ibid., 448, 1963</td>
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<tr>
<td>4</td>
<td>3-Methyl phenyl isothiocyanate</td>
<td>244/773 m.m.</td>
<td>Werner J. Chem. Soc., 59, 404 (1891)</td>
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<td>5</td>
<td>4-Methyl-phenyl isothiocyanate</td>
<td>26-7 m.p.</td>
<td>Dains, Brewster and Olander, loc. cit.</td>
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<td>7</td>
<td>4-Methoxy phenyl isothiocyanate</td>
<td>111-5 m.m.</td>
<td>Coghil and Johnson, J. Amer. Chem. Soc., 187, 47 (1925)</td>
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<tr>
<td>8</td>
<td>4-Dimethyl amino phenyl isothiocyanate</td>
<td>69-70 M.P.</td>
<td>Erich Schmidt, Erich Kammerl, Dietrich Ross &amp; Frank Zaller at 94 Ann., 594, 233-7 (1955)</td>
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<td>9</td>
<td>Benzyl isothiocyanate</td>
<td>140/17 m.m.</td>
<td>Schneider et al. Ber., 47, 1248</td>
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<td>11</td>
<td>4-Bromobenzyl isothiocyanate</td>
<td>140/5</td>
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</tr>
<tr>
<td>12</td>
<td>4-Methylbenzyl isothiocyanate</td>
<td>155/17 m.m.</td>
<td>Trivedi et al. J. Indian Chem. Soc., 658, 35, 35 (1958)</td>
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<td>13</td>
<td>4-Methoxybenzyl isothiocyanate</td>
<td>128/3 m.m.</td>
<td>- do -</td>
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General Method for the Synthesis of Benzoyl Isothiocyanates:

45 g. (0.6 mole) potassium sulfocyanate finely powdered and thoroughly dried at 110°C for ten hours was suspended in dry benzene containing 56.5 g. (0.4 mole) benzoyl chloride. The mixture is then refluxed at 110-120°C for six hours till no odour of the chloride is left. The salt is filtered and the liquid product is vacuum distilled at 135°C/18 m.m. The yield was 64%(99).

The isothiocyanates prepared by this method are described in Table III.
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<th>No.</th>
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<th>Reference</th>
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<td>Benzoyl isothiocyanate</td>
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<td>J. Am. Chem. Soc., 61, 632, (1939)</td>
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<td>2</td>
<td>p-Chloro-benzyl, isothiocyanate</td>
<td>130-133°/2.0 m.m.</td>
<td>J. Chem. Soc., 1160-3, (1949)</td>
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<td>3</td>
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FRIEDEL AND CRAFT'S REACTION

Typical Procedure:

4-Hydroxy-N-p-Anisyl thio-benzamide: To a mixture of (0.0149 g.; 0.001 M.) p-methoxy phenyl isothiocyanate, anhydrous aluminium chloride (2.6 g.; 0.02 mole) and carbon disulfide 3.0 ml. was gradually added with shaking phenol solution, (0.47 g.; 0.005 mole) in carbon disulfide 5 ml. During the addition of the phenol, the mixture of the isothiocyanate and anhydrous aluminium chloride was cooled to 0°C in an ice salt bath, as the reaction is spontaneous and exothermic. An immediate colour change took place during the addition. Care should be taken that the mixture is well protected from moisture during and after the addition. When the addition was complete and the reaction subsided it was treated in the following different ways.

a) The mixture was decomposed immediately with ice cold hydrochloric acid and ether extracted. The ether was distilled, the product thus obtained was steam-distilled to remove the phenol and traces of carbon disulfide. This was then ether extracted, ether distilled and then crystallised from ethyl alcohol or ethyl acetate. The yield in this case was only 20% and most of the unreacted products were recovered during steam distillation.

b) The mixture was kept in the ice bath for four hours and then given the above treatment and the product thus obtained was crystallised from ethyl acetate or alcohol. The yield in this case was found to increase by 5%.

c) The mixture was kept in the ice bath for four hours and
then refluxed on a water bath at 60°C for two hours, cooled and then decomposed as above. The yield in this case still increased and was found to be 35%.

d) The reaction mixture after the addition of phenol when the reaction had subsided was removed from the ice bath and kept over-night at room temperature care being taken that it is well protected from moisture. The next day it was refluxed on a water bath at 60°C for two hours and then decomposed as above. It was found that the yields increased to a great extent i.e. 60%.

Any other changes in the conditions of the reaction were found to be of little importance and had no significant effect on the yields.

**Effect of Solvents:** When the reaction was carried out in the absence of carbon disulfide the yields were very poor. Use of carbon disulfide greatly increased the yield. Nitro-benzene was also tried out, but again the yields were found to be very poor. Table \( \text{F} - \text{H} \) describes the yields prepared.
### TABLE IV

**Aryl Thioamides**

![Chemical structure](chart)

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**TABLE VI**

Aryl Thio carbamates

![Aryl Thio carbamates structure](image)
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### TABLE VII

**Aryl Thiocarbamates**

![Chemical structure](image)

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SYNTHESIS OF THIOAMIDES BY THE GRIGNARD REACTION

Typical Procedure:

Preparation of the Grignard reagent: In a round bottom flask fitted with a double surface refluxing condenser was taken pure magnesium (0.25 mole) and to it 10 c.c. of anhydrous ether was added. The apparatus was well protected from moisture by a guard tube. Then butyl iodide (0.25 mole) diluted with ether was added dropwise and the mixture was mechanically stirred. When half the butyl iodide had been added the reaction started with the evolution of heat. The rest of the butyl iodide was added at such a rate that the reaction did not become very vigorous. When all the butyl iodide had been added stirring was continued for about half an hour and the reaction subsided. The completion of the reaction is marked by most of the magnesium being dissolved. The reaction mixture was then warmed on a water bath for fifteen minutes to ensure the completion of the reaction. The butyl magnesium iodide is then filtered on a hot Buchner funnel to remove some suspended magnesium particles. It is necessary that the grignard solution should be filtered while it is hot, or it invariably solidifies.

Preparation of Thiovalero-p-Toluide: To a warm solution of butyl magnesium iodide (0.40 mole) in ether taken in a round bottom flask fitted with a double surface water condenser is added p-tolyl isothiocyanate (0.17 mole) drop-wise. Sufficient heat was evolved to cause vigorous boiling of the ether solution. A bulky precipitate of ball-like aggregate of white crystals was
obtained from the mixture on standing it overnight. This addition product was filtered off by suction washed with ether and added to hydrochloric acid containing crushed ice during much mechanical stirring. A solid separated, which was filtered off, dried and crystallised from alcohol, m.p. 70°C. The yield was 90% calculated on the bases of the isothiocyanate.

Preparation of S-methyl N-benzyl-thio-acetamide: 0.3 mole of benzyl isothiocyanate dissolved in ether was slowly added to a cool well stirred ether solution containing 0.4 mole of methyl magnesium iodide. After warming the mixture for two hours 0.5 mole of dimethyl sulfate in ether was slowly added. The contents of the flask thickened quite appreciably and became yellow. It was then again refluxed for two more hours and the reaction mixture was hydrolysed with iced hydrochloric acid. The ether layer was washed with water. On evaporation of most of the ether slightly yellow needles melting at 80°C were obtained. Following tables describe thioamides thus prepared.
### TABLE VIII

**N-Aryl Alkyl Thioamides**

![Chemical Structure]

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### TABLE IX

**N-Benzyl Alkyl Thioamides**

![Chemical Structure](image)

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