

// A STUDY OF THE REACTIONS OF THE HALOCARBONYLS,
 $\text{Mo}(\text{CO})_4\text{X}_2$ (X = Cl, Br) WITH VARIOUS ALKYL AMINES //

BY
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A THESIS SUBMITTED FOR PARTIAL FULFULMENT FOR
THE DEGREE OF MASTER OF SCIENCE OF KENYATTA
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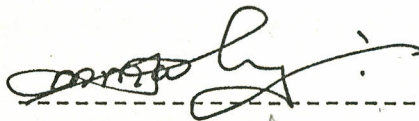
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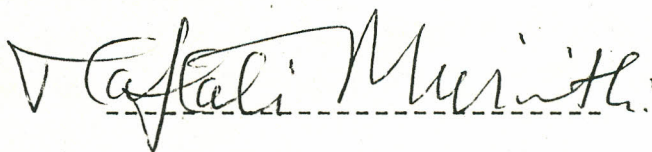
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This Thesis is my original work and has not
been presented for a degree in any other University.



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This Thesis has been submitted for examination
with my approval as University Supervisor.



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Dedicated to my wife Esther Wangechi and
our daughter Eddah Wanjiru

(i)

A B S T R A C T

This thesis describes the reactions of dihalotetracarbonylmolybdenum (II), $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}$), complexes with various alkyl amines. The aim of the project was to find out whether these halocarbonyls react via a solvolytic or a redox mechanism with alkyl amines.

The highly reactive halocarbonyls, $\text{Mo}(\text{CO})_4\text{X}_2$, were prepared following literature methods. These halocarbonyls reacted with neat piperidine giving the zerovalent molybdenum complex, tetracarbonylbis(piperidine)molybdenum(0), $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$. The amine salt, $\text{C}_5\text{H}_{10}\text{NH}\cdot\text{HX}$, for the respective halogen was isolated. The NMR spectrum of the basic distillate from the reaction mixture showed a singlet signal at $\delta=6.1\text{ppm}$ which is in the olefinic region. The signal was not affected by deuterating the distillate with deuterated water.

When the reaction was carried out using either tetrahydrofuran (T.H.F.) or methanol which had been cooled in dry-ice/acetone mixture as solvents, the same products as those mentioned above were obtained.

Treatment of the halocarbonyls, $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}$), with neat butylamine or propylamine which had been cooled in dry-ice/acetone mixture gave the trisubstituted zerovalent molybdenum complexes,

$\text{Mo}(\text{CO})_3\text{L}_3$ (L = butylamine, propylamine). The NMR spectrum of each basic distillate from these reaction mixtures showed a singlet signal at $\delta = 5.8$ ppm for butylamine reaction and at $\delta = 5.3$ ppm for propylamine reaction. These singlet signals are in the olefinic region thus showing that the amines have been dehydrogenated. These signals were not affected by deuterating the distillates with deuterated water.

The zerovalent molybdenum complex, tris(butylamine)tricarbonylmolybdenum(0), was also isolated when the halocarbonyl, $\text{Mo}(\text{CO})_4\text{Br}_2$, was treated with butylamine/methanol mixture. This mixture had been cooled in dry-ice/acetone mixture before being added onto the halocarbonyl, $\text{Mo}(\text{CO})_4\text{Br}_2$.

The infrared spectra of the zerovalent molybdenum complexes have been studied. Various assignments for the carbonyl stretching modes have been made. The N-H stretching frequency of the coordinated amine was found to be significantly lower than that for the free amine.

A careful analysis of the NMR spectra shows that piperidine reacts with the halocarbonyls, $\text{Mo}(\text{CO})_4\text{X}_2$ forming 1,4,5,6-tetrahydroanabasine. The high reactivity of the enamines formed from butylamine and propylamine made it impossible to isolate

any identifiable organic products.

The present work has shown that the halocarbonyls, $\text{Mo(CO)}_4\text{X}_2$ ($\text{X} = \text{Cl, Br}$) react with alkyl amines via a redox mechanism.

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TABLE OF CONTENTS:

	<u>PAGE.</u>
ABSTRACT:	i
<u>CHAPTER 1:</u>	
INTRODUCTION	1
<u>CHAPTER 2:</u>	
A. HANDLING OF COMPOUNDS AND GLASSWARE	
CLEANING	10
(i) Handling of Compounds	10
(ii) Routine glassware cleaning	10
B. MATERIALS AND PURIFICATIONS	12
(i) Molybdenum Hexacarbonyl	12
(ii) Halogens	12
(iii) Hydrogen Halides	14
(iv) Amines	14
(v) Organic solvents	16
(vi) Dry Oxygen-Free Nitrogen	20
(vii) Sodium naphthalide solution	20
C. ANALYTICAL TECHNIQUES	21
(a) General	21
(b) Determination of chloride and bromide using silver nitrate solution	21

	<u>PAGE</u>
D. METHODS OF HANDLING AIR-SENSITIVE COMPOUNDS	26
E. PHYSICAL MEASUREMENTS	28
1. Infrared spectra	28
2. Nuclear Magnetic Resonance	29
<u>CHAPTER 3:</u>	
PREPARATIVE WORK	30
INTRODUCTION	30
3.1 Preparation of dibromotetracarbonylmolybdenum(II)	30
3.2 preparation of dichlorotetracarbonylmolybdenum(II)	33
3.3 Reaction of dibromotetracarbonylmolybdenum(II) with piperidine	35
3.4 Reaction of dichlorotetracarbonylmolybdenum(II) with neat piperidine	42
3.5 Reaction of dibromotetracarbonylmolybdenum(II) with butylamine	44
3.6 Reaction of dichlorotetracarbonylmolybdenum(II) with butylamine	47

	<u>PAGE</u>
3.7 Reaction of Dibromotetracarbonylmolybdenum(II) with propylamine	48
3.8 Reaction of dichlorotetracarbonylmolybdenum(II) with propylamine	49
<u>CHAPTER 4:</u>	
RESULTS AND DISCUSSION	52
I PREPARATIVE	52
A. THE REACTION OF $\text{Mo}(\text{CO})_4\text{X}_2$ WITH PIPERIDINE	52
(a) Tetracarbonylbis(piperidine) molybdenum(0)	52
(b) The oxidation product of piperidine	55
(c) The amine salt	62
B. THE REACTION OF $\text{Mo}(\text{CO})_4\text{X}_2$ WITH BUTYLAMINE OR PROPYLAMINE	64
II PHYSICAL MEASUREMENTS	65
A. IR Spectra	65
B. NMR Spectra	67
III CONCLUSION	68
REFERENCES	80

CHAPTER 1INTRODUCTION.

Most compounds of molybdenum(II) which appear simple from the empirical formulae are, in fact, cluster compounds containing metal-metal bonds. Thus, molybdenum dichloride, MoCl_2 , should be formulated as $\text{Mo}_6\text{Cl}_{12}$ (1). It has eight chlorides covalently bonded to an octahedral cluster Mo_6 to form the basic unit $\text{Mo}_6\text{Cl}_8^{4+}$ (1). The structure for this unit is shown in figure 1.

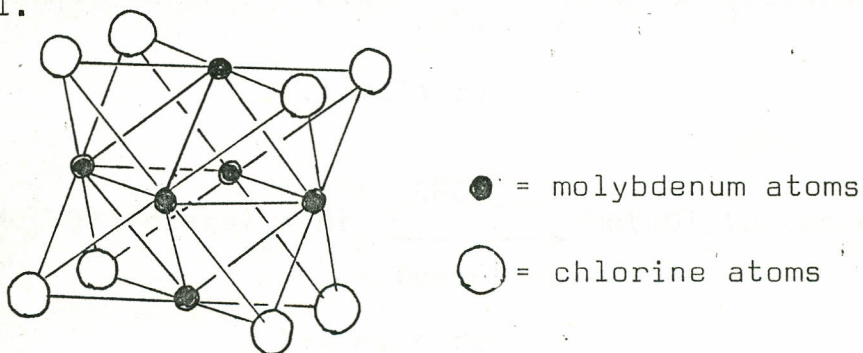
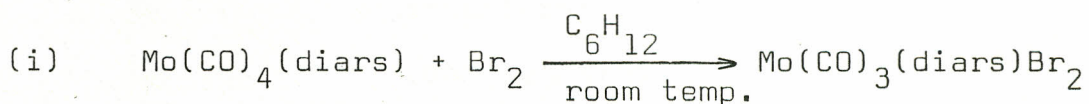


Fig. 1. The structure of the complex ion
 $\text{Mo}_6\text{Cl}_8^{4+}$

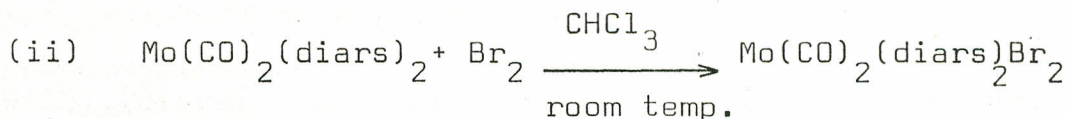
The bromide (2) and the iodide (3) have similar structures.

The formation of cluster compounds is commonest among elements with high heats of atomization (4) especially in the low formal oxidation states (5). It is for this reason that mononuclear complexes of Molybdenum(II) do not exist unless they are stabilized by π -bonding ligands such as phosphines and arsines(6).

The first mononuclear complexes of molybdenum(II) were reported by Nyholm and Co-workers in 1960 (7). These workers showed that substituted molybdenum carbonyls of the type $\text{Mo}(\text{CO})_4\text{D}$ or $\text{Mo}(\text{CO})_2\text{D}_2$ (D = bidentate ligand such as diarsine, diarsine \equiv o-phenylenebisdimethylarsine) react with the calculated amount of bromine to give molybdenum(II) complexes e.g.



1:1 mole ratio



1:1 mole ratio

Table 1. gives examples of other complexes prepared using this technique.

TABLE 1

SOME COMPLEXES FROM HALOGEN OXIDATION OF SUBSTITUTED
MOLYBDENUM AND TUNGSTEN CARBONYLS.

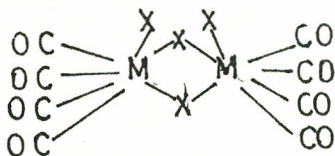
<u>REACTANTS</u>	<u>CONDITIONS</u>	<u>PRODUCT</u>	<u>REF</u>
I $\text{Mo}(\text{CO})_4(\text{diars}) + \text{I}_2$	1:1 mole ratio in chloroform at room temp.	$\text{Mo}(\text{CO})_3(\text{diars})\text{I}_2$	(7)
II $\text{W}(\text{CO})_4(\text{diars}) + \text{I}_2$	Excess iodine in chloroform at room temperature	$[\text{W}(\text{CO})_4(\text{diars})\text{I}]\text{I}_3$	(8)
III $\text{Mo}(\text{CO})_4(\text{bipy}) + \text{X}_2$ (X = Br, I)	1:1 mole ratio	$\text{Mo}(\text{CO})_3(\text{bipy})\text{X}_2$	(9)
IV $\text{W}(\text{CO})_4(\text{diars}) + \text{Br}_2$	1:1 mole ratio in CCl_4 at 0°	$\text{W}(\text{CO})_3(\text{diars})\text{Br}_2$	(10)
V $\text{Mo}(\text{CO})_4(\text{PEt}_3)_2 + \text{X}_2$ (X = Br, I)	1:1 mole ratio	$\text{Mo}(\text{CO})_3(\text{PEt}_3)_2\text{X}_2$	(11)
VI $\text{W}(\text{CO})_4(\text{AsMe}_2\text{Ph})_2 + \text{X}_2$ (X = Br, I)	1:1 mole ratio	$\text{W}(\text{CO})_3(\text{AsMe}_2\text{Ph})_2\text{X}_2$	(11)

It should be noted that treatment of molybdenum hexacarbonyl with bromine at room temperature leads to loss of all carbonyls giving MoBr_4 (12), whereas chlorine gives MoCl_5 (13).

Another method of preparing the mononuclear halocarbonyl complexes of molybdenum(II) is that developed by Brennze (14). It was shown that reduction of MoCl_4 and WCl_4 with EtAlCl_2 in heptane in the presence of carbon monoxide gives acetone soluble products. Addition of phosphine ligands to these solutions precipitated the complexes $\text{Mo}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}_2$ and $\text{W}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}_2$ (14).

Probably the most interesting method of preparing mononuclear molybdenum(II) complexes is that developed by Colton and Co-workers in 1966 (15). These workers showed that when molybdenum hexacarbonyl, $\text{Mo}(\text{CO})_6$, is cooled to -78° and then treated with chlorine, the molybdenum(II) complex, $\text{Mo}(\text{CO})_4\text{Cl}_2$, is formed (15). Treatment of this material, $\text{Mo}(\text{CO})_4\text{Cl}_2$, with phosphines gave complexes like the ones prepared by Nyholm and co-workers using a different route (10). The method was used to prepare the bromine analogue, $\text{Mo}(\text{CO})_4\text{Br}_2$, and similar tungsten complexes $\text{W}(\text{CO})_4\text{Cl}_2$ and $\text{W}(\text{CO})_4\text{Br}_2$ (16).

The halocarbonyl complexes, $\text{M}(\text{CO})_4\text{X}_2$ ($\text{M}=\text{Mo}, \text{W}$; $\text{X}=\text{Cl}, \text{Br}$) were found to be diamagnetic and on the basis of susceptibility measurements, it has been proposed that these complexes are dimeric (15) with halogen bridging as shown below.



These complexes were found to be thermally unstable. Thus, Schaefer and Holste have shown that when $\text{Mo}(\text{CO})_4\text{Cl}_2$ is heated to 100°C , it decomposes to give molybdenum(II) chloride whose composition was shown to be $\text{Mo}_6\text{Cl}_{12}$ (17). The complexes were also found to be highly reactive. By using them as the starting materials, a wide range of complexes has been prepared by many workers. Typical examples of these are given in Table 2.

TABLE 2

SOME COMPLEXES PREPARED USING $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$)

AS STARTING MATERIALS.

<u>REACTION</u>	<u>CONDITIONS</u>	<u>PRODUCTS</u>	<u>REF</u>
I $\text{Mo}(\text{CO})_4\text{Cl}_2 + 2\text{AsPh}_3$	Stoichiometric amounts in CH_2Cl_2 at room temperature	$\text{Mo}(\text{CO})_3(\text{AsPh}_3)_2\text{Cl}_2$	(15)
II $\text{Mo}(\text{CO})_4\text{Cl}_2 + 2\text{PPh}_2$	Stoichiometric amounts in CH_2Cl_2 at room temperature	$\text{Mo}(\text{CO})_3(\text{PPh}_2)_2\text{Cl}_2$	(15)
III $\text{Mo}(\text{CO})_4\text{Cl}_2 + \text{CH}_3\cdot\text{CN}$	ether solution at room temperature	$\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$	(18)

TABLE 2 (continued)

<u>REACTION</u>	<u>CONDITIONS</u>	<u>PRODUCTS</u>	<u>REF</u>
IV $\text{Mo}(\text{CO})_4\text{Br}_2 + \text{P}(\text{OCH}_3)_3$	ligand used as solvent at room temperature	$\text{Mo}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_3\text{Br}_2$	(19)
V $\text{Mo}(\text{CO})_4\text{Br}_2 + \text{HS}_2\text{PPh}_2$	methanol as solvent at room temperature	$\text{Mo}(\text{CO})_3(\text{S}_2\text{PPh}_2)_2$	(20)
VI $\text{Mo}(\text{CO})_4\text{Cl}_2 + \text{dmpe}$	THF as solvent at 0°	$\text{Mo}(\text{CO})_2(\text{dmpe})_2\text{Cl}_2$	(21)

Bonati and Menghetti showed that all CO groups in $\text{Mo}(\text{CO})_4\text{X}_2$ can be replaced by isocyanide ligands to form the products of the type $\text{Mo}(\text{CNR})_5\text{X}_2$ (22). This takes place when $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}$) is treated with excess isocyanide. The above examples show that substitution in $\text{Mo}(\text{CO})_4\text{X}_2$ occurs mostly with good π - bonding ligands.

A new aspect of the chemistry of molybdenum(II) was revealed by the work of Muriithi and Westland (18, 19). These workers showed that the halocarbonyl complexes $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}$) react with neat ligands

of poor π - bonding ability to give molybdenum(0) and molybdenum (III) complexes. This is, in fact, a disproportionation reaction in which molybdenum(II) disproportionates to molybdenum(0) and molybdenum (III) (18,19). The disproportionation reaction takes place as shown below.

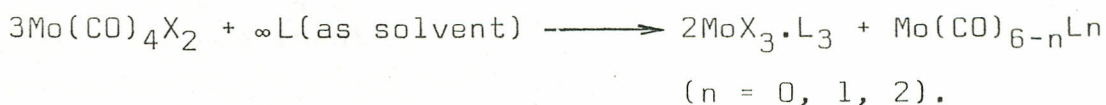


Table 3. gives a list of some molybdenum(III) complexes isolated using this reaction.

TABLE 3

SOME MOLYBDENUM(III) COMPLEXES ISOLATED AFTER
DISPROPORTIONATION OF MOLYBDENUM (II).

