Purification of solvents:

**Benzene:**

Benzene (BDH, thiophene free) was refluxed over $\text{P}_2\text{O}_5$ for 4 hrs. and then distilled. The distillate so obtained was kept over sodium wire for 24 hrs. and distilled. Fractions distilling between 72-74°C/540 mm were collected and kept over activated molecular sieves $1 \text{A}^0$ for 48 hrs. in properly stoppered bottles before use.

**Carbon tetrachloride:**

Carbon tetrachloride (BDH) was refluxed over mercury for 3 hrs. to remove any carbon disulphide present and then distilled. The distillate so obtained was refluxed over $\text{P}_2\text{O}_5$ for 4 hrs. and then redistilled. The fraction distilling at 70°C/560 mm was collected and kept over activated molecular sieves $1 \text{A}^0$ for 48 hrs. before use.

**Petroleum ether:**

Petroleum ether (BDH, 60-80°C) was successively distilled over sodium wire and $\text{P}_2\text{O}_5$ respectively. The fraction distilling between 60-80°C was collected and stored over activated molecular sieves $1 \text{A}^0$ for 48 hrs. before use.

**Chloroform:**

Chloroform (E. Merck) was shaken with about half of its
volume of water for 5 or 6 times in a separating funnel. The chloroform layer was kept over anhydrous calcium chloride for 24 hrs. and then distilled. Fraction distilling at 55°C/560 mm was collected and stored in a dark bottle over activated molecular sieves 4 Å and then used.

**Nitrobenzene:**

Nitrobenzene (A.R.) was kept over anhydrous calcium chloride for overnight and then distilled. The distillate was kept over activated molecular sieves for 24 hrs. and finally fractionally distilled. The fraction distilling at 193-195°C/540 mm was collected and stored over activated molecular sieves for 48 hrs. before use.

**Acetonitrile:**

Acetonitrile (Reidel) was kept over molecular sieves for 48 hrs. and was then distilled twice over anhydrous calcium chloride. The fraction distilling at 65°C/520 mm was collected and kept over molecular sieves before use.

**Xylene:**

Xylene (BDH) was refluxed over P₂O₅ for 3 hrs. and then distilled. The distillate so obtained was kept over sodium wire for 24 hrs. and distilled. Fractions distilling between
128-130°C were collected and kept over activated molecular sieves \( A^0 \) for 48 hrs. in properly stoppered bottles before use.

**Phenol:**

Phenol was purified by crystallising twice from carbon tetrachloride. It was further purified by distilling and collecting the fraction boiling at 169°C/540 mm. Samples having specific conductance more than \( 1.8 \times 10^{-8} \text{ ohm}^{-1}\text{cm}^{-1} \) were rejected. The purity of the sample was checked by its melting point (43°C).

**Phosphorus(V) chloride:**

Phosphorus(V) chloride was purified by sublimation in an all glass apparatus and used immediately.

**Arsenic(III) and antimony(III) chlorides:**

Arsenic(III) and antimony(III) chlorides (BDH) were used as such without further purification.

**Organic nitrogenous bases:**

Pyridine, \( \alpha \)-picoline and piperidine, all of AnalaR grade, were kept over potassium hydroxide pellets for 24 hrs. and fractionally distilled in an all glass apparatus. The fractions
distilling at the following temperatures were collected for use:

<table>
<thead>
<tr>
<th>Base</th>
<th>Temperature °C (b.pt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>106/540 mm</td>
</tr>
<tr>
<td>Piperidine</td>
<td>99.5-100.5/540 mm</td>
</tr>
<tr>
<td>α-picoline</td>
<td>122-123/560 mm</td>
</tr>
</tbody>
</table>

2,2'-Bipyridyl:

2,2'-Bipyridyl (A.R., BDH) was kept over H₂O₅ in a vacuum desiccator for 48 hrs. before use (m.pt. 69.5°C).

1,10-Phenanthroline:

1,10-Phenanthroline (R. Merck) was kept in an oven at low temperature for about one hr. and then placed over H₂O₅ in a vacuum desiccator for 48 hrs. before use (m.pt. 117°C).

Pyridine N-oxide:

Pyridine N-oxide was prepared by the following standard method (409):

40 gm of pyridine was mixed with 300 ml of glacial acetic acid and then 60 ml of 30% aqueous hydrogen peroxide was added to the above mixture dropwise with constant shaking. The contents were stirred till the solution became homogeneous.
The solution so obtained was heated on a water bath at 70-80°C for 3 hrs. followed by the addition of 40 ml more of hydrogen peroxide (altogether 1.7 moles). The resulting solution was further maintained at this temperature for 9 hrs. It was then concentrated to about 100 ml by distillation under reduced pressure. The concentrated solution was then diluted with 100 ml of water, stirred well and concentrated again under vacuum.

The solution thus obtained was made strongly alkaline with anhydrous sodium carbonate. It was then shaken with 250 ml of chloroform and allowed to stand for some time when sodium carbonate and sodium acetate separated out which were removed by filtration. The filtrate containing pyridine N-oxide was dried by keeping over anhydrous sodium sulphate for 3 hrs. It was then freed of sodium sulphate by filtration. The solvent from the filtrate was removed by simple distillation. Last traces of the solvent were then removed under reduced pressure leaving behind pyridine N-oxide (yield 46 gm).

$\alpha$-Picoline N-oxide:

$\alpha$-Picoline N-oxide (A.R.) was available commercially and was used as such without further purification.

2,2'-Bipyridyl N,N'-dioxide:

It was prepared by the method already reported in literature (299).
To a solution of 10 gm of 2,2'-bipyridyl in 75 ml of glacial acetic acid, 13 ml of 30% hydrogen peroxide was added. The contents were heated at 70-80°C for 3 hrs. followed by the addition of 9 ml of hydrogen peroxide. The contents were again maintained at 70-80°C for 19 hrs. These were brought to room temperature and one litre of dried acetone was added. Precipitates of 2,2'-bipyridyl N,N'-dioxide were obtained. These were filtered and recrystallised from hot water by the addition of a large excess of acetone, when fine white needles were obtained (m.pt. 297°C).

1,10-Phenanthroline N,N'-dioxide:

1,10-Phenanthroline N,N'-dioxide was prepared by the following standard method (410):

1,10-Phenanthroline monohydrate (10.0 gm) was dissolved in 60 ml of glacial acetic acid, 12 ml of 30% hydrogen peroxide was added to it. The contents were maintained at 70-75°C for 3 hrs. Then 12 ml of additional hydrogen peroxide was added. Heating was continued for another six hrs. The resulting solution was concentrated to approximately 30 ml using a rotatory evaporator and then 30 ml of water was added. The concentration was continued to approximately 15 ml. The mixture was then neutralised with a sodium carbonate-water paste. The solid mass so obtained was extracted repeatedly with several
portions of chloroform and the resulting extracts were evaporated. The residue left was dried in an oven at 50°C. It was then ground to a fine powder and re-extracted with chloroform. The combined chloroform extracts were dried over sodium sulphate, boiled with decolourising charcoal and evaporated to dryness. It was recrystallised from chlorobenzene. Fine pale yellow needles were obtained (m.pt. 185°C).

**Triphenylphosphine oxide:**

Commercially available triphenylphosphine oxide (A.R.) was used as such without further purification.

**Triphenylarsine oxide:**

Triphenylarsine oxide (Koch-Light) was used as such without further purification.

**Amides and dimethylsulphoxide:**

N-Methylformamide, dimethylformamide, N-methylacetamide, N,N'-dimethylacetamide, hexamethylphosphoramide and dimethylsulphoxide were purified by the standard methods.

**Acetylacetone and ethyl acetoacetate:**

Acetylacetone and ethyl acetoacetate were repeatedly shaken with small amounts of saturated aqueous sodium bicarbonate
solution. The whole lots were then washed with water and were dried over anhydrous calcium chloride. The fractions at the following temperatures were collected for use:

- Acetylacetone 128°C/550 mm
- Ethyl acetoacetate 167-168°C/540 mm

Dibenzoylmethane:

Dibenzoylmethane (A.R.) was recrystallised from methanol. The compound used had melting point (79°C).

Benzoin:

Benzoin (E. Merck) was recrystallised from hot benzene. The purity of the sample was checked from its melting point (137°C).

Salicylaldehyde:

Salicylaldehyde (Reidel) was used after distillation in an all glass apparatus under reduced pressure.

2-Hydroxyacetophenone:

2-Hydroxyacetophenone (A.R.) was used as such without further purification.
Acetophenone:

Acetophenone (A.R.) was first dried by keeping over anhydrous calcium chloride followed by fractional distillation in an all glass apparatus under reduced pressure. The fractions distilling at 188°C/540 mm was collected for use.

Acetyl chloride:

Acetyl chloride (BDH) was refluxed over sodium metal for 3 hrs. to remove any trace of acetic acid present in the commercial sample. It was then distilled and the fraction distilling at 44.5°C/540 mm was collected and used immediately.