	<u>REACTANTS</u>	\longrightarrow	<u>MOLYBDENUM(III) PRODUCT</u>
I	$\text{Mo}(\text{CO})_4\text{Cl}_2 + \text{Ph} \cdot \text{CN}$ (neat)		$\text{MoCl}_3(\text{NC} \cdot \text{Ph})_3$
II	$\text{Mo}(\text{CO})_4\text{Cl}_2 + \text{CH}_3\text{CN}$ (neat)		$\text{MoCl}_3(\text{NCCH}_3)_3$
III	$\text{Mo}(\text{CO})_4\text{Cl}_2 + \text{CH}_3\text{CH}_2\text{CH}_2 \cdot \text{CN}$ (neat)		$\text{MoCl}_3(\text{NCCH}_2\text{CH}_2\text{CH}_3)_3$
IV	$\text{Mo}(\text{CO})_4\text{Br}_2 + (\text{CH}_3)_2\text{CH} \cdot \text{CN}$ (neat)		$\text{MoBr}_3[\text{NC} \cdot \text{CH}(\text{CH}_3)_2]_3$
V	$\text{Mo}(\text{CO})_4\text{Br}_2 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \cdot \text{CN}$ (neat)		$\text{MoBr}_3(\text{NC} \cdot \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$

Table 3 (continued)

<u>REACTANTS</u>	<u>MOLYBDENUM (III) PRODUCT</u>
VI $\text{Mo}(\text{CO})_4\text{Cl}_2 + \text{C}_5\text{H}_5\text{N} \longrightarrow$ (neat)	$\text{MoCl}_3(\text{C}_5\text{H}_5\text{N})_3$
VII $\text{Mo}(\text{CO})_4\text{Cl}_2 + \text{C}_4\text{H}_8\text{O} \longrightarrow$ (neat)	$\text{MoCl}_3(\text{C}_4\text{H}_8\text{O})_3$
VIII $\text{Mo}(\text{CO})_4\text{Br}_2 + \text{C}_4\text{H}_8\text{S} \longrightarrow$ (neat)	$\text{MoCl}_3(\text{C}_4\text{H}_8\text{S})_3$

In this work it is reported that $\text{Mo}(\text{CO})_4\text{Br}_2$ reacts with the secondary amine piperidine (\equiv PiP) to give the complex $\text{Mo}(\text{CO})_4(\text{PiP})_2$ as the main product (23). The reaction of tmen (N,N,N',N' - tetramethylethylenediamine \equiv tmen) with $\text{Mo}(\text{CO})_4\text{Cl}_2$ is reported to give $\text{Mo}(\text{CO})_4(\text{tmen})$ (23). The isolation of these products suggests strongly that the halocarbonyls, $\text{Mo}(\text{CO})_4\text{X}_2$ (X=Cl, Br) react with amines via a redox mechanism. No mechanistic studies were carried out during this work. Furthermore, McDonald et. al. (24) have reported that $\text{Mo}(\text{CO})_4\text{Cl}_2$ reacts with $\text{H}_2\text{S}_2\text{P}(\text{i-Pr})_2$ to give $\text{Mo}(\text{CO})_2\text{S}_2\text{P}(\text{i-Pr})_2$ in which molybdenum is in oxidation state +2. This reaction must be proceeding via a solvolytic mechanism. Recently, Ambrosius et. al. have reported that $\text{Mo}(\text{CO})_4\text{Cl}_2$ reacts with $\text{RNHC}(\text{S})\text{PPh}_2$ in dichloromethane in the presence of excess triethylamine,

Et_3N , to form $\text{Mo}(\text{CO})_2[\text{Ph}_2\text{PC}(\text{S})\text{NR}]_2$ which does not contain any halogen (25, 26). This reaction is interesting in that amines are reacting in the presence of dichloromethane whereas Nevstad et. al. have shown that dichloromethane reacts with amines forming the hydrogen chloride salt of the amine (27). In fact, during the course of this work, it was found that mixing piperidine with dichloromethane and leaving the mixture overnight, long colourless crystals formed. (see preparative section)

When the various literature reports mentioned above are taken into consideration, it is of interest to find out how molybdenum(II) halocarbonyls react with amines. The purpose of the present work was to carry out a systematic study of the reactions of alkyl amines with the halocarbonyls $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) with a view of discovering whether they undergo a solvolytic mechanism or a redox mechanism. This would help in gaining a better understanding of the chemistry of molybdenum(II).

CHAPTER 2EXPERIMENTAL TECHNIQUES

In this chapter, the following experimental techniques will be discussed.

- (a) Purification and handling of materials.
- (b) Details of making various physical measurements e.g. IR and NMR.
- (c) Analytical methods.

Procedures for preparation of specific compounds will be discussed in chapter 3.

A. HANDLING OF COMPOUNDS AND GLASSWARE CLEANING

(i) HANDLING OF COMPOUNDS

Unless otherwise specified, all preparations were carried out in an atmosphere of dry oxygen-free nitrogen.

(ii) ROUTINE GLASSWARE CLEANING

(a) Glassware with no grease:

The glassware was cleaned with liquid detergent and tap water. The glassware was then filled with chromic acid and kept thus overnight. The chromic

acid was removed and the glassware rinsed with tap water followed by distilled water. It was then dried at 130°C in an electric oven for at least two hours. Glassware like test tubes and adapters was put in a desiccator filled with chromic acid and then treated as above.

(b) Glassware with grease

The grease was washed off the joints with halogenated organic solvents like dichloromethane. The glassware was then filled with chromic acid and kept thus overnight. The filtering apparatus (Fig. 2) could not be filled with chromic acid in both chambers simultaneously. Instead, one chamber was filled with acid and the acid allowed to pass through the glass frit. This process was repeated with the second chamber. The apparatus was washed with tap water and rinsed with distilled water. It was then dried at 130°C for at least two hours in an electric oven.

(c) NMR tubes

These were rinsed with carbon tetrachloride and then washed with liquid detergent and tap water. They were later rinsed with distilled water and dried at 130°C in an electric oven.

(d) IR cells

These were washed with a suitable organic solvent e.g. acetone.

B. MATERIALS AND PURIFICATIONS(i) Molybdenum hexacarbonyl

The molybdenum hexacarbonyl was obtained from Aldrich Chemical Co. Ltd. (U.K.). The molybdenum hexacarbonyl was in all cases ground thoroughly using a mortar and pestle and dried over phosphorous pentoxide overnight in a desiccator.

(ii) Halogens(a) Chlorine

This was generated and dried using the set-up shown in figure 3. Analar grade materials were used.

(b) Bromine

Analar grade bromine from BDH Chemicals Ltd (England) was used without further purification.

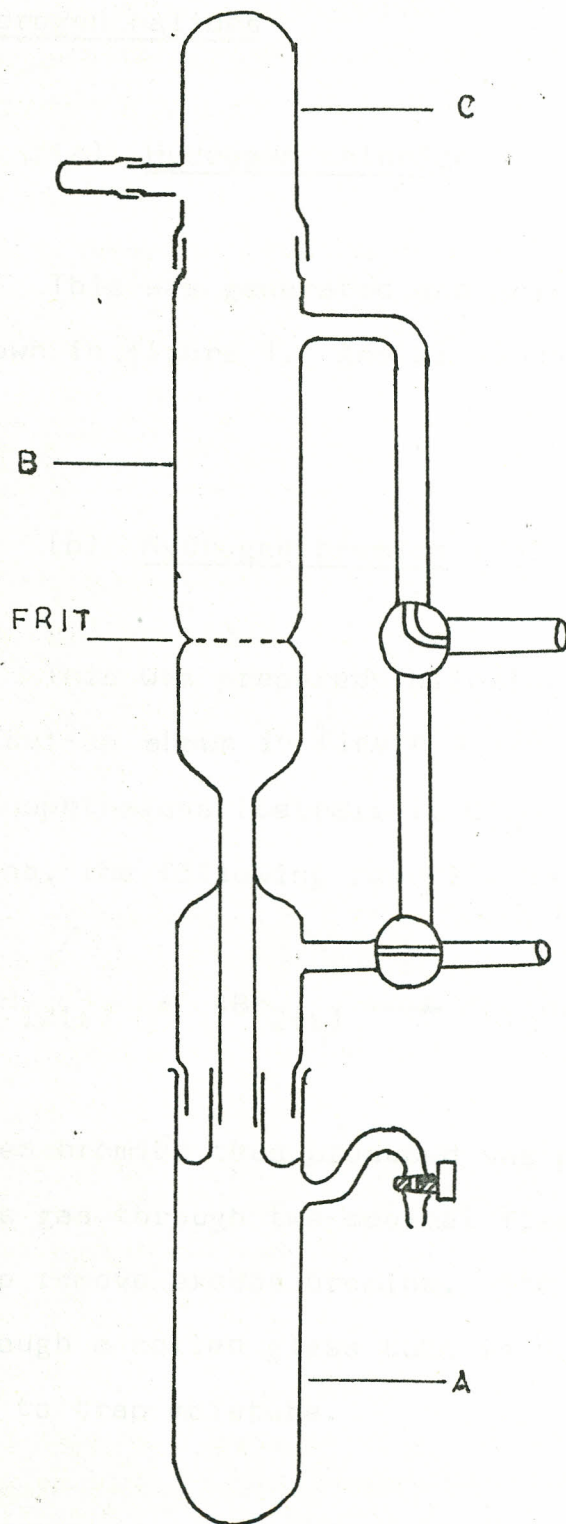


Fig. 2 Apparatus for filtration under nitrogen.

(iii) Hydrogen halides(a) Hydrogen chloride

This was generated and dried using the set-up shown in figure 4. Analar grade materials were used.

(b) Hydrogen bromide (28)

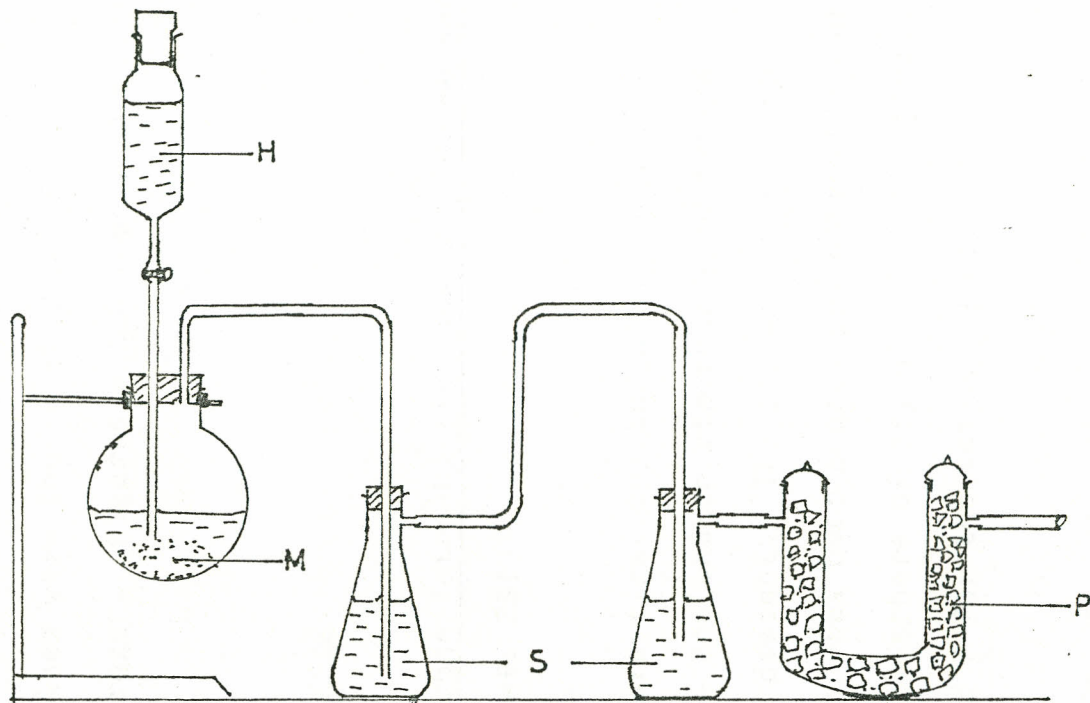
This was prepared following literature methods using the set-up shown in figure 5 (28). When tetrahydronaphthalene (tetralin), $C_{10}H_{12}$, is treated with bromine, the following reaction takes place:



The hydrogen bromide thus produced was purified by passing the gas through two conical flasks containing tetralin to remove excess bromine. The gas was finally passed through a coiled glass tube in dry-ice/acetone slush bath to trap moisture.

(iv) Amines

The amines were refluxed over calcium oxide



H = Concentrated hydrochloric acid

P = Phosphorus Pentoxide supported on pumice stones

M = Manganese(IV) Oxide

S = Concentrated sulphuric acid

Fig. 3 Apparatus for generating dry chlorine.

for 40 minutes in an atmosphere of dry oxygen-free nitrogen. The amines were then distilled in an atmosphere of nitrogen. Figures 6 and 7 show the set-up used.

(v) Organic solvents

(a) Carbon Tetrachloride and Dichloromethane

(Ref. 29)

These were first treated with anhydrous magnesium sulphate and shaken vigorously to remove most of the water present. The solvents were then refluxed for 40 minutes over phosphorus pentoxide and distilled in an atmosphere of dry oxygen-free nitrogen. (see figures 6 and 7 for the set-up used).

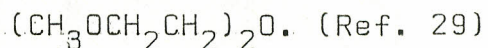
(b) n-Hexane and n-Pentane (Ref. 29)

About 200 ml of either n-hexane or n-pentane were treated with 5 ml. of analar grade concentrated sulphuric acid. This mixture was refluxed for 40 minutes and distilled in an atmosphere of dry oxygen-free nitrogen. The distillate collected was refluxed for 40 minutes over sodium metal and distilled in an atmosphere of dry oxygen-free nitrogen (see figures 6 and 7 for the set-up used).

(c) Tetrahydrofuran (T.H.F.) (Ref. 29)

The T.H.F. was first treated with anhydrous magnesium sulphate to remove the bulk of the water. This mixture was refluxed for 40 minutes over sodium metal and distilled in an atmosphere of dry oxygen-free nitrogen. (see figures 6 and 7 for the set-up used).

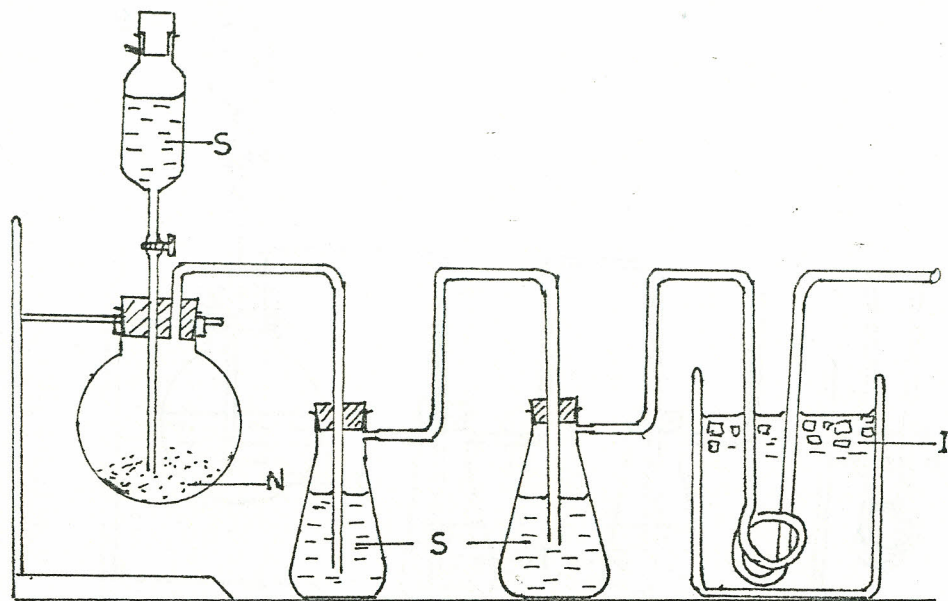
Note: Figures 6 and 7 all contain a rubber tubing and a glass tube dipped in toluene. The purpose of this set-up is to monitor the flow of nitrogen properly.

(d) Diethyleneglycoldimethylether (Diglyme)

The diglyme was treated with anhydrous magnesium sulphate to remove the bulk water. It was then refluxed for 40 minutes over sodium metal in an atmosphere of dry oxygen-free nitrogen. It was then distilled and collected using the set-up shown in figure 8.