Aluminium(III) chloride:

Anhydrous aluminium(III) chloride (BDH) was purified by sublimation in an atmosphere of chlorine in a specially designed tube having 5 or 6 bulbs. The material was successively sublimed from one bulb to another. The final product so obtained was kept under vacuum for 48 hrs. to remove any excess of chlorine. Purity of the compound was checked by elemental analysis.

Iron(III) chloride:

Iron(III) chloride anhydrous (BDH) was used as such without further purification.
Antimony(V) chloride:

Antimony(V) chloride (Reidel) was used after distillation under reduced pressure.

Preparation of alkali metal phenoxides:
(Phenoxides of sodium, potassium and lithium)

These phenoxides were prepared by the following standard method:

Freshly cut pieces of the metals (1C gm) dried between the folds of filter paper were added in small amounts to phenol in predetermined molar ratios in 500 ml of benzene. The contents were vigorously stirred with a magnetic stirrer. The reaction was quite rapid and after 4-5 hrs. a thick white compound started separating out. It was filtered, washed with benzene to remove any excess of phenol and finally dried under vacuum. The purity of the compounds was checked by elemental analysis (% Na = 19.78(19.82), % K = 16.92(16.96), % Li = 6.96(7.00) Found(Calcd).

Preparation of sodium isopropoxide:

Sodium isopropoxide was prepared by adding freshly cut pieces of sodium metal (5 gm) to isopropanol (13.5 ml) in 500 ml of benzene. The flask was warmed slightly (50-60°C) to enhance the reaction. It was then vigorously stirred with a magnetic
stirrer. A white fluffy compound so obtained was filtered, washed repeatedly with hot benzene to remove any unreacted isopropanol and finally dried under vacuum. The purity of the compound was checked by elemental analysis (% Na = 28.11 (28.04) Found(Calcd).

**Preparation of pentaphenoxy phosphorus(V) P(OC₆H₅)₅:**

Pentaphenoxy of phosphorus was prepared by taking together phosphorus(V) chloride (3.74 g; .0179 moles) and phenol (8.43 g; .089 moles) in dry carbon tetrachloride in the presence of a base. A liquid layer of the compound so formed was separated out. It was successively washed with carbon tetrachloride and petroleum ether. Last traces of the solvent were removed under reduced pressure. Stoichiometry of the compound was established by elemental analysis (% P = 6.27(6.25) Found(Calcd) (Yield = 1.08 gm).

**Preparation of monochlorophosphorus(V) phenoxide FC₁(OC₆H₅)₄:**

Monochlorophosphorus(V) phenoxide was prepared by taking together phosphorus(V) chloride (4.31 g; .08 moles) and phenol (7.77 g; .082 moles) in dry carbon tetrachloride. The completion of the reaction was ensured when there was no evolution of hydrogen chloride gas under anhydrous conditions. Two different liquid layers of the solvent and the compound were separated out through separating funnel. The liquid compound so formed was
filtered, washed repeatedly with carbon tetrachloride to remove any excess of reactants. Last traces of the solvent were removed under reduced pressure. Stoichiometric composition was established by elemental analysis (% P = 7.04(7.06); % Cl = 8.06(8.09); Found(Calcd) (Yield = 2.52 gm).

Preparation of dichlorophosphorus(V) phenoxide PCl$_2$(OC$_6$H$_5$)$_3$:

Dichlorophosphorus(V) phenoxide was prepared by taking together phosphorus(V) chloride (1.5 g; 0.0071 mole) and phenol (2.02 g; 0.0204 mole) in dry carbon tetrachloride. The contents of the mixture were stirred for 2 hrs. at room temperature and then refluxed on a water bath for about 18 hrs. when the evolution of hydrogen chloride gas stopped. The resulting compound was filtered under anhydrous conditions. The residue was successively washed with carbon tetrachloride and petroleum ether and then dried under vacuum. Stoichiometry composition of the compound was established by elemental analysis (% P = 8.22 (8.26); % Cl = 18.92(18.93); Found(Calcd) (Yield = 1.89 gm).

Preparation of trichlorophosphorus(V) phenoxide PCl$_3$(OC$_6$H$_5$)$_2$:

Trichlorophosphorus(V) phenoxide was prepared by taking together phosphorus(V) chloride (1.8 g; 0.0086 mole) and phenol (1.62 g; 0.0172 mole) in dry carbon tetrachloride. The contents were refluxed on a water bath. The completion of the reaction was ensured when there was no evolution of hydrogen chloride gas.
The solid compound so formed was filtered under anhydrous conditions, washed repeatedly with carbon tetrachloride to remove any excess of reactants and finally dried under vacuum. Stoichiometric composition was established by elemental analysis (% F = 9.57(9.58); % Cl = 32.93(32.90); Found(Calcd) (Yield = 1.2 gm).

**Preparation of tetrachlorophosphorus(V) phenoxide $\text{PCl}_4(\text{OC}_6\text{H}_5)$:**

Tetrachlorophosphorus(V) phenoxide was prepared by stirring a solution of phosphorus(V) chloride (4.0 g; 0.019 moles) and phenol (1.8 g; 0.019 moles) in dry carbon tetrachloride. The contents were stirred at room temperature for about 24 hrs. when the evolution of hydrogen chloride gas ceased. The solid compound so obtained was washed repeatedly with carbon tetrachloride to remove any excess of reactants and finally dried under vacuum. Stoichiometric composition of the compound was established by elemental analysis (% F = 11.63(11.65); % Cl = 53.36(53.38); Found(Calcd) (Yield = 2.1 gm).

**Preparation of arsenic(III) phenoxide $\text{As(OC}_6\text{H}_5)_3$:**

Arsenic(III) chloride (25 g; 0.13 mole) was mixed with phenol (51 g; 0.541 mole) in xylene. The contents were refluxed for about 12 hrs. when the evolution of hydrogen chloride gas ceased. Then reaction mixture was subjected to distillation. Xylene was distilled between 128-130°C. The major quantity of
material was obtained at 207°C. Stoichiometry composition of the compound was established by elemental analysis (% As = 21.19(21.16); Found(Calcd) (Yield = 55%).

**Preparation of monochloroarsenic(III) phenoxide AsCl(OC₆H₄)₂:**

Monochloroarsenic(III) phenoxide was prepared by mixing arsenic(III) chloride (15 g; .082 mole) with phenol (15.54 g; .165 mole) in xylene. The contents were refluxed for about 8 hrs. Then the reaction mixture was distilled to remove xylene. From the fraction between 165-205°C about 3 gms of oily liquid was obtained. Stoichiometry composition of the compound was established by elemental analysis (% As = 25.29(25.25); % Cl = 11.95(11.97); (Found(Calcd) (Yield = 15%).

**Preparation of dichloroarsenic(III) phenoxide AsCl₂(OC₆H₄)₂:**

Arsenic(III) chloride (40 g; .275 mole) was mixed with phenol (20.7 g; .22 mole) in xylene. The contents were refluxed for about 5 hrs. Then the reaction mixture was distilled to remove xylene. The remaining portion was redistilled in a small column under vacuum. Fraction obtained between 115-150°C contained the compound. Stoichiometric composition of the compound was established by elemental analysis (% As = 31.38 (31.35); % Cl = 29.67(29.71); Found(Calcd) (Yield = 40%).
Preparation of antimony(III) phenoxide Sb(O\textsubscript{C,H\textsubscript{5}}\textsubscript{3}):  
Antimony(III) chloride (2.67 g; .0116 moles) was mixed with phenol (3.28 g; .0348 moles) in xylene. The contents were refluxed for about 25 hrs. when the evolution of hydrogen chloride stopped. Then the reaction mixture was distilled to remove xylene. From the remaining portion colourless crystalline material was obtained by the addition of petroleum ether. Stoichiometric composition of the compound was established by elemental analysis (% Sb = 30.35(30.38) Found(Calcd) (Yield = 1.72 gm).

Preparation of monochloroantimony(III) phenoxide SbCl(O\textsubscript{C,H\textsubscript{5}}):  
Monochloroantimony(III) phenoxide was prepared by refluxing a solution of antimony(III) chloride (2.83 g; .0123 moles) with phenol (2.33 g; .0347 moles) in xylene for about 12 hrs. The reaction mixture was then distilled to remove xylene and any unreacted phenol. Colourless crystalline material separated out by the addition of petroleum ether from the solution. Stoichiometric composition of the compound was established by elemental analysis (% Sb = 35.47(35.46); % Cl = 10.37(10.34); Found(Calcd) (Yield = 1.87 gm).

Preparation of dichloroantimony(III) phenoxide SbCl\textsubscript{2}(O\textsubscript{C,H\textsubscript{5}}):  
Antimony(III) chloride (3.65 g; .015 moles) was mixed with
phenol (1.503 g; .015 moles) in xylene. The contents were refluxed in carbon tetrachloride for about 6 hrs. The completion of the reaction was ensured when there was no more evolution of hydrogen chloride gas. The solid compound so formed was filtered, washed repeatedly with carbon tetrachloride to remove any excess of reactants and finally dried under vacuum. Stoichiometric composition of the compound was established by elemental analysis (% Sb = 42.63(42.60); Cl = 24.88(24.84); Found(Calcd) (Yield = 1.47 gms).