(e) Ethanol (Ref. 29)

95% ethanol was refluxed for 20 hours over plenty of calcium oxide under an atmosphere of dry

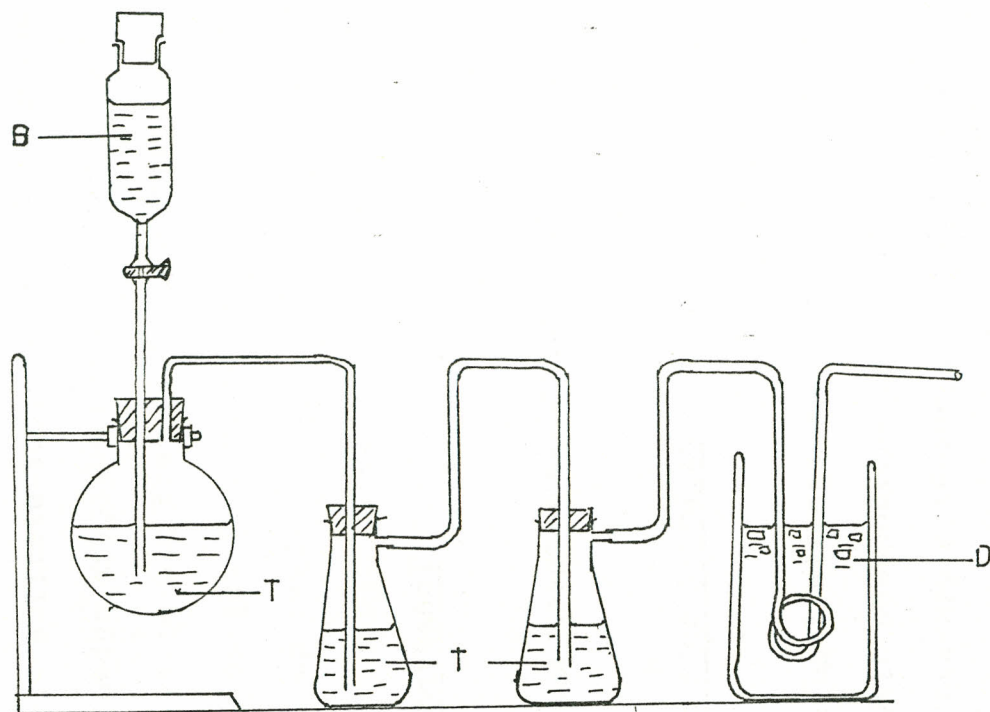


I = Dry-ice/Acetone mixture

S = Concentrated sulphuric acid

N = Sodium chloride

Fig. 4. Apparatus for generating dry hydrogen chloride.



B = Bromine

I = Dry-ice/Acetone mixture

T = Tetraline

Fig. 5. Apparatus for generating dry hydrogen bromide.

oxygen-free nitrogen. The refluxed ethanol was distilled under nitrogen and magnesium turnings added to the distillate. A little iodine was added and the mixture refluxed under dry oxygen-free nitrogen for 5 hours. This mixture was then distilled in an atmosphere of dry oxygen-free nitrogen (see figure 6 and 7 for the set-up used).

(f) Methanol

This was treated as ethanol above.

(vi) Dry-Oxygen free nitrogen

White spot nitrogen was passed through two columns packed with phosphorous pentoxide supported on dry pumice. The dry nitrogen was then bubbled through a solution of sodium naphthalide in diglyme to remove oxygen. See figure 9 for the set-up used.

(vii) Sodium Naphthalide solution

Sodium metal was dissolved in freshly distilled diglyme which had been treated with naphthalene crystals. All this was performed in an atmosphere of dry oxygen-free nitrogen. A dark green solution formed. The dark green solution gave a

whitish solid when exposed to air. This served as an indicator to show if air was leaking into the solution or when the solution had expired.

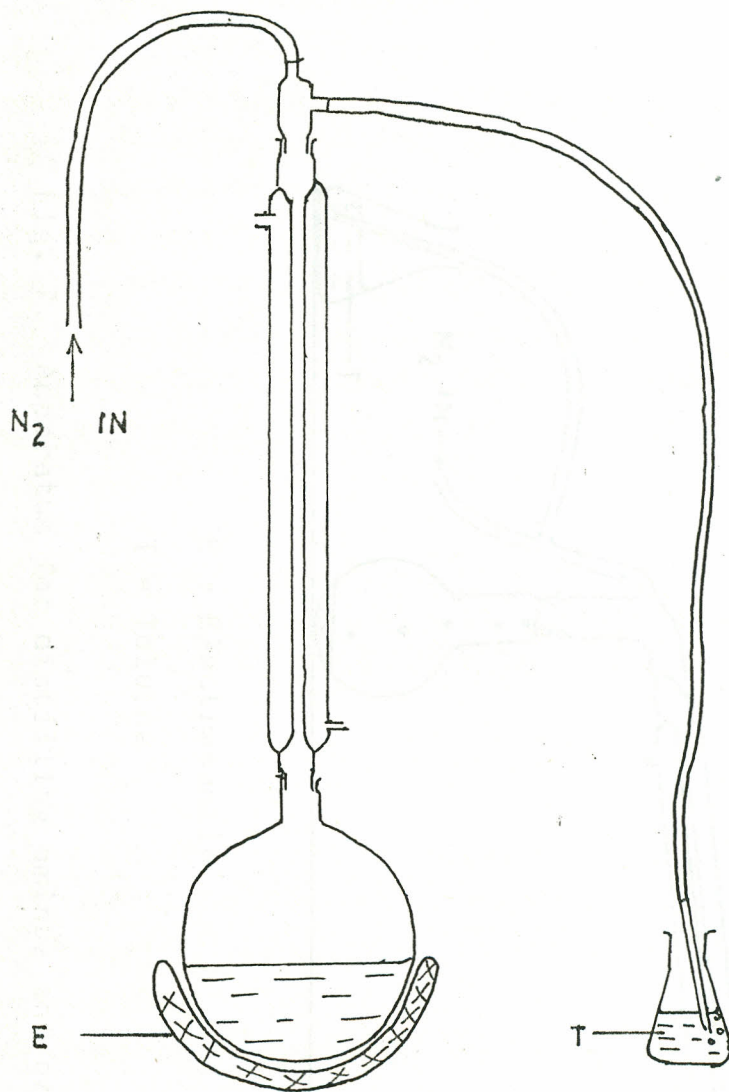
C. ANALYTICAL TECHNIQUES

(a) General

Carbon, hydrogen, nitrogen, chlorine and bromine were estimated by Butterworth Laboratories Ltd., Middlesex, U.K. Occasionally the halogens were determined by the present author following standard literature methods (30).

(b) Determination of Chloride and bromide using Silver nitrate solution (Ref. 30)

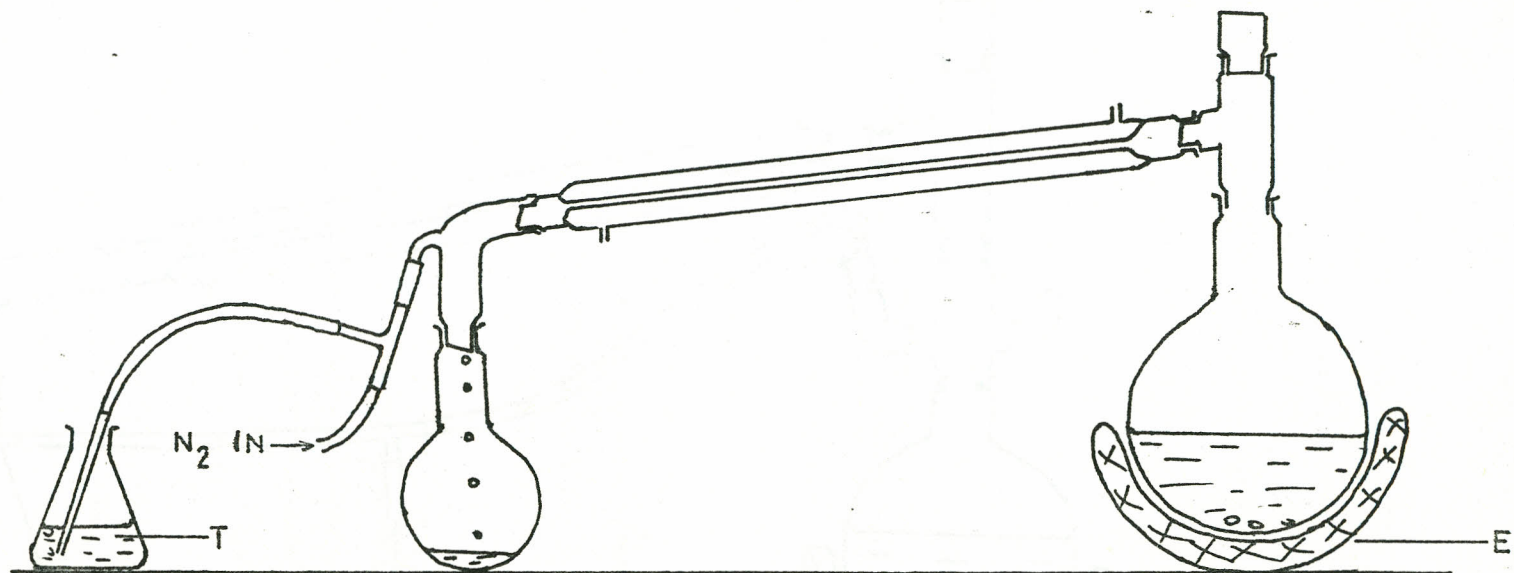
About 0.2 gm. of the sample were dissolved in 150 cm³ of distilled water in a 250 cm³ beaker. To this solution was added 25 cm³ of 1M sulphuric acid and the beaker wrapped with an aluminium foil. To this solution was added 0.1M AgNO₃ solution drop by drop with stirring until no more precipitate formed. The top of the beaker was covered with a watch glass and aluminium foil. The mixture was warmed until the supernatant liquid was clear. A few drops of AgNO₃ were added and when no turbidity was seen, the beaker was



E = Electromantle

T = Toluene

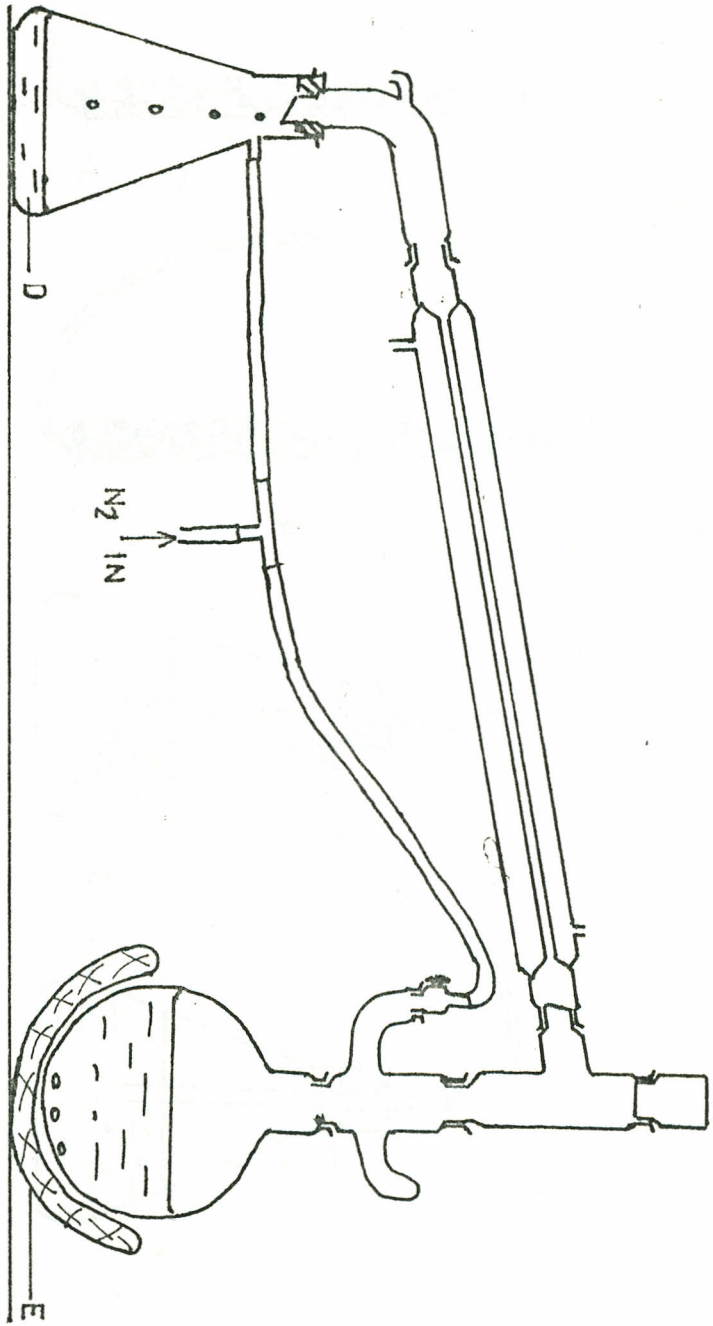
Fig. 6. Apparatus for refluxing under nitrogen.



E = Electromantle

T = Toluene

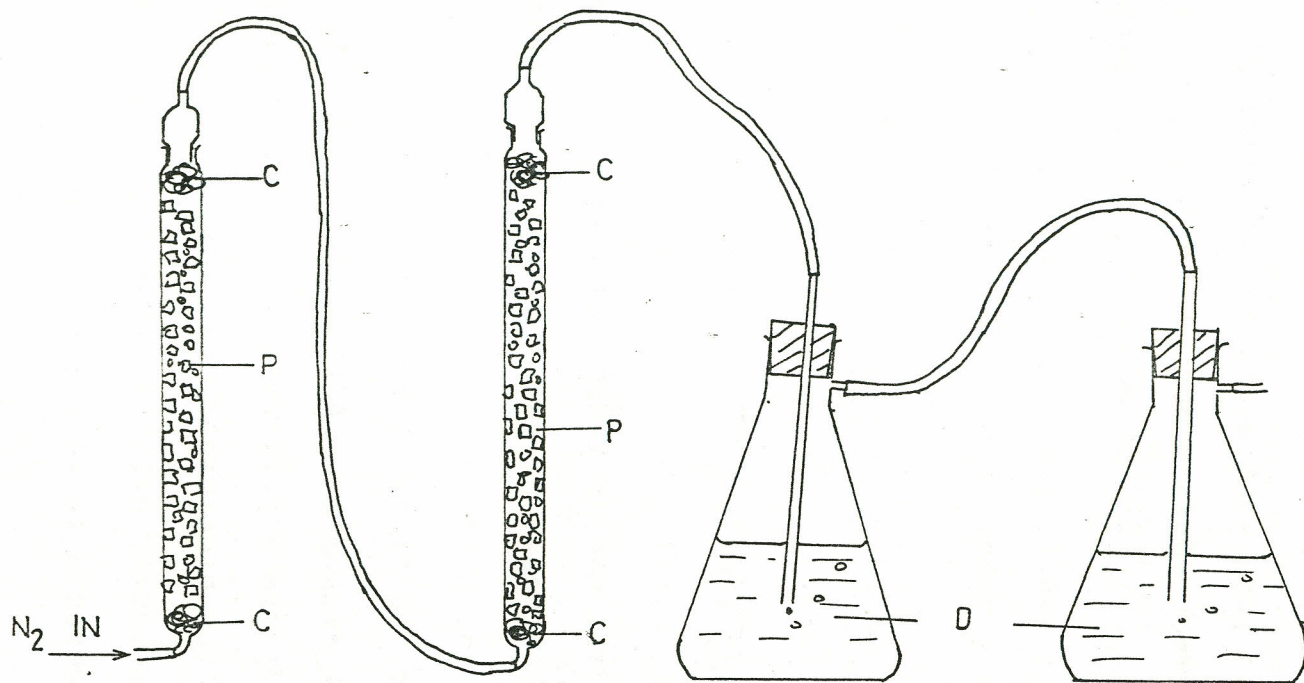
Fig. 7. Apparatus for distilling amines and organic solvents.



D = Diglyme

E = Electromantle

Fig. 8. Apparatus for distilling Diglyme.



C = Cotton wool

D = Sodium naphthalide in diglyme

P = Phosphorus Pentoxide supported on pumice stones

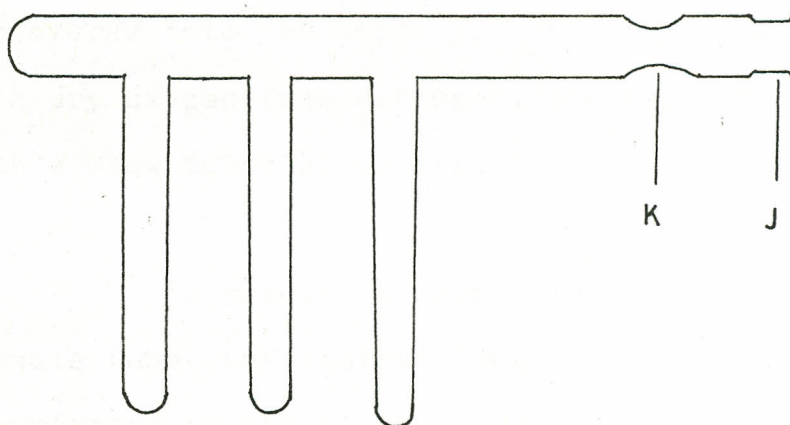
Fig. 9. Apparatus for purifying nitrogen.

Kept in a dark cupboard to cool for one hour. The precipitate was filtered using a pre-weighed sintered glass crucible. The precipitate was washed several times with very dilute nitric acid until the filtrate gave no turbidity with 0.1 M hydrochloric acid. The precipitate was dried at 140°C in an electric oven, cooled in a desiccator containing phosphorus pentoxide and weighed. The process of heating and cooling was repeated until there was no significant change in weight.

D. METHODS OF HANDLING AIR-SENSITIVE COMPOUNDS

1. Apparatus:

Figure 2 shows an apparatus described by Fritz et. al. (31) for filtration in an atmosphere of nitrogen. Essentially, the apparatus has three separate parts viz two Schlenk tubes A and C, and a middle part, B, provided with a fritted glass disc for filtration. Throughout the rest of this thesis, reference to the filtration apparatus will mean this apparatus (figure 2) whereas "Schlenk tube" will be used to mean a Schlenk tube such as A.