Preparation of the adducts of phenoxides of phosphorus(V), arsenic(III) and antimony(III) with nitrogenous bases:

Addition compounds of the phenoxides of phosphorus(V), arsenic(III) and antimony(III) with organic tertiary bases were prepared by a general procedure which involves the mixing of the benzene solution of the parent phenoxide and the bases in predetermined molar ratios. The reactants were then stirred for about 24 hrs. at room temperature. The addition compounds so formed separated out as solids or were isolated from the solutions by the addition of petroleum ether to the clear solution of the reactants. Compounds so isolated were filtered in a dry atmosphere and were washed with petroleum ether to remove any excess of reactants and finally dried under vacuum. Stoichiometry of the adducts was established by elemental analysis details of which are included in Tables IX, XXIV and XXV.
Preparation of the adducts of phenoxides of phosphorus(V), arsenic(III) and antimony(III) with amine oxides:

The addition compounds of the phenoxides of phosphorus(V), arsenic(III) and antimony(III) with various oxides viz. pyridine N-oxide, α-picoline N-oxide, 2,2'-bipyridyl N,N'-dioxide, 1,10-phenanthroline N,N'-dioxide and of phenoxide of phosphorus(V) with triphenylphosphine oxide were prepared by mixing their solutions or suspension in chloroform in predetermined molar ratios under controlled experimental conditions. The contents were stirred for about ten hrs. when components went into solution. The compounds were isolated by the addition of petroleum ether. These were then filtered under anhydrous conditions, washed 2-3 times with petroleum ether and finally dried under vacuum. Stoichiometric composition was established by elemental analysis (Tables XIV, XX, XXIV and XXV).

Preparation of the adducts of phenoxides of phosphorus(V) with amides, dimethylsulphoxide and hexamethylphosphoramidate:

Addition compounds of phenoxides of phosphorus(V) with various amides, dimethylsulphoxide and hexamethylphosphoramidate were prepared by mixing the solution of the parent phenoxide in benzene with solution of the respective ligands in the same solvent. The contents were stirred for about 24 hrs. The addition compounds either separated out as solids or were isolated by the addition of petroleum ether to the resulting
solution. These were then filtered under anhydrous conditions. The residue was washed with petroleum ether to remove any excess of the reactants and finally dried under vacuum. Stoichiometric composition was established by elemental analysis, details of which are given in Tables XVIII and XX.

**Reaction products of the phenoxides with hydrogen chloride and acetyl chloride:**

Through a known weight (0.2-0.3 g) of the phosphorus(V) phenoxide in carbon tetrachloride, a slow stream of dry hydrogen chloride gas was slowly bubbled through the suspension. The compounds were isolated by chilling the solution and finally dried under vacuum. The stoichiometric composition of the compounds was established by elemental analysis.

To a known weight (0.2-0.3 g) of the phosphorus(V) phenoxide in benzene, acetyl chloride was added in 1:1, 1:2 and 1:3 molar ratio. The contents were refluxed over a water bath for about 1 hr. The contents were then cooled and the compounds were isolated by the addition of petroleum ether. These were filtered and finally dried under vacuum. The stoichiometric composition of the compounds was established by elemental analysis.
Preparation of double phenoxides of phosphorus(V) phenoxide and arsenic(III) phenoxide:

Double phenoxides of composition $\text{M} \left[ \text{As(O}_6\text{H}_5\right]_6$ and $\text{M}\left[\text{P(O}_6\text{H}_5\right]_6$ $\text{M} = \text{Li, Na, K}$ were prepared by refluxing phosphorus(V) and arsenic(III) phenoxides and alkali metal phenoxides in 1:1 molar ratio in carbon tetrachloride till the components went into solution. The components were isolated by cooling the solution supplemented by the addition of petroleum ether, filtered and finally dried under vacuum.

Preparation of complexes of monochlorophosphorus(V) phenoxide with Lewis acids:

Complexes of composition $\text{F(O}_6\text{H}_5\right]_4 \cdot \text{MC}_4$ ($\text{M} = \text{Al, Fe}$) were prepared by taking monochlorophosphorus(V) phenoxide and the Lewis acids in exactly 1:1 molar ratio in carbon tetrachloride. The contents were refluxed on a water bath for 2-3 hrs. The completion of the reaction was indicated by a colour change. The solid complexes separated out on cooling which were filtered under dry atmosphere, washed repeatedly with petroleum ether and then dried under vacuum.

In the case of the complex of composition $\text{SbC}_6\text{F(O}_6\text{H}_5\right]_4$, however, the components were refluxed in dichloromethane instead of carbon tetrachloride. Rest of the procedure being the same as discussed above.
Preparation of phenolic trimethylsilyl ether $\text{Me}_3\text{Si}(\text{OC}_6\text{H}_5)$:

Trimethylsiloxybenzene was prepared by the following method:

To 37.4 g of phenol (0.4 mole), 54.5 g of trimethylchlorosilane (0.5 mole) was added. After 7 hrs. of refluxing, 50 ml of petroleum ether (b.p. 60-68°) was added. The reaction solution was then refluxed for 4 hrs. and then distilled. After stripping a total of 56.6 g of material, b.p. 166-178° was recovered. This product was distilled through a 2 foot Podbielniak column to give 2 g of material, b.p. 112-174°, and 27.0 g of material with a boiling point of 174° to 181.9°. Much of the latter was an azeotrope with a b.p. of 175.5°. The rest of the trimethylsilylphenyl ether product had b.p. 181.9-182.4°.

Preparation of solvate of tellurium(IV) chloride with phenol $\text{TeCl}_4 \cdot 2\text{C}_6\text{H}_5\text{OH}$:

Compound of composition $\text{TeCl}_4 \cdot 2\text{C}_6\text{H}_5\text{OH}$ was prepared by mixing tellurium(IV) chloride with excess of phenol in dry benzene. The mixture was stirred constantly for 24 hrs. at room temperature. A yellowish green compound separated out was filtered and washed repeatedly with dry benzene to remove any excess of phenol left. It was then dried under anhydrous conditions. Composition of the compound was established by
elemental analysis (% Te = 27.81 (27.78); % Cl = 31.05 (31.07)
Found (Calcd) (Yield = 45%).

Preparation of tellurium(IV) phenoxide $\text{Te}(\text{OC}_6\text{H}_5)_4$:

Tellurium(IV) phenoxide was prepared by the addition of
tellurium(IV) chloride (5.38 g; 0.19 moles) to a solution of
trimethylsilyl ether (13.25 g; 0.79 moles) in dry xylene under
anhydrous conditions. The contents were refluxed for about
2 hrs. when dark green compound separated out. It was filtered,
washed and dried under anhydrous conditions under vacuum. The
composition of the compound was established by elemental
analysis (% Te = 25.58 (25.54) Found (Calcd) (Yield = 3.38 gm).

Preparation of trichlorotellurium(IV) phenoxide $\text{TeCl}_3(\text{OC}_6\text{H}_5)_2$:

Tellurium(IV) chloride (7.46 g; 0.27 moles) was added to a
solution of trimethylsilyl ether (4.58 g; 0.27 moles) in xylene.
The contents were stirred for 4 hrs. at room temperature. The
compound thus separated out was filtered and dried under
anhydrous conditions. Composition of the compound was established
by elemental analysis (% Te = 38.87 (39.00); % Cl = 32.49 (32.55);
Found (Calcd) (Yield = 4.18 gm).

Preparation of dichlorotellurium(IV) phenoxide $\text{TeCl}_2(\text{OC}_6\text{H}_5)_2$:

Dichlorotellurium(IV) phenoxide was prepared by refluxing
tellurium(IV) chloride (8.12 g; 0.30 moles) and trimethylsilyl
ether (9.62 g; .057 moles) in xylene for about 4 hrs. The resulting compound was filtered, washed repeatedly with dry benzene and dried under anhydrous conditions. Composition of the compound was established by elemental analysis (% Te = 33.19 (33.17); % Cl = 18.43(18.46); Found(Calcd) (Yield = 5.28 gm).

Preparation of monochlorotellurium(IV) phenoxide TeCl(OC₆H₅)₃:

Tellurium(IV) chloride (6.58 g; .024 moles) was added to a solution of trimethylsilyl ether (12.15 g; .073 moles) in xylene. The contents were refluxed for about 4 hrs. The brownish solid compound obtained was filtered, washed and dried under vacuum. The composition of the compound was assigned on the basis of elemental analysis (% Te = 28.82(28.86); % Cl = 8.07(8.02); Found(Calcd) (Yield = 3.54 gm).