J = Joint 19/26

K = Constriction

Fig. 10. Ampoule for storing air-sensitive compounds.

2. Procedure:

Samples to be stored

With the sample in B (Fig. 2) and dry oxygen-free nitrogen flowing through the system, the ampoule (Figure 10) was fitted onto the filtration apparatus, the system evacuated and all the sample transferred into the ampoule. The system was filled with dry oxygen-free nitrogen, and the ampoule sealed with a blow torch at constriction K.

To recover a sample from the sealed storage ampoule tube, the desired amount of the substance was transferred to one of the side tubes. The other tubes were put in Dewar Flask containing dry-ice/acetone mixture and the tube with the desired amount of the sample was cut off from the rest with a blow torch. The sample was used for elemental analysis or physical measurements.

E. PHYSICAL MEASUREMENTS

1. Infrared Spectra

(a) Instrumentation:

Infrared spectra were recorded on a Perkin-Elmer Model 598 Spectrophotometer which has the

range 4000 cm^{-1} to 200 cm^{-1} .

(b) Procedure:

(i) Solid Samples:

The spectra were recorded using pellets made using either potassium bromide or cesium bromide as supports.

(ii) Liquid Samples:

Samples were dissolved in suitable organic solvents and the solutions put in solution cells.

2. Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance spectra were recorded on either a Perkin-Elmer Model 12B Nuclear Magnetic Resonance Spectrometer or JEOL FX - 100 NMR Spectrometer. Tetramethylsilane (TMS) was used as the internal reference.

CHAPTER 3
PREPARATIVE WORK

INTRODUCTION:

In this chapter, the preparation of the molybdenum (II) complexes, $\text{Mo}(\text{CO})_4\text{X}_2$, ($\text{X} = \text{Cl}, \text{Br}$) is given. The reactions of these halocarbonyls with various alkyl amines under different reaction conditions are also described. The various reactions are indicated with numerals. Thus, the first reaction is 3.1, the second reaction is 3.2 and so on. All preparative work was carried out in an atmosphere of dry oxygen-free nitrogen.

3.1 Preparation of dibromotetracarbonylmolybdenum (II),
 $\text{Mo}(\text{CO})_4\text{Br}_2$. (Ref. 16, 23)

Apparatus:

A modified Schlenk tube, illustrated in figure 11, was used. The contents were stirred with a 1 cm piece of iron nail sealed in a glass tube.

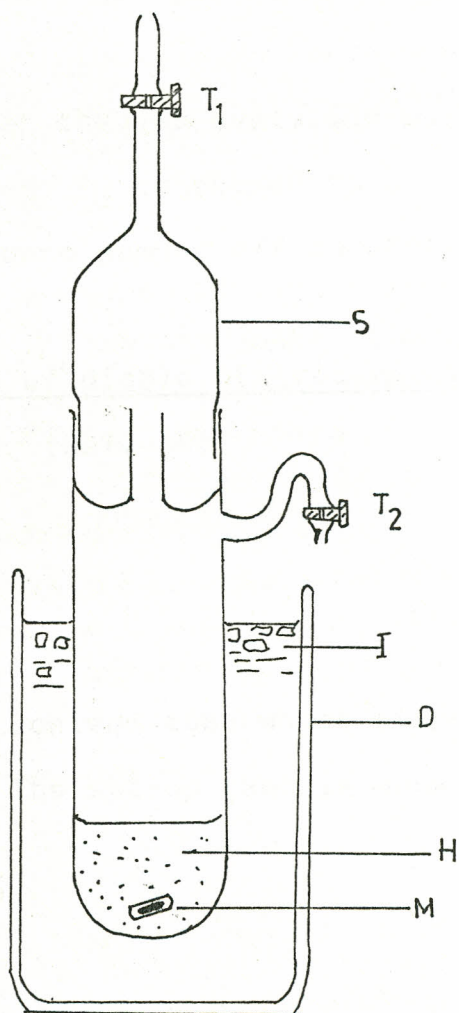
Procedure:

The Schlenk tube was dried at 120° for one hour then cooled by flushing it with dry oxygen-free nitrogen through stopcock T_2 . The joints of the cool Schlenk tube and stopper S. were lightly greased with silicon

grease.

As nitrogen was passing through the system, a suitable quantity (e.g. 3 - 8 gm) of pulverized molybdenum hexacarbonyl, $\text{Mo}(\text{CO})_6$, which had been dried over phosphorus pentoxide, P_2O_5 , in a desiccator were accurately weighed and put into the Schlenk tube. About 30 cm^3 of dry freshly distilled dichloromethane were added. A bar magnet was put in the Schlenk tube and stopper S replaced and the mixture stirred. Stopcocks T_2 and T_1 were closed, the nitrogen flow quickly closed, and the mixture pumped off by opening stopcock T_1 when the system was connected to a vacuum. The evacuating was done only for a few seconds. Stopcock T_1 was closed and stopcock T_2 opened to fill the tube with dry oxygen-free nitrogen. The Schlenk tube was placed in a dry-ice/acetone slush bath and cooled for about 30 minutes.

The calculated amount of bromine was accurately measured with an all plastic syringe and dissolved in about 10 cm^3 of dry freshly distilled dichloromethane. The bromine solution was added onto the cold suspension of the hexacarbonyl, $\text{Mo}(\text{CO})_6$, while dry oxygen-free nitrogen was being passed through stopcock T_2 . The stopper S was quickly replaced and the Schlenk tube removed from the dry-ice/acetone slush bath. The mixture was stirred vigorously as the tube was allowed to warm-up



D = Dewar flask

H = $\text{Mo}(\text{CO})_6/\text{CH}_2\text{Cl}_2$

I = Dry-ice/Acetone

M = Magnetic bar

Fig. 11. Apparatus for the preparation of $\text{Mo}(\text{CO})_4\text{Br}_2$.

slowly. A vigorous reaction took place with evolution of a colourless gas giving an orange product, $\text{Mo}(\text{CO})_4\text{Br}_2$.

When the gas evolution was complete, stopcock T_2 was closed, T_1 connected to a vacuum pump and dichloromethane pumped off completely.

3.2 Preparation of dichlorotetracarbonylmolybdenum (II),

$\text{Mo}(\text{CO})_4\text{Cl}_2$. (Ref. 15)

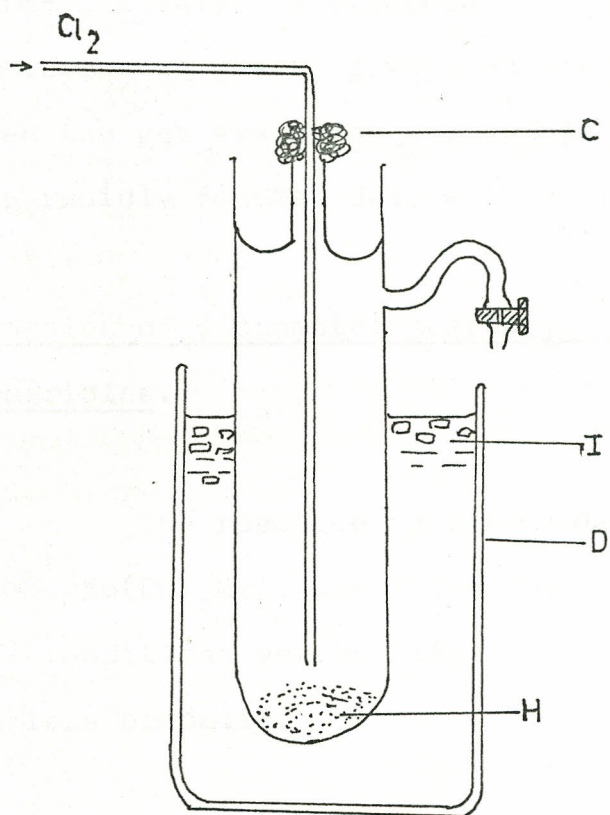
Apparatus:

A Schlenk tube whose stopper had been removed was used. The set-up used is shown in figure 12.

Procedure:

A suitable quantity (e.g. 3 - 7 gm) of pulverized molybdenum hexacarbonyl, $\text{Mo}(\text{CO})_6$, which had been dried over phosphorus pentoxide, P_2O_5 , in a desiccator was accurately weighed and put in a clean dry Schlenk tube and thoroughly flushed with dry oxygen-free nitrogen.

The Schlenk tube was then cooled in dry-ice/acetone slush bath for about 30 minutes as nitrogen flowed through the system. Purified chlorine gas was



C = Cotton wool

D = Dewar flask

H = Molybdenum hexacarbonyl

I = Dry-ice/Acetone

Fig. 12. Apparatus for the preparation of $\text{Mo}(\text{CO})_4\text{Cl}_2$.

condensed on the hexacarbonyl until excess liquid chlorine was visible. The Schlenk tube was removed from the dry-ice/acetone slush bath and allowed to warm-up slowly. A vigorous reaction took place with evolution of gas to give a yellow product, $\text{Mo(CO)}_4\text{Cl}_2$. When the gas evolution was complete, excess chlorine was rapidly flushed away with nitrogen.

3.3 Reaction of dibromotetracarbonylmolybdenum (II) with Piperidine.

The reaction of dibromotetracarbonylmolybdenum(II), $\text{Mo(CO)}_4\text{Br}_2$, with piperidine was carried out and the conditions varied slightly in order to isolate the various products.

(a) Procedure for isolation of the zerovalent Molybdenum complex, $\text{Mo(CO)}_4(\text{C}_5\text{H}_{10}\text{N})_2$.

(i) Using neat Piperidine as solvent

About 4 gm of molybdenum hexacarbonyl were used to prepare the molybdenum halocarbonyl as described in 3.1. As nitrogen flowed through the system, 30 cm³ of dry freshly distilled piperidine were added onto $\text{Mo(CO)}_4\text{Br}_2$, and the mixture stirred vigorously. A vigorous reaction took place with evolution of a lot of heat. As the orange solid, $\text{Mo(CO)}_4\text{Br}_2$, dissolved, a

a dark orange solution formed which turned dark yellow later. This reaction mixture was stirred overnight under nitrogen to ensure completion of the reaction. The yellowish solid precipitated was recovered by filtration under nitrogen. The solid was washed twice with dichloromethane, then several times with distilled water. Finally, it was washed several times with ether and dried in vacuo. A bright yellow solid was left. Elemental analysis showed that the product was tetracarbonylbis(piperidine)molybdenum(O), $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$.

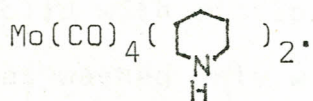
	C	H	N	Br
Found	43.96	5.75	7.27	0.38 %
$\text{C}_{14}\text{H}_{22}\text{MoN}_2\text{O}_4$ req.	44.45	5.86	7.41	0.00 %

As the product was not recrystallized, the bromine present is believed to be an impurity.

(ii) Using Piperidine dissolved in
Tetrahydrofuran (T.H.F.)

About 5 gm of molybdenum hexacarbonyl were used to prepare the halocarbonyl, $\text{Mo}(\text{CO})_4\text{Br}_2$. The orange solid, $\text{Mo}(\text{CO})_4\text{Br}_2$, was cooled for about 10 minutes in dry-ice/acetone slush bath. About 6.65 cm³ of dry, freshly distilled piperidine dissolved in dry, freshly distilled T.H.F. were cooled in dry-ice/acetone mixture.

The cold piperidine/T.H.F. mixture was added onto the cold molybdenum halocarbonyl, $\text{Mo}(\text{CO})_4\text{Br}_2$. The solid dissolved forming a dark yellowish solution. This solution was stirred overnight under nitrogen. A yellow solid was precipitated and it was recovered by filtration under nitrogen. This solid was washed several times with distilled water and the water washings kept in order to isolate the halogen-containing product. The bright yellow solid left was washed several times with acetone and dried in vacuo. Elemental analysis showed that the product was the zerovalent molybdenum complex, tetracarbonylbis(piperidine)molybdenum (0),

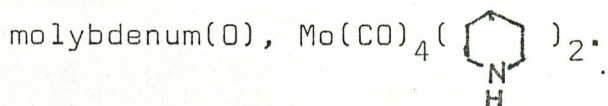


	C	H	N	Br
Found	43.04	5.74	7.21	0.24 %
$\text{C}_{14}\text{H}_{22}\text{MoN}_2\text{O}_4$ req.	44.45	5.86	7.41	0.00 %

The bromine present is an impurity.

(iii) Using Piperidine dissolved in methanol.

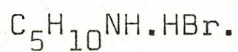
The reaction of $\text{Mo}(\text{CO})_4\text{Br}_2$ with piperidine described in 3.3(a) (ii) above was repeated using methanol as the solvent. A bright yellow solid was recovered. Elemental analysis of the yellow solid showed that the product was tetracarbonylbis(piperidine)



	C	H	N	Br
Found	43.85	5.90	7.11	0.13 %
$C_{14}H_{22}MoN_2O_4$ req.	44.45	5.86	7.41	0.00 %

The present bromine is from an impurity.

(b) Procedure for the isolation of the amine salt,



(i) Using neat piperidine as solvent.

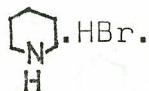
The reaction of $Mo(CO)_4Br_2$ with piperidine described in 3.3 (a) (i) above was repeated with the following modification. Instead of washing the yellow solid with dichloromethane and distilled water, it was washed only with 95% ethanol. The ethanol washings were passed through a silica gel column and eluted with acetone. The first portions were yellowish and had no halogen. The middle colourless portions which showed the presence of halogen were heated in a water bath to remove excess acetone. Long colourless crystals were formed. The crystals were washed several times with acetone and dried at $120^{\circ}C$. Elemental analysis showed that the product was the amine salt, $C_5H_{10}NH.HBr.$

	C	H	N	Br	
Found	35.98	7.32	8.57	48.44	%
$C_5H_{12}BrN$ req.	36.16	7.28	8.43	48.11	%

The melting point and IR Spectrum of this product were identical to those of the synthetic salt prepared by bubbling hydrogen bromide gas through piperidine and recrystallizing the product from methanol.

(ii) Using Piperidine dissolved in
Tetrahydrofuran (T.H.F.)

The water washings of the yellow solid isolated in reaction 3.3 (a) (ii) above were evaporated to dryness. The long colourless crystals formed were dissolved in 95% ethanol and the solution boiled with powdered charcoal. The solution was filtered and precipitated with ether. The white crystalline solid precipitated was washed several times with ether and dried at 120°C. Elemental analysis showed that the product was the amine salt,



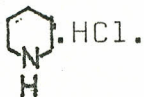
	C	H	N	Br	
Found	35.47	7.23	7.97	48.56	%
$C_5H_{12}Br_2N$ req.	36.16	7.28	8.43	48.11	%

(c) Procedure for isolation of the Piperidine Product

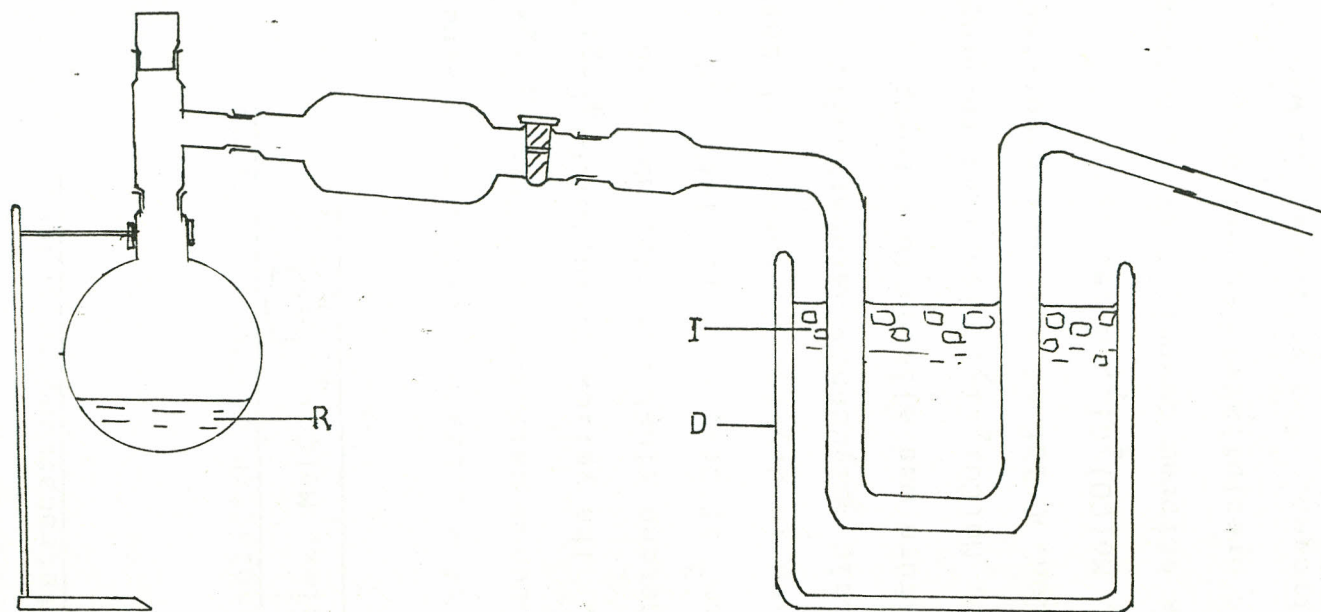
The reaction of $\text{Mo(CO)}_4\text{Br}_2$ with piperidine described in 3.3 (a) (i) above was repeated using about 22 gm of molybdenum hexacarbonyl and 40 cm³ of piperidine. The reaction mixture which had turned into a solid was vacuum distilled using the set-up shown in figure 13. A colourless basic distillate was collected. The NMR Spectrum of this distillate showed a peak at $\delta=6.1$ which was absent in the NMR Spectrum of piperidine. (see chapter 4 for details). This peak is in the olefinic region.