Preparation of tellurium isopropoxide Te(OiPr)₄:

To tellurium tetrachloride (3.8 g; .014 moles) dissolved in isopropanol and cooled by ice, sodium isopropoxide (4.62 g; .0563 moles) was added with constant shaking. Then benzene was added and the contents were refluxed for an hour. The excess of the solvent was distilled. On drying the contents under reduced pressure at the room temperature, a colourless liquid was obtained which distilled at 46°. Stoichiometric composition of the compound was established on the basis of elemental analysis (% Te = 28.36(28.32); Found(Calcd).
Preparation of the adducts of phenoxides of tellurium(IV) with nitrogen bases and amine oxides:

Addition compounds of the phenoxides of tellurium(IV) with nitrogen bases and amine oxides were prepared by a general procedure which involves the mixing of the suspension of the phenoxides in dry benzene with various ligands in predetermined molar ratios. The reactants were then stirred for about 12 hrs. and were isolated either by cooling the contents or by the addition of petroleum ether. Compounds so isolated were filtered, and were washed with petroleum ether and finally dried under vacuum. Stoichiometry of the adducts was established by elemental analysis, details of which are included in Tables XXX and XXXa.

Preparation of the chelates of phenoxides of tellurium(IV) with acetyl acetone, dibenzoylmethane, ethylacetoacetate, benzoin, salicylaldehyde, acetophenone and 2-hydroxyacetophenone:

Monochloro-, dichloro- and trichloro-tellurium(IV) phenoxides were taken as suspensions in benzene and to this solution the ligands were added in 1:1 and 1:2 molar ratio. The contents were refluxed on a water bath till there was no more evolution of hydrogen chloride gas. The contents were cooled and the compounds so formed separated out as solids or were isolated from the solutions by the addition of petroleum ether. These were filtered in dry atmosphere, washed repeatedly with
dry petroleum ether and finally dried under vacuum. Stoichiometric composition of all these compounds was established by elemental analysis, details of which are given in Tables XXXV, XXXVIII, XLI and XLII.

Preparation of tungsten hexa-o-chlorophenoxide and tungsten hexa-o-nitrophenoxide:

Tungsten(VI) chloride (3.18 g; .008 moles) was refluxed with o-chlorophenol (6.12 g; .048 moles) and o-nitrophenol (6.63 g; .048 moles) in chlorobenzene. The red solution was passed through a column of alumina which retained some coloured impurities, and the column was washed with 1:1 benzene/light petroleum. The combined eluates were concentrated to a syrup under reduced pressure and the compounds were crystallized from ethanol. Stoichiometric composition of the compounds was established by elemental analysis (Table XLIV).

Preparation of trichloro derivatives of tungsten(VI) with phenol, o-chlorophenol and o-nitrophenol:

Tungsten(VI) chloride (2.78 g; .0070 moles) was refluxed with phenol (1.97 g; .021 moles), o-chlorophenol (2.67 g; and o-nitrophenol (2.9 g; .021 moles) in chlorobenzene in predetermined molar ratios till there was no more evolution of hydrogen chloride gas. The solutions were then passed through a column of alumina which retained some coloured impurities and
the column was washed with 1:1 benzene/light petroleum. The combined eluates were concentrated to a syrup under reduced pressure and the compounds were crystallised from petroleum ether. Stoichiometric composition of the compounds was established by elemental analysis (Table XLIV).

Preparation of addition compounds of trichloro derivatives of tungsten(VI) with nitrogenous bases and amine oxides:

Addition compounds of the compounds of composition

\[ \text{WCl}_3(\text{OC}_6\text{H}_5)_3, \text{WCl}_3(\text{o-OC}_6\text{H}_4\text{Cl})_3\]  and \[ \text{WCl}_3(\text{o-OC}_6\text{H}_4\text{NO}_2)_3 \]

with nitrogenous bases and amine oxides were prepared by mixing of the benzene solution of the parent phenoxydes, o-chlorophenoxydes and o-nitrophenoxydes and ligands in predetermined molar ratios. The reactants were then stirred for about 12 hrs. at room temperature and the addition compounds were isolated from the solutions by the addition of petroleum ether to the clear solution of the reactants. Compounds so isolated were dried under vacuum. Washing with petroleum ether were avoided due to high solubility of adducts in petroleum ether. Stoichiometry of the adducts was established by elemental analysis, details of which are included in Tables XLVI and XLVIA.

Conductivity measurements:

Molar conductance measurements of the compounds were made by dissolving a known amount of (.01-.05 gm) of the complexes
in dry nitrobenzene. The volume of the solution was made to a definite volume in a measuring flask. The solution was then transferred in a specially designed conductivity cell having a cell constant 3.17 cm⁻¹. The conductance of the solution was measured at 25 ± 0.1°C using precision measuring Elico Conductivity Bridge type CM-82T. Specific conductance was calculated by multiplying the observed conductance with the cell constant and the molar conductance of the compounds were calculated using the relation:

\[
\text{Molar conductance} = \frac{\text{Sp. conductance} \times 1000}{\text{Conc. in g mole/litre}}
\]

For all measurements, millimolar solutions (10⁻³ M) in nitrobenzene was used.

**Conductometric titrations in nitrobenzene and fused phenol:**

Conductometric titrations in nitrobenzene and fused phenol were carried out in a cell fitted with replaceable electrodes and was fitted with a calcium chloride guard tube. But in a particular titration, the position of the electrodes was kept fixed.

In the case of titrations carried out in nitrobenzene, conductance measurement was carried out at 25 ± 0.1°C by immersing the cell in a water bath maintained at that temperature.
A small amount of the compound (0.001 mole) to be titrated was taken in the conductivity cell and dissolved in nitrobenzene. Conductance of the resulting solution was noted when it became constant. A concentrated solution of the titrant in nitrobenzene was prepared by a specially designed liquid weighing bottle. The addition of the titrant in each case was made in very small amounts. Sufficient time was given after addition for the equilibrium to be attained. The titrations were continued till the titrant was in excess than the anticipated result required.

Molten phenol, which was just sufficient to dip the electrodes, was taken in the conductivity cell. The cell was then placed in a thermostat maintained at a temperature of 50 ± 0.5°C. A known weight of the solvo acid was now added to the solvent. The resulting solution was allowed to attain equilibrium. The conductance of the solution was noted when it became constant. Concentrated solution of the solvo base in phenol, prepared directly in standard joint liquid weighing bottle was added in small instalments to the solvo acid solution and the solution stirred vigorously. Conductance was taken only when it attained a constant value. The solvo base was added in excess than the anticipated result required.

Infrared spectra:

The infrared spectra of the compounds under study was
recorded in potassium bromide pellets or as nujol mull using
double grating infrared spectrophotometer Perkin Elmer model
337 and 621 for the far infrared study. The pellets and mulls
were prepared in a dry box to avoid the action of moisture.

**Determination of molecular weights:**

**Cryoscopic method:**

Molecular weights were determined by finding the depression constant in freezing point. Beckmann thermometer was first set for freezing point of benzene or nitrobenzene as the case may be and then freezing point was noted on it.

A known weight of the compound was dissolved in a known weight of pure solvent and the depression in freezing point noted. Some more compound was weighed out in the same solution and further depression in freezing point was noted. Three to four observations were taken in the same manner. Molecular weight was then determined by using the following relationship:

\[
M = \frac{K_f \times w \times 1000}{T_f \times W}
\]

where

- \(K_f\) = Molal freezing point constant of the solvent
- \(w\) = Weight of the compound
- \(T_f\) = Depression in freezing point
- \(W\) = Weight of the solvent.
Estimation of phosphorus, arsenic, antimony and tellurium:

These were estimated separately on different aliquots of the filtrate employed; the method referred to in the appendix.

Appendix-I

"A Text book of Quantitative Inorganic Analysis" by A.I. Vogel, 3rd edition, Longman, Green and Co. Ltd., London (1961), has been consulted for the estimation of various elements and metals and the pages are given below:

a) Determination of phosphorus as magnesium pyro-phosphate P. 635, 575
b) Determination of arsenic and antimony volumetrically with potassium iodate P. 376
c) Determination of tellurium P. 508
d) Determination of tungsten as $\text{WO}_3$: A known weight of the compound was moistened with nitric acid and charred at 200-250°C, then heated in air at 500°C for 15 min. The residue was allowed to cool and from the weight of $\text{WO}_3$ amount of tungsten was estimated.

Preparation of aqueous solution of complexes:

Due to the insoluble nature of most of these complexes in water, the halide ions were brought into aqueous solution as follows:
A known weight of the complex was taken in a nickel crucible containing a thick layer of anhydrous sodium carbonate (A.R.). Three or four beads of potassium hydroxide (A.R.) and a small piece of freshly cut sodium metal were added. The whole mass was then covered with another layer of sodium carbonate. The mixture was fused using oxygen flame for fifteen minutes. Then it was allowed to cool and the crucible was placed in a beaker containing distilled water. It was heated on a burner and the fused mass was dissolved in water completely and the nickel crucible was removed after thorough washing with distilled water. The solution(s) thus obtained was employed for the estimation of halide ions in the complexes.

Estimation of chlorine:

The solution(s) was acidified with nitric acid (A.R.) and the contents of the beaker were heated to 60-70°C. Then to this solution was added a known excess of standard silver nitrate solution keeping the beaker wrapped with black paper. The contents were stirred and allowed to stand in the dark place for about an hour. The silver halide precipitates were filtered. The filtrate, obtained after the removal of silver halide, was titrated against standard ammonium sulphocyanide solution, using 1-2 mls of ferric alum as an internal indicator. From the volume of silver nitrate solution used for halide ion, the percentage of halogen was calculated.