NOTE:

During these preparations, dichloromethane was pumped off completely from the complex, $\text{Mo(CO)}_4\text{Br}_2$. This was necessary since it was found that mixing piperidine with dichloromethane and leaving the mixture overnight produced long colourless crystals. Elemental analysis of these crystals showed that the product was the amine salt,



	C	H	N	Cl
Found	49.10	9.85	11.27	28.71 %
$\text{C}_5\text{H}_{12}\text{ClN}$ req.	49.38	9.95	11.52	29.15 %



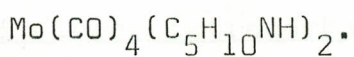
D = Dewar flask
I = Dry-ice/Acetone
R = Reaction mixture

Fig. 13. Apparatus for vacuum distillation.

3.4 Reaction of dichlorotetracarbonylmolybdenum (II)
with neat Piperidine

(a) Procedure for isolation of the Zerovalent
Molybdenum Complex, $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{N})_2$

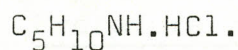
About 4 gm of molybdenum hexacarbonyl were used to prepare the molybdenum halocarbonyl, $\text{Mo}(\text{CO})_4\text{Cl}_2$, as described in 3.2. The yellow solid, $\text{Mo}(\text{CO})_4\text{Cl}_2$, was cooled in dry-ice/acetone slush bath for about 10 minutes. About 30 cm³ of dry, freshly distilled piperidine were cooled in dry-ice/acetone slush bath and added onto the cold molybdenum halocarbonyl, $\text{Mo}(\text{CO})_4\text{Cl}_2$. The mixture was allowed to warm-up slowly and the solid, $\text{Mo}(\text{CO})_4\text{Cl}_2$, dissolved forming a dark yellow solution. A lot of heat was generated as the yellow solid, $\text{Mo}(\text{CO})_4\text{Cl}_2$, dissolved. The reaction mixture was stirred overnight under nitrogen and the yellow solid precipitated recovered by filtration under nitrogen. The yellow solid was washed several times with methanol and the methanol washings kept in order to recover the halogen containing product. The bright yellow solid left was washed several times with petroleum spirit (b.p. 40 - 60°) and dried in vacuo. Elemental analysis of the bright yellow solid showed that the product was tetracarbonylbis(piperidine)molybdenum(0),



	C	H	N	Cl	
Found	45.00	5.5	7.45	0.02	%
$\text{C}_{14}\text{H}_{22}\text{MoN}_2\text{O}_4$ req.	44.45	5.86	7.41	0.00	%

The chlorine present is an impurity.

(b) Procedure for isolation of amine salt,



The volume of the methanol washings of the yellow solid in 3.4 (a) was reduced by evaporation. The methanol washings were then kept in a conical flask and allowed to evaporate slowly. After one week, long colourless crystals were formed. These were washed several times with petroleum ether and recrystallized from methanol. Elemental analysis showed that the product was the amine salt, $\text{C}_5\text{H}_{10}\text{NH.HCl}$.

	C	H	N	Cl	
Found	49.58	10.01	11.63	28.65	%
$\text{C}_5\text{H}_{12}\text{ClN}$ req.	49.38	9.95	11.52	29.15	%

The melting point and IR Spectrum of this sample were identical to those of the synthetic salt prepared by bubbling hydrogen chloride gas through piperidine dissolved in petroleum ether (b.p. 40 - 60°) and recrystallizing the product from methanol.

3.5 Reaction of dibromotetracarbonylmolybdenum(II)
with butylamine.

The reaction of the halocarbonyl, $\text{Mo}(\text{CO})_4\text{Br}_2$, and butylamine was carried out and the conditions varied slightly in order to isolate the various products.

(a) Procedure for isolation of the zerovalent molybdenum complex, $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3$

(i) Using neat butylamine as solvent

About 5 gm of molybdenum hexacarbonyl were used to prepare the halocarbonyl, $\text{Mo}(\text{CO})_4\text{Br}_2$, as described in 3.1. About 35 cm³ of dry, freshly distilled butylamine were cooled in dry-ice/acetone mixture for 10 minutes and then added onto the cold solid, $\text{Mo}(\text{CO})_4\text{Br}_2$. The reaction mixture was allowed to warm-up slowly. As the solid dissolved, the Schlenk tube became quite warm and a dark yellow solution formed. The reaction mixture was stirred overnight under nitrogen. The volume of the reaction mixture was reduced by pumping off excess amine. Onto the dark yellow solution left was added 70 cm³ of petroleum spirit (b.p. 40-60°) and the mixture stirred overnight under nitrogen. A lot of pale yellow solid was formed and it was recovered by filtration under nitrogen. This solid was washed several times

with butylamine. Finally it was washed several times with petroleum spirit (b.p 40 - 60^o) and dried in vacuo. Elemental analysis showed that the product was the zerovalent molybdenum complex, tris(butylamine)tricarbonylmolybdenum(0), $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3$.

	C	H	N	Br
Found	44.99	8.33	10.46	0.24 %
$\text{C}_{15}\text{H}_{33}\text{MoN}_3\text{O}_3$ req.	45.11	8.33	10.52	0.00 %

The small amount of bromine present must be an impurity.

(ii) Using butylamine dissolved in methanol

The reaction of the halocarbonyl complex, $\text{Mo}(\text{CO})_4\text{Br}_2$, with butylamine dissolved in methanol was carried out following the procedure described in 3.3 (a) (iii). About 4.7 gm of molybdenum hexacarbonyl were used to prepare the complex, $\text{Mo}(\text{CO})_4\text{Br}_2$. About 10 cm³ of dry, freshly distilled butylamine were dissolved in 20 cm³ of dry, freshly distilled methanol.

The pale yellow solid precipitated was recovered by filtration under nitrogen. The solid was washed several times with methanol and dried in vacuo.

Elemental analysis showed that the product was the zerovalent complex, tris(butylamine)tricarbonylmolybdenum(0), $\text{Mo}(\text{CO})_3(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3$.

	C	H	N	Br
Found	44.8	8.23	10.34	0.16 %
$\text{C}_{15}\text{H}_{33}\text{MoN}_3\text{O}_3$ req.	45.11	8.33	10.52	0.00 %

This product was not recrystallized, hence the bromine present is from an impurity.

(b) Procedure for isolation of the butylamine product.

The reaction of the halocarbonyl, $\text{Mo}(\text{CO})_4\text{Br}_2$, with neat butylamine described in 3.5 (a) (i) was repeated using about 21 gm of molybdenum hexacarbonyl and 50 cm³ of butylamine. The reaction mixture was vacuum distilled using the set-up shown in figure 13. A colourless basic distillate was collected. The NMR spectrum of this distillate had two peaks one at $\delta = 5.8$ and the other at $\delta = 5.3$ which are not present in the NMR spectrum of butylamine. (see chapter 4 for details). These peaks are in the olefinic region.

3.6 Reaction of dichlorotetracarbonylmolybdenum(II),
Mo(CO)₄Cl₂, with neat butylamine

About 7.4 gm of molybdenum hexacarbonyl were used to prepare the halocarbonyl, Mo(CO)₄Cl₂, as described in 3.2. Onto the yellow solid, Mo(CO)₄Cl₂, was added 25 cm³ of dry, freshly distilled butylamine that had been cooled in dry-ice/acetone slush bath. On allowing the mixture to warm-up slowly, the yellow solid dissolved with generation of heat and formed a dark yellow solution. The reaction mixture was stirred overnight under nitrogen and the pale yellow solid recovered as in 3.5 (a) (i). Elemental analysis of this solid showed that the product was the zerovalent molybdenum complex, tris(butylamine)tricarbonylmolybdenum(0), Mo(CO)₃(CH₃CH₂CH₂CH₂.NH₂)₃.

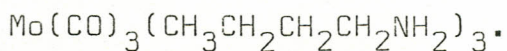
	C	H	N	Cl
Found	44.64	8.06	9.86	0.13 %
C ₁₅ H ₃₃ MoN ₃ O ₃ req.	45.11	8.33	10.52	0.00 %

The present chlorine must be from an impurity.

3.7 Reaction of dibromotetracarbonylmolybdenum(II),
 $\text{Mo(CO)}_4\text{Br}_2$, with propylamine

The reaction of the halocarbonyl, $\text{Mo(CO)}_4\text{Br}_2$, with propylamine was carried out and the conditions varied slightly in order to isolate the various products.

(a) Procedure for isolation of the zerovalent complex



The procedure followed for the reaction of the halocarbonyl, $\text{Mo(CO)}_4\text{Br}_2$, with propylamine is as described in 3.5 (a) (i). About 1.5 gm of molybdenum halocarbonyl, $\text{Mo(CO)}_4\text{Br}_2$, and about 20 cm³ of dry, freshly distilled propylamine were used. Elemental analysis of the pale yellow solid recovered showed that the product was the zerovalent molybdenum complex, tricarbonyltris(propylamine)molybdenum(0), $\text{Mo(CO)}_3(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_3$.

	C	H	N	Br
Found	39.57	7.94	11.54	0.25 %
$\text{C}_{12}\text{H}_{27}\text{MoN}_3\text{O}_3$ req.	40.34	7.62	11.76	0.00 %

Since the product was not recrystallized, the bromine present must be from an impurity.

(b) Procedure for isolation of the propylamine product

The reaction of, $\text{Mo}(\text{CO})_4\text{Br}_2$, with propylamine described in 3.7 (a) above was repeated with the following modifications. About 5.3 gm of molybdenum hexacarbonyl, $\text{Mo}(\text{CO})_6$, were used to prepare the halocarbonyl $\text{Mo}(\text{CO})_4\text{Br}_2$. About 40 cm³ of dry, freshly distilled propylamine were used.

The reaction mixture was vacuum-distilled using the set-up shown in figure 13. A colourless basic distillate was collected whose NMR spectrum had a peak at $\delta = 5.3$ which was absent in the NMR spectrum of propylamine (see chapter 4 for details). This peak is in the olefinic region.

3.8 Reaction of dichlorotetracarbonylmolybdenum(II) with neat propylamine

The procedure followed for the reaction of the halocarbonyl, $\text{Mo}(\text{CO})_4\text{Cl}_2$, with propylamine is as described in 3.6 above. About 6.7 gm of molybdenum hexacarbonyl, $\text{Mo}(\text{CO})_6$, were used to prepare the halocarbonyl, $\text{Mo}(\text{CO})_4\text{Cl}_2$. About 25 cm³ of dry, freshly distilled propylamine were used.

(a) Procedure for the isolation of the zerovalent Molybdenum complex, $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_3$.

The pale yellow solid was recovered as described in section 3.5 (a) (i). The propylamine washings were kept in order to recover the halogen-containing product. Elemental analysis of the pale yellow solid recovered showed that the product was the zerovalent molybdenum complex, tricarbonyltris(propylamine)molybdenum(0), $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_3$.

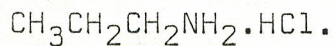
	C	H	N	Cl
Found	39.37	7.11	10.95	0.27 %
$\text{C}_{12}\text{H}_{27}\text{MoN}_3\text{O}_3$ req.	40.34	7.62	11.76	0.00 %

The chlorine is believed to be an impurity.

(b) Procedure for isolation of amine salt, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \cdot \text{HCl}$.

The propylamine washings were kept in a beaker and allowed to evaporate slowly. After three weeks, long colourless crystals were formed. They were filtered, washed with petroleum spirit and recrystallized from methanol. Elemental analysis

showed that the product was the amine salt



	C	H	N	Cl
Found	37.80	10.66	14.52	37.24 %
$\text{C}_3\text{H}_{10}\text{ClN}$ req.	38.10	10.51	14.81	37.49 %

The melting point and IR spectrum of this sample were identical to those of the synthetic salt prepared by bubbling hydrogen chloride gas through propylamine dissolved in petroleum ether (b.p. 40 - 60^o) and recrystallizing the product from methanol.

CHAPTER 4RESULTS AND DISCUSSIONI PREPARATIVEA. The reaction of $\text{Mo}(\text{CO})_4\text{X}_2$ (X = Cl, Br)
with Piperidine (23)

When the halocarbonyls, $\text{Mo}(\text{CO})_4\text{X}_2$ (X = Cl, Br) were treated with neat piperidine, the following products were isolated:

- (a) Tetracarbonylbis(piperidine)molybdenum(0),
 $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$.
- (b) A basic distillate whose NMR spectrum showed presence of olefinic protons.
- (c) The amine salts, $\text{C}_5\text{H}_{10}\text{NH}\cdot\text{HX}$ (X = Cl, Br).

A brief discussion of each of these products and the possible mechanism by which the product may be formed are given below.

(a) Tetracarbonylbis(Piperidine)molybdenum(0).

This product was isolated when the halocarbonyls $\text{Mo}(\text{CO})_4\text{X}_2$ (X = Cl, Br) were treated

with excess piperidine under the following conditions:

- (i) when the ligand was used neat.
- (ii) when the ligand was dissolved in methanol and cooled to -78°C .
- (iii) when the ligand was dissolved in tetrahydrofuran and cooled to -78°C .

(i) Use of the neat ligand

This procedure is as described by Muriithi et. al. (23) and repeated preparations showed that $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$ is indeed the main product. This was confirmed by elemental analysis and infrared data of the complex. The halocarbonyls $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) react with neat non π -bonding ligands such as nitriles to give molybdenum (III) and molybdenum(0) complexes via a disproportionation mechanism (18,19). The molybdenum(0) complex $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$, isolated in this case cannot be via such a mechanism since there was no evidence of molybdenum (III) species.

(ii) Use of methanol as a solvent

Chou et. al. have reported that when $\text{Mo}(\text{CO})_4\text{Br}_2$ is dissolved in methanol and treated with HS_2PPh_2 , a solvolytic reaction takes place giving $\text{Mo}(\text{CO})_3(\text{S}_2\text{PPh}_2)_2$ (20). During the present work, it was found that when $\text{Mo}(\text{CO})_4\text{Br}_2$ was dissolved in methanol which had been cooled to -78°C and a solution of piperidine in methanol added, the product isolated was $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$. This result is identical to the one got when $\text{Mo}(\text{CO})_4\text{Br}_2$ is treated with neat piperidine. It is also worth noting that there was no evidence of any molybdenum (III) species.

(iii) Use of Tetrahydrofuran as a solvent.

The piperidine was dissolved in T.H.F. and the mixture cooled to -78°C before adding to the solid, $\text{Mo}(\text{CO})_4\text{Br}_2$. The cooling of the piperidine/T.H.F. mixture was necessary since it is known that at room temperature, T.H.F. reacts with $\text{Mo}(\text{CO})_4\text{Br}_2$ via a disproportionation mechanism (18). Furthermore, it is known that at 0°C , the disproportionation reaction does not take place (21). When the reaction was carried

out under these conditions, the major product was $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$.

CONCLUSIONS DRAWN FROM SECTION (a)

In all the three cases discussed, there was no evidence of either molybdenum (III) species or $(\text{C}_5\text{H}_{10}\text{N})_2\text{Mo}(\text{CO})_4$. The molybdenum (III) species would suggest a disproportionation mechanism whereas presence of $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{N})_2$ suggests a solvolytic mechanism. The isolation of $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$ as the only molybdenum complex (if there were others at all, these were not detected) suggests very strongly that the halocarbonyls $\text{Mo}(\text{CO})_4\text{X}_2$ react with piperidine via a redox mechanism. It is therefore necessary to find out what piperidine is converted to when molybdenum (II) in $\text{Mo}(\text{CO})_4\text{X}_2$ is reduced to molybdenum (0).

(b) The Oxidation Product of Piperidine during oxidation by molybdenum (II).

There were two main problems in trying to isolate the oxidation product of piperidine.

- (i) The oxidized amine (enamine) produced was in very small quantities compared to the parent amine.
- (ii) Enamines are extremely unstable at room temperature and usually polymerize (32, 33, 34, 35).

It is probably because of these reasons that attempts to isolate some pure products by column chromatography were unsuccessful. A comparison of NMR spectra of the starting amine and the distillate from the reaction mixture of $\text{Mo}(\text{CO})_4\text{Br}_2$ with piperidine showed very clearly, however, that the reaction mixture contained a product with olefinic protons. The NMR data are summarized in Table 4.

The fact that the NMR spectrum of the distillate shows a singlet at $\delta = 6.1$ ppm rules out the presence of any of the following species which should have split signals in the olefinic region.



I



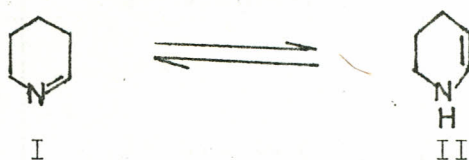
II



III

In any case species (I) and (II) which are likely to be the oxidation products of piperidine are highly unstable (32, 36). Species II can be formed in one of the two ways namely:

- (i) tautomerization of the imine(I) to enamine (II) as is the case with other imines (32).



- (ii) direct formation from the reaction of piperidine with molybdenum(II) as happens when 1-methylpiperidine is oxidized with mercuric acetate (34,35).

It has been shown that once species (I) is formed, it trimerizes (36) readily to form the species shown below.

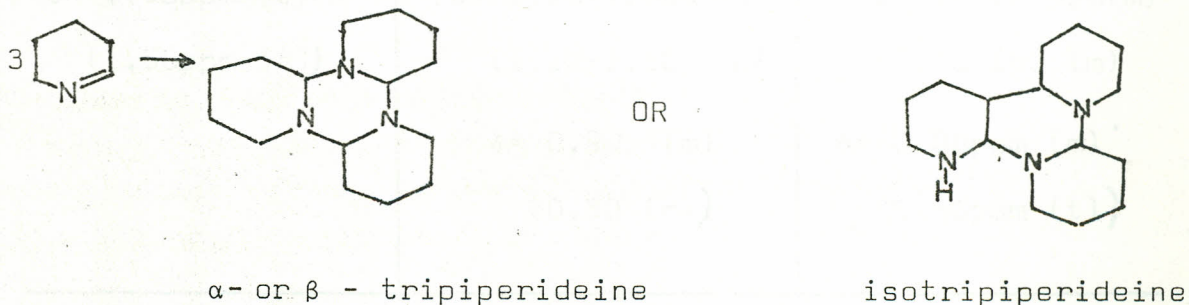
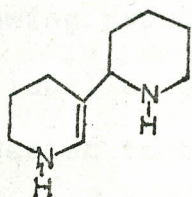


TABLE 4: NMR DATA FOR THE DISTILLATES
OBTAINED FROM THE REACTION OF
 $\text{Mo}(\text{CO})_4\text{Br}_2$ AND ALKYL AMINES
(DATA IN PARENTHESIS ARE FOR
THE PURE AMINES).

DISTILLATE FROM PIPERIDINE	DISTILLATE FROM BUTYLAMINE	DISTILLATE FROM PROPYLAMINE
(i) $\delta = 6.10\text{ppm}$ (s) ()	$\delta = 5.80\text{ppm}$ (s) ()	$\delta = 5.30\text{ppm}$ (s) ()
(ii) $\delta = 3.10\text{ppm}$ (t) ()	$\delta = 5.30\text{ppm}$ (s) ()	$\delta = 4.25\text{ppm}$ (s) ()
(iii) $\delta = 2.90\text{ppm}$ (s) (2.90ppm (s))	$\delta = 3.30\text{ppm}$ (s) ()	$\delta = 3.30\text{ppm}$ (s) ()
(iv) $\delta = 2.40\text{ppm}$ (t) (2.10ppm (s))	$\delta = 2.85\text{ppm}$ (t) (2.70ppm (t))	$\delta = 3.75\text{ppm}$ (t) (2.65ppm (t))
(v) $\delta = 1.75\text{ppm}$ (m)	$\delta = 2.40\text{ppm}$ (t) ()	$\delta = 2.40\text{ppm}$ (m) ()
(vi) $\delta = 1.50\text{ppm}$ (s) (1.50ppm (s))	$\delta = 1.10-1.80\text{ppm}$ (m) (1.10-1.50 (m)) $\delta = 0.90$ (m) (0.90 (m))	$\delta = 1.20-1.70\text{ppm}$ (m) (1.10-1.60 (m)) $\delta = 0.90\text{ppm}$ (m) (0.90ppm (t))

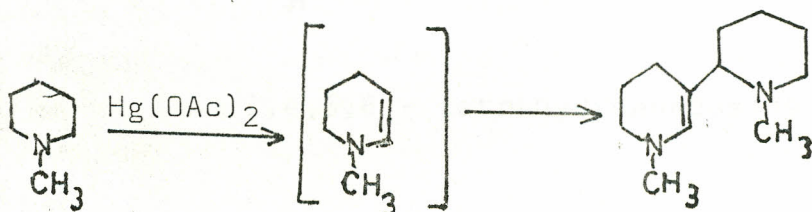
m = multiplet ; s = singlet ; t = triplet.

Species II, 1, 4, 5, 6 - tetrahydropyridine is an enamine and like other enamines (32, 33, 34, 35), it should be very unstable and dimerize to 1,4,5,6 - tetrahydroanabasine shown below.



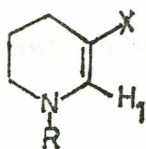
1,4,5,6 - tetrahydroanabasine.

A similar reaction has been shown to take place when 1-methylpiperidine is oxidized with mercuric acetate (34, 35).



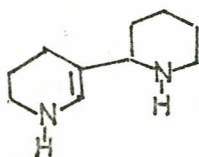
Thus, these workers (34,35) isolated the dimer 1,1 - dimethyl - 1,4, 5, 6 - tetrahydroanabasine instead of 1 - methyl - 1, 4, 5, 6-tetrahydropyridine.

NMR studies of partially reduced pyridines especially



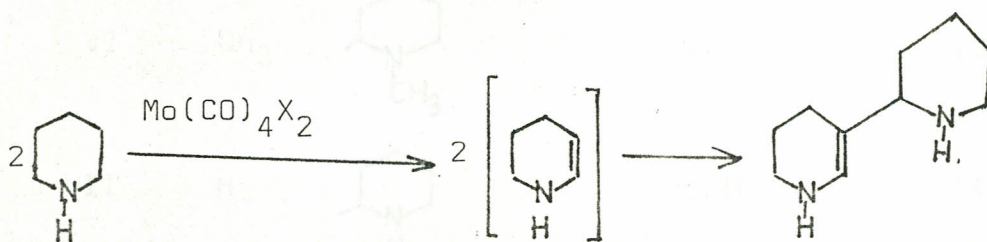
strongly support the proposed structure. The data for these are summarized in Table 5.

As can be seen from Table 5, electron withdrawing groups X tend to give high δ values for proton labelled H_1 . The δ - value for compound VII is expected to be intermediate between the values for compounds V and VI. This is found to be the case. It is proposed that piperidine is oxidized by $Mo(CO)_4X_2$ to give the compound,



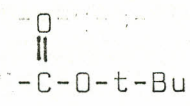
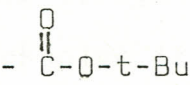
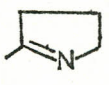
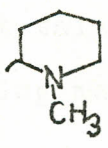
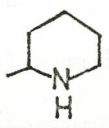
1,4,5,6 - tetrahydroanabasine.

Possibly via the reaction;



Although several derivatives of this compound have been reported in the literature (34,42), this substance has not been reported previously.

TABLE 5: NMR DATA FOR THE OLEFINIC HYDROGEN IN
THE SUBSTITUTED 1,4,5,6-TETRAHYDROPYRIDINE

COMPOUND	R	X	δ VALUES FOR H_1 (PPM)	REF.
I	CH ₃		7.21	(37)
II	H		7.37	(37)
III	CH ₃	- CH ₃	5.42	(38)
IV	PhCH ₂	-C ₂ H ₅	5.60	(39)
V	H		6.80	(40)
VI	CH ₃		5.75	(37)
VII	H		6.10	(41)

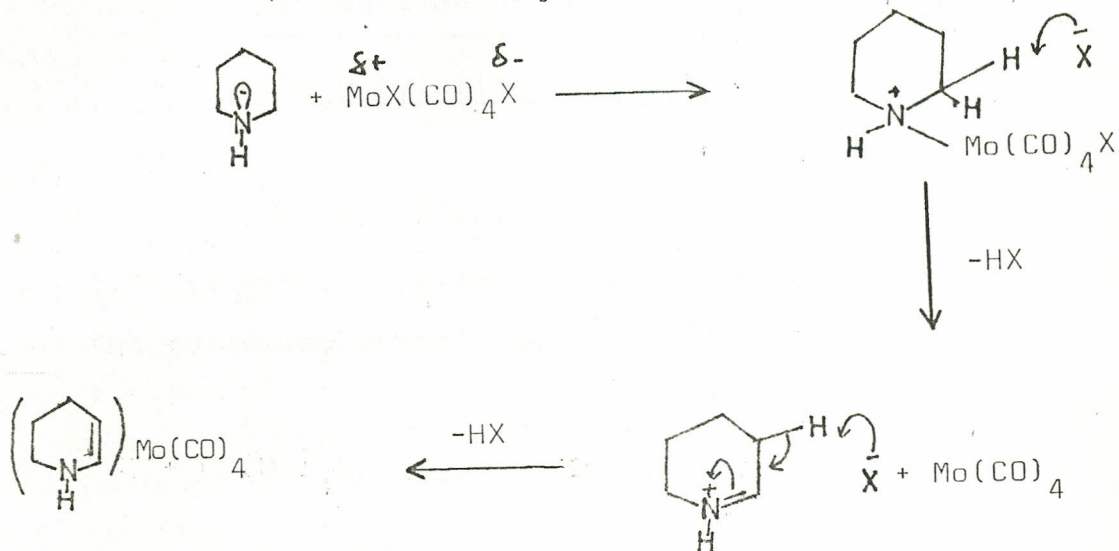
(c) The Amine Salts, C₅H₁₀NH.HX (X = Cl, Br)

As noted in the preparative section, the reaction of Mo(CO)₄X₂ with piperidine gave the salt, C₅H₁₀NH.HX (X = Cl, Br), as one of the products. This was the case whichever method was used. It should be noted that the formation of the salt would result whether Mo(CO)₄X₂ reacts with piperidine via a solvolytic mechanism or via a redoxy mechanism. A possible redoxy mechanism is discussed later. Thus, if a solvolytic mechanism took place, the halocarbonyl and piperidine would react as follows:

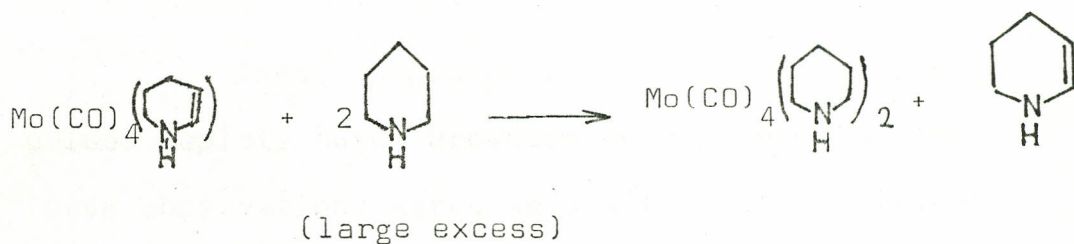


It is believed that this is not the case since the molybdenum-containing material (C₅H₁₀N)₂Mo(CO)₄ should not show any presence of N-H Stretching Frequency in the IR Spectrum. In molybdenum complex isolated, the presence of N-H Stretching Frequency is very distinct and this, therefore, rules out a solvolytic mechanism.

A possible redox mechanism is as follows:



This mechanism is similar to that proposed for the oxidation of amines by mercuric acetate (43). The zerovalent molybdenum complex formed is coordinatively unsaturated (44). It should be remembered that the bulk of the liquid is piperidine itself. Hence, this will not only replace the enamine (45) but more will coordinate to form $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$.



Hence, reason for the complex $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$.

B. The reaction of $\text{Mo(CO)}_4\text{X}_2$ (X = Cl, Br)
with butylamine or propylamine.

The zerovalent complexes, $\text{Mo(CO)}_3\text{L}_3$
(L = butylamine, propylamine) were obtained in each
of the following reactions.

(i) Reaction of $\text{Mo(CO)}_4\text{X}_2$ with neat
amine.

(ii) Reaction of $\text{Mo(CO)}_4\text{Br}_2$ with the
amine in methanol.

In both cases, it was necessary to cool the reaction
mixture failing which, only resinous materials were
obtained and the amine lost due to the heat produced.

These complexes which are pale yellow in
colour rapidly turn brownish on exposure to air.
These observations agree well with those of Tripathi
et. al. (46).

The basic distillate isolated from the
reaction mixture gave an NMR spectrum showing a
singlet peak in the olefinic region. As in the case
of the reaction between $\text{Mo(CO)}_4\text{X}_2$ and piperidine
discussed in the previous section, these results

suggest very strongly that the reaction between alkyl amines and the halocarbonyls $\text{Mo}(\text{CO})_4\text{X}_2$ proceeds via a redox mechanism rather than a disproportionation mechanism. In the latter case, a molybdenum (III) species would be expected to form (18). There was no evidence, however, for any molybdenum (III) species.

II PHYSICAL MEASUREMENTS

A. IR Spectra:

The IR data for the zerovalent molybdenum complexes isolated during the present work are summarized in Table 5. The various assignments for the carbonyl stretching modes have been assigned.

The observation of N-H stretching frequency is significant in that it shows that the complexes formed contain the amine and not the solvolytic product. The N-H stretching frequency in the free amine occurs in the 3500 cm^{-1} to 3000 cm^{-1} region and is lowered by as much as 200 cm^{-1} on coordination (47). From the results in table 5, this is found to be the case. See also figures 14-16.

TABLE 5: CO AND N-H STRETCHING FREQUENCIES FOR THE
COMPLEXES $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$ AND $\text{Mo}(\text{CO})_3\text{L}_3$
(L = BUTYLAMINE, CYCLOHEXYLAMINE, PROPYLAMINE).
DATA IN PARENTHESIS IS N-H STRETCHING FREQUENCY
FOR THE FREE AMINE (48).

COMPLEX	CO STRETCHING FREQUENCY CM^{-1}	TYPE OF MODE	N-H STRETCHING FREQUENCY
$\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$	2010 (m)	A_1	3260 (m)
	1890 (s)	A_1	(3333)
	1840 (s)	B_1	
	1770 (s)	B_2	
$\text{Mo}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3$	1870 (s)	A_1	3310 (w)
	1720 (s)	E	(3380)
			3260 (w)
			(3300)
$\text{Mo}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_3$	1870 (s)	A_1	3310 (w)
	1690 (s)	E	(3380)
			3260 (w)
			(3300)
$\text{Mo}(\text{CO})_3(\text{C}_6\text{H}_{11}\text{NH}_2)_3$	1880 (s)	A_1	3310 (w)
	1730 (s)	E	(3333)
			3260 (w)

m = medium ; s = strong ; w = weak

B. NMR SPECTRA

As mentioned in section I.A.(b) the identification of the oxidation products of the amines was extremely difficult because of:

(i) The products (imines and enamines) are extremely unstable.

(ii) These products form a very small proportion of the bulk of the reaction mixture.

For these reasons, it was not possible to isolate the pure amine oxidation products. The NMR technique was, therefore, extremely useful in following the course of the reaction between $\text{Mo}(\text{CO})_4\text{X}_2$ and alkyl amines. The spectra are given in figures 17-19.

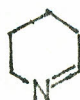
For all the cases studied, the general observation is that, the amine is converted to products containing carbon double bonds. The NMR data are summarised in Table 4. A discussion of the possible mechanism for the reaction between $\text{Mo}(\text{CO})_4\text{X}_2$ and piperidine has already been given in section I.A.(c) and will not be repeated here.

Whereas it has not been possible to identify the oxidation products between $\text{Mo}(\text{CO})_4\text{X}_2$ and butylamine or propylamine, it is believed that the enamines formed form polymeric materials as has been shown by Ripoll et. al. (33). Ripoll et. al. obtained primary enamines by flash thermolysis technique (33) and therefore examined relatively simple reaction mixtures at low temperatures. During the present work, it was necessary to pump off the amine product from the reaction mixture which contained the metal complex. It was necessary to warm the reaction mixture to room temperature so that the amine product could be distilled off. Ripoll et. al (33) have indicated that primary enamines are only stable below -50°C and hence warming to room temperature converts them to polymeric materials.

III CONCLUSION

The reaction between $\text{Mo}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) and the alkyl amines (butylamine, cyclohexylamine, piperidine, propylamine) has been studied. The reaction between $\text{Mo}(\text{CO})_4\text{X}_2$ and piperidine gives 1,4,5,6 - tetrahydroanabasine. This material could be formed via:

(i) Formation of



which

from amines complexes and

could tautomerize to



(ii) Direct formation of the enamine



which would then dimerize to

1,4,5,6 - tetrahydroanabasine.

The molybdenum (II) in the halocarbonyl, $\text{Mo}(\text{CO})_4\text{X}_2$ is converted to the molybdenum (0) complex, $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$. The other product isolated from this reaction of $\text{Mo}(\text{CO})_4\text{X}_2$ and alkyl amines is the amine salts.

Studies of this reaction under different conditions rule out the possibility of a disproportionation reaction or a solvolytic reaction.

The primary alkyl amines react with $\text{Mo}(\text{CO})_4\text{X}_2$ to give the molybdenum (0) complexes, $\text{Mo}(\text{CO})_3\text{L}_3$ (L = butylamine, propylamine) and enamines which readily polymerize to materials that were difficult to identify. Cyclohexylamine is believed to react similarly.

The general conclusion that can be made from these studies is that $\text{Mo}(\text{CO})_4\text{X}_2$ reacts with alkyl amines via a redox mechanism giving molybdenum(0) complexes and enamines.

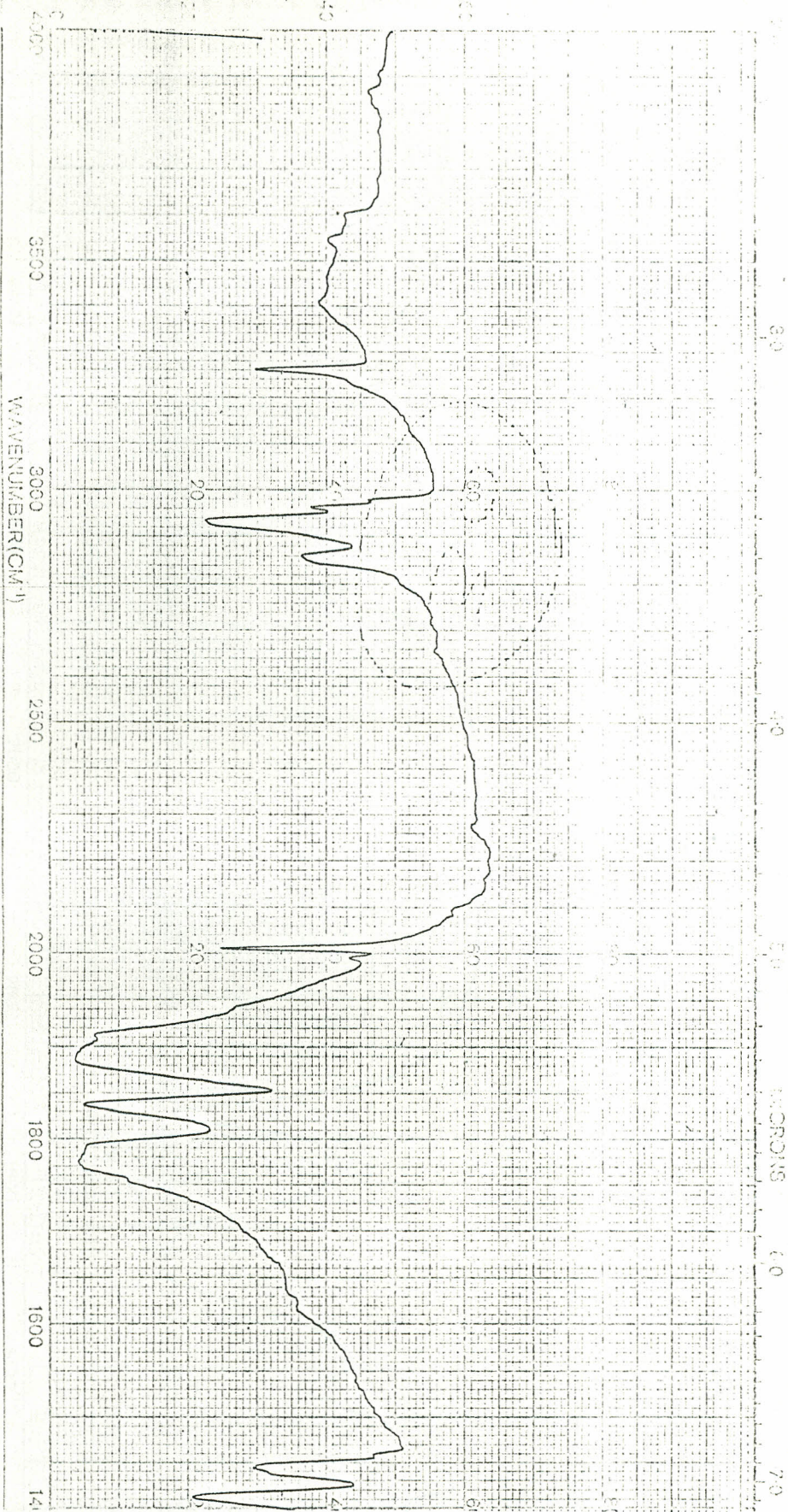


Fig. 14. IR spectrum of $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$.

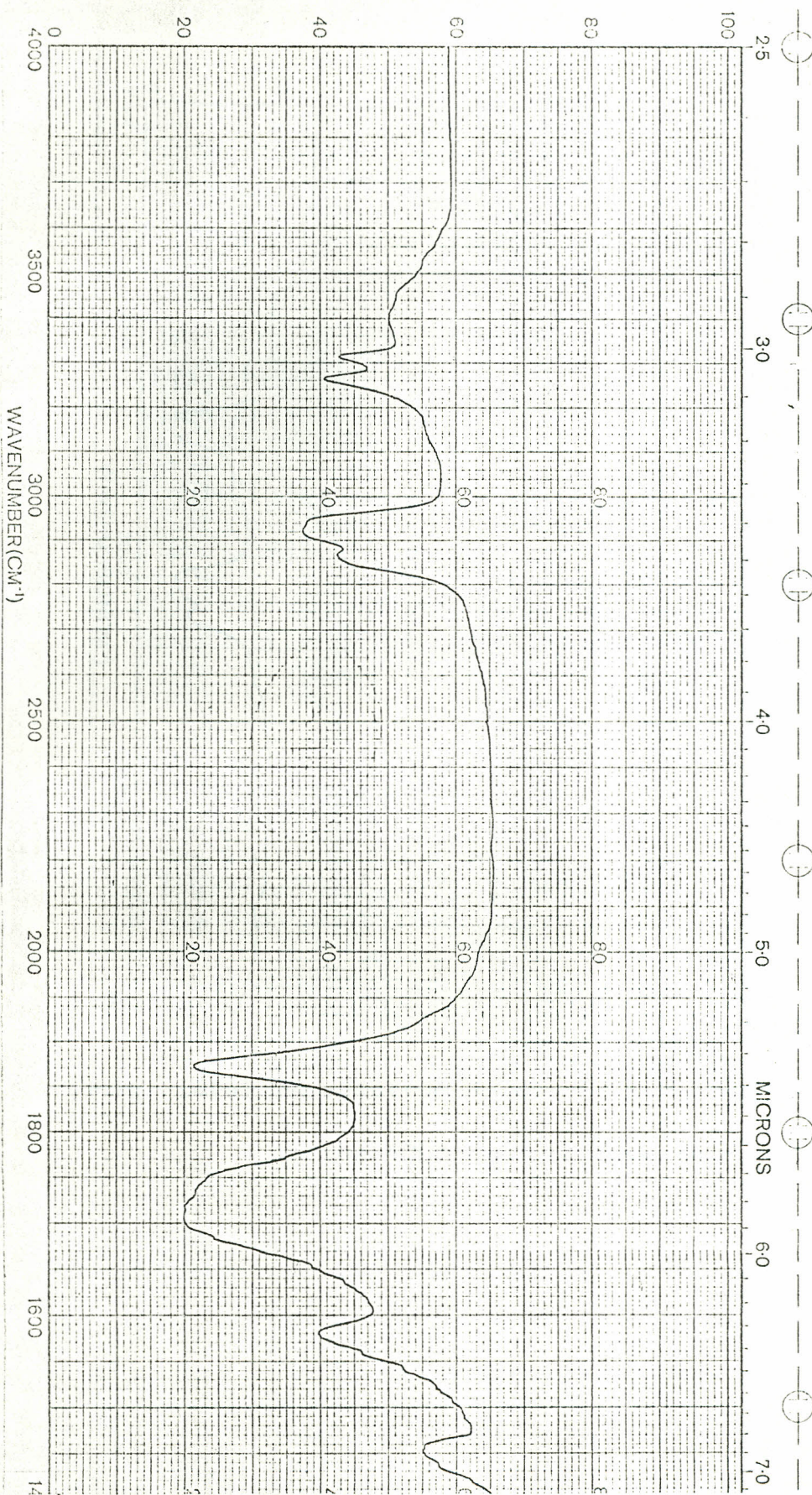


Fig. 15. IR spectrum of $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_3$

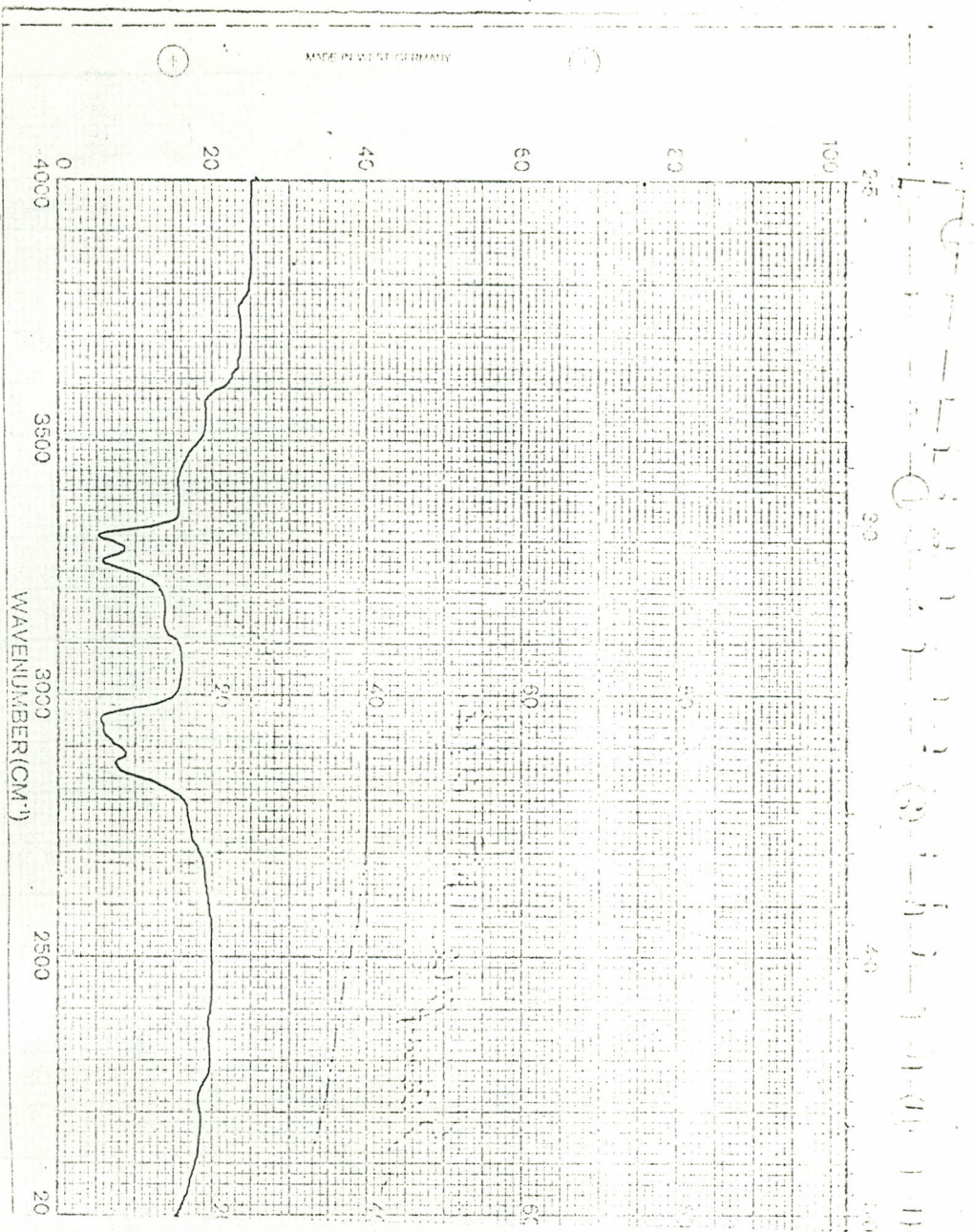


Fig. 16(a) IR spectrum of $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_3$
in the 4000 cm^{-1} to 2000 cm^{-1} range.

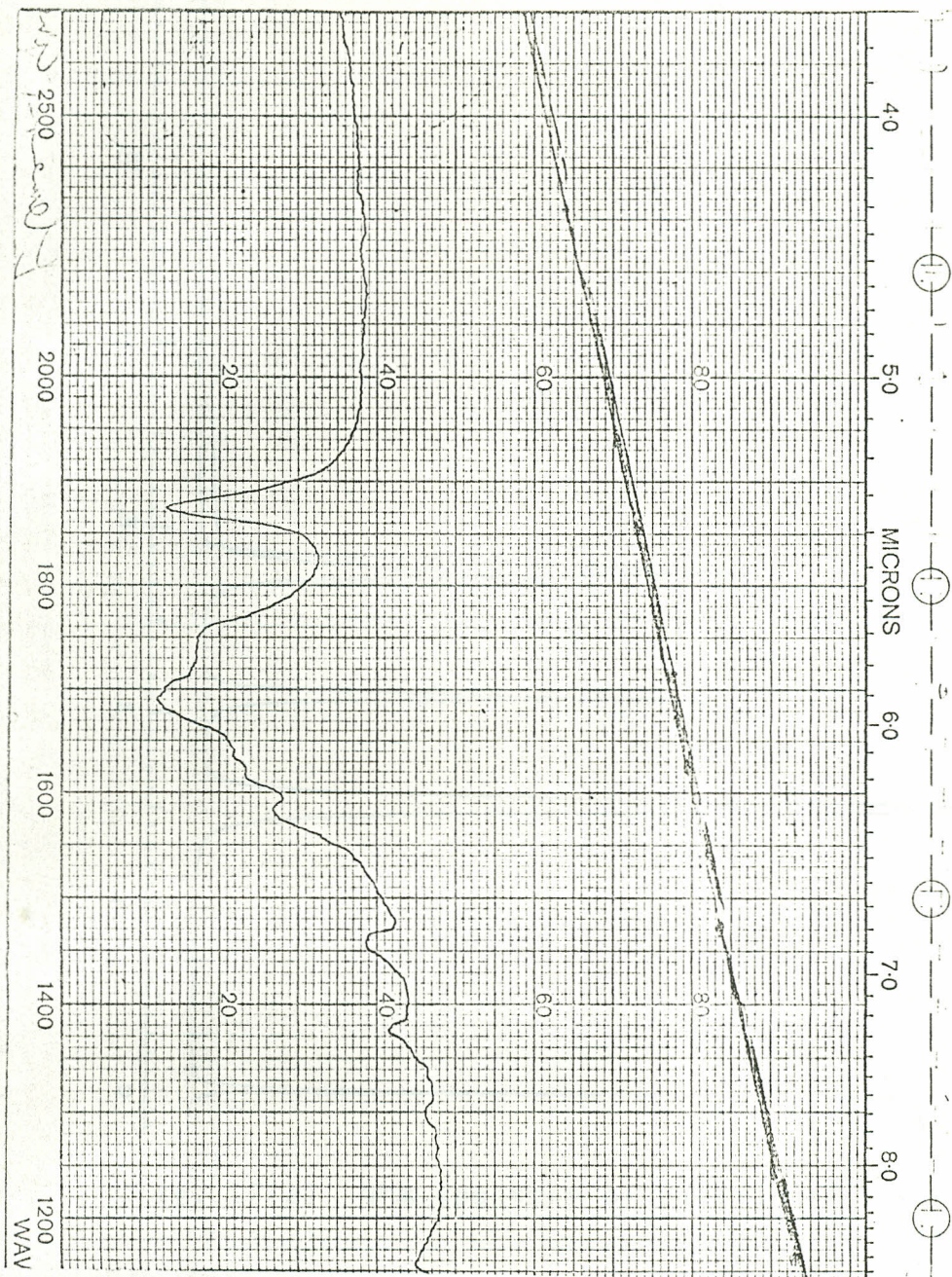


Fig. 16(b) IR spectrum of $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_3$
 in the 2500 cm^{-1} to 1200 cm^{-1} range..

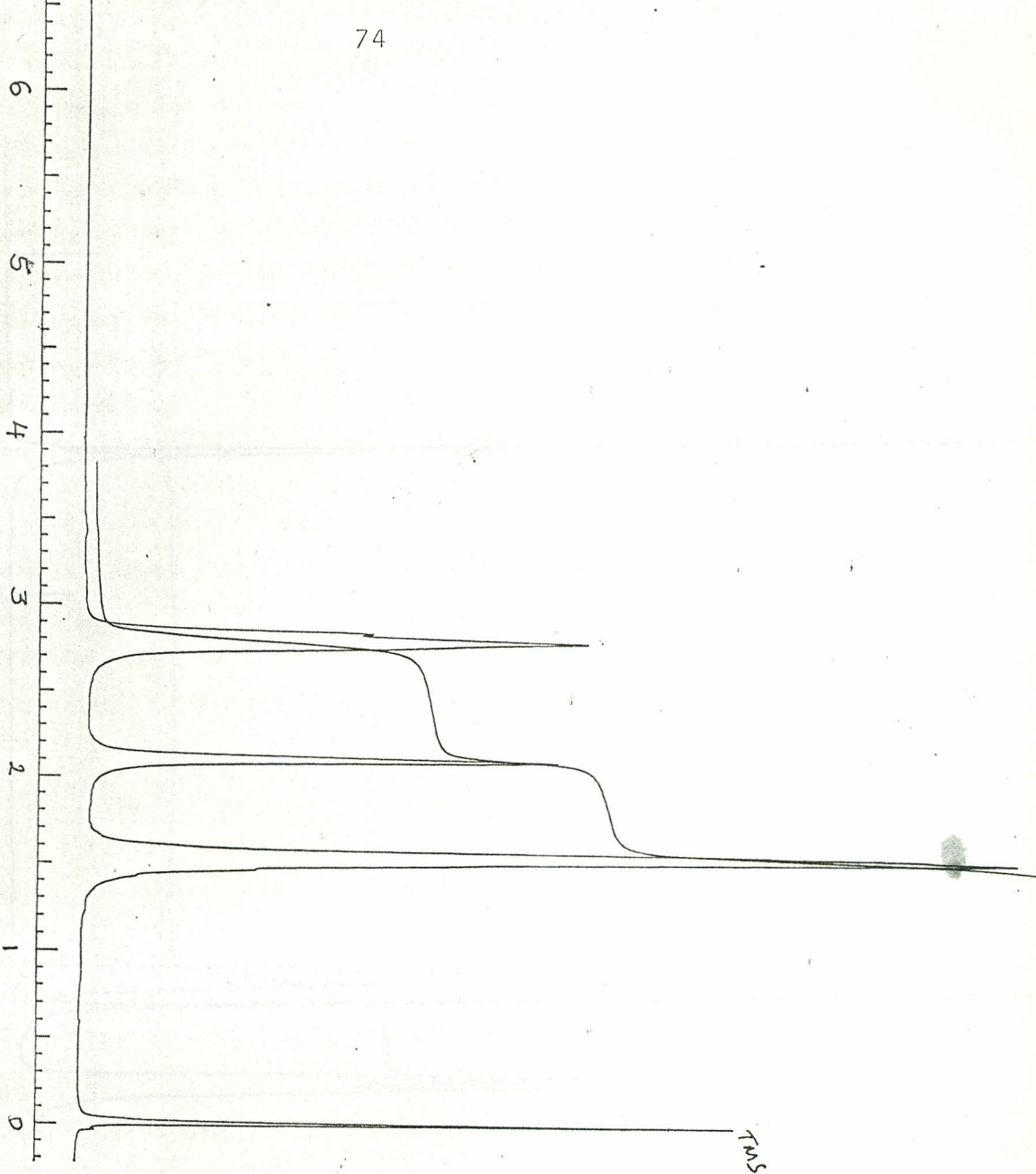


Fig. 17(a) NMR spectrum of piperidine.

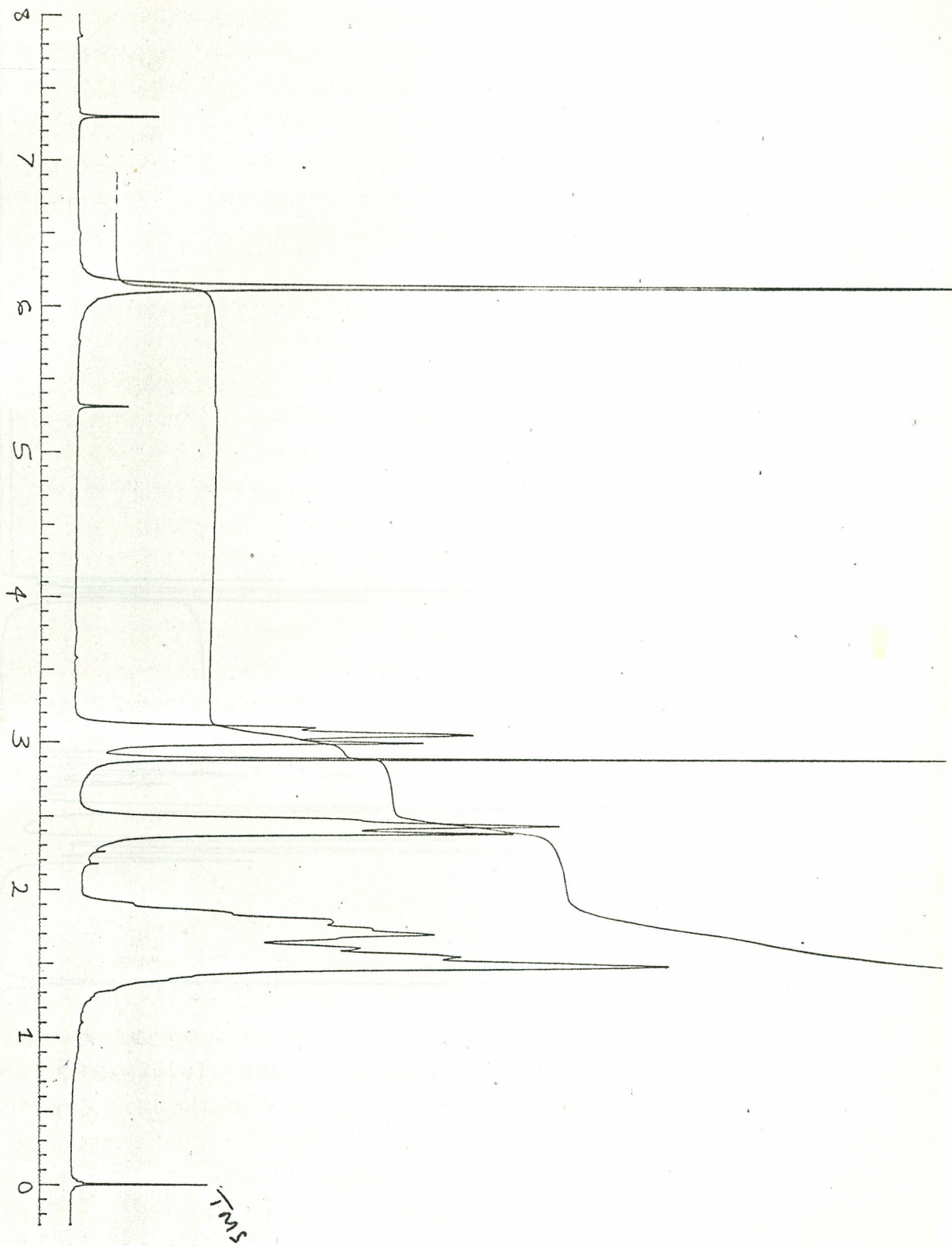


Fig. 17(b). NMR spectrum of distillate from the reaction of $\text{Mo(CO)}_4\text{Br}_2$ with piperidine.

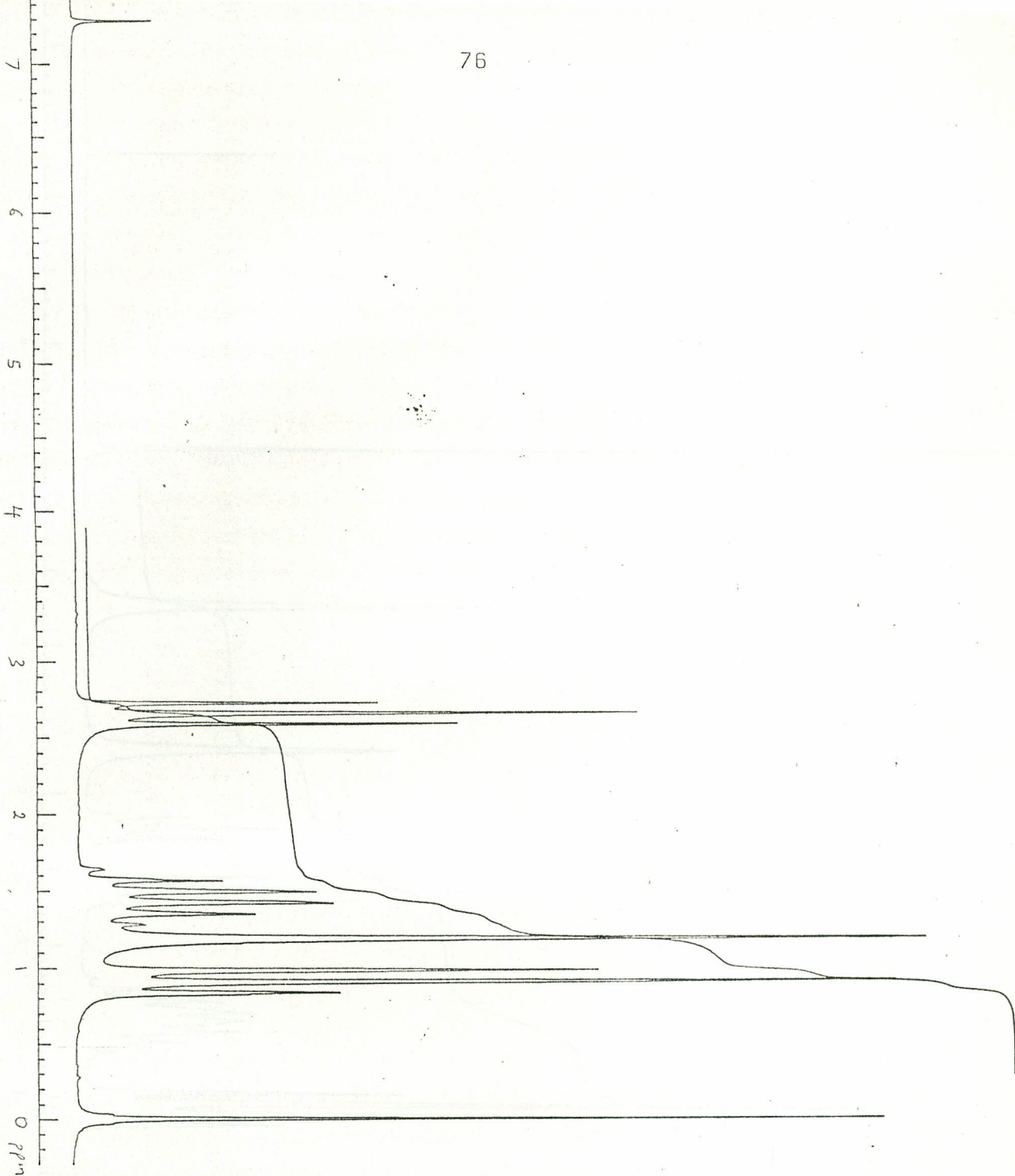


Fig. 18(a) NMR spectrum of propylamine.

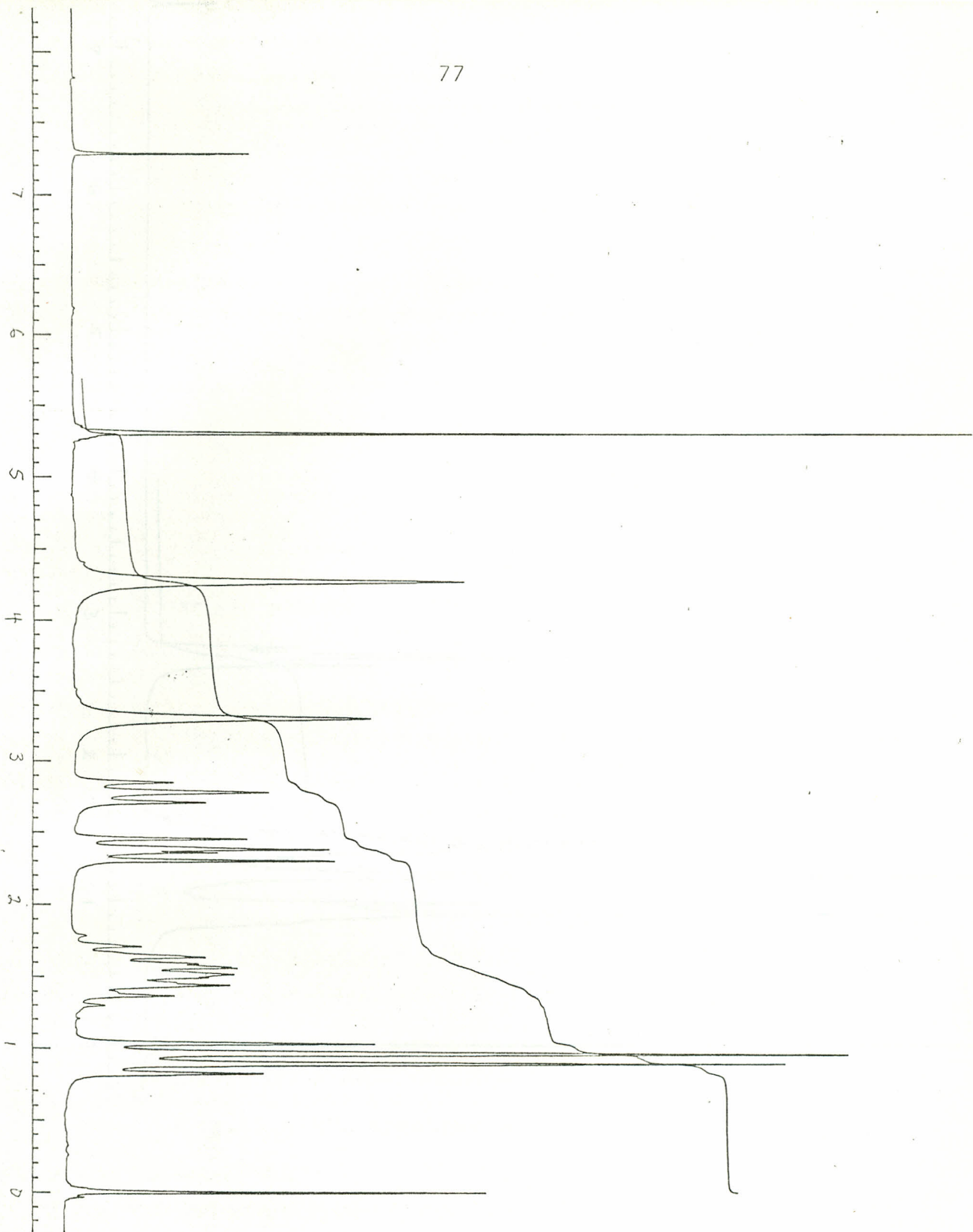


Fig.18(b) NMR spectrum of distillate from the reaction of $\text{Mo}(\text{CO})_4\text{Br}_2$ with propylamine.

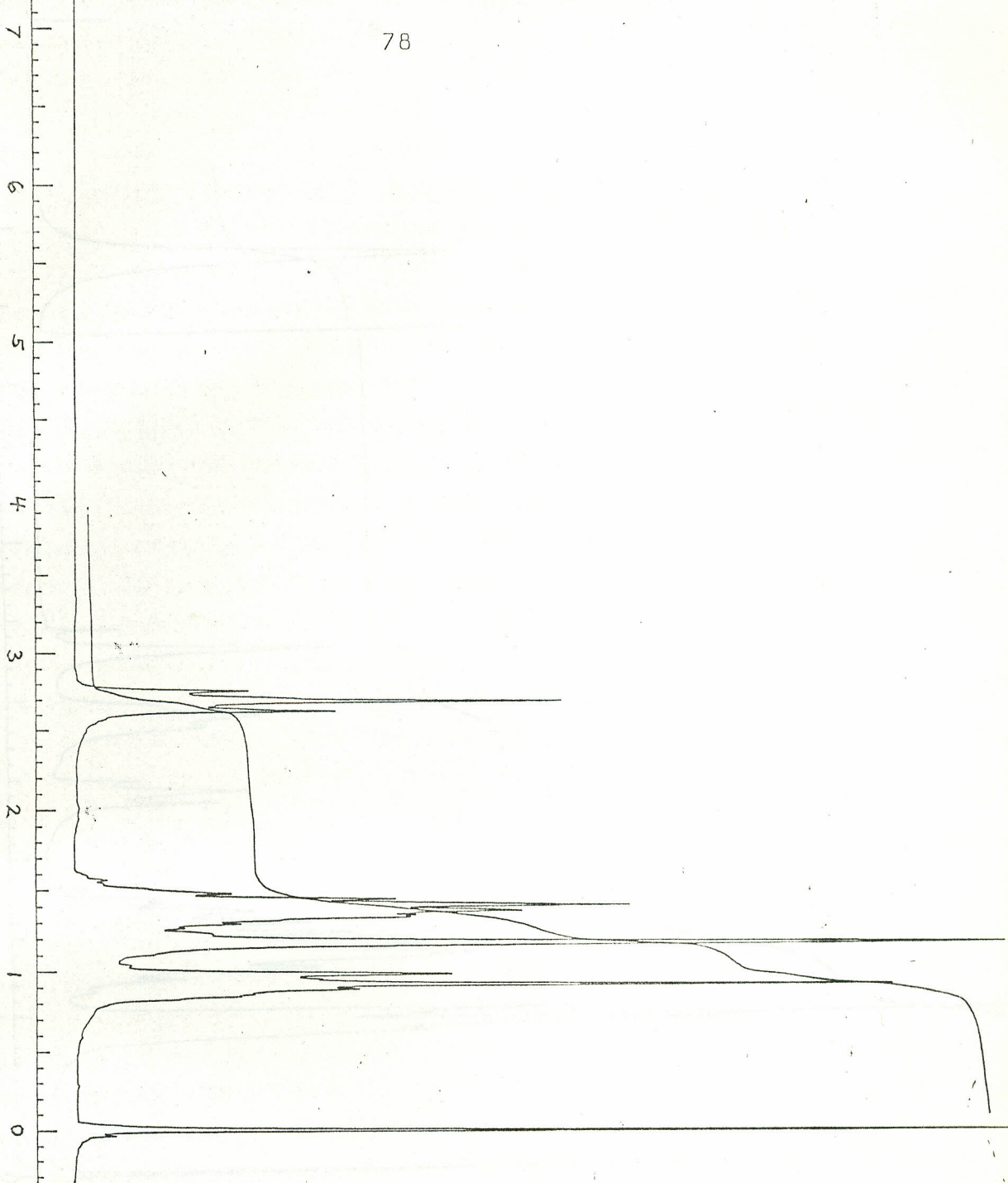


Fig.19(a)NMR spectrum of butylamine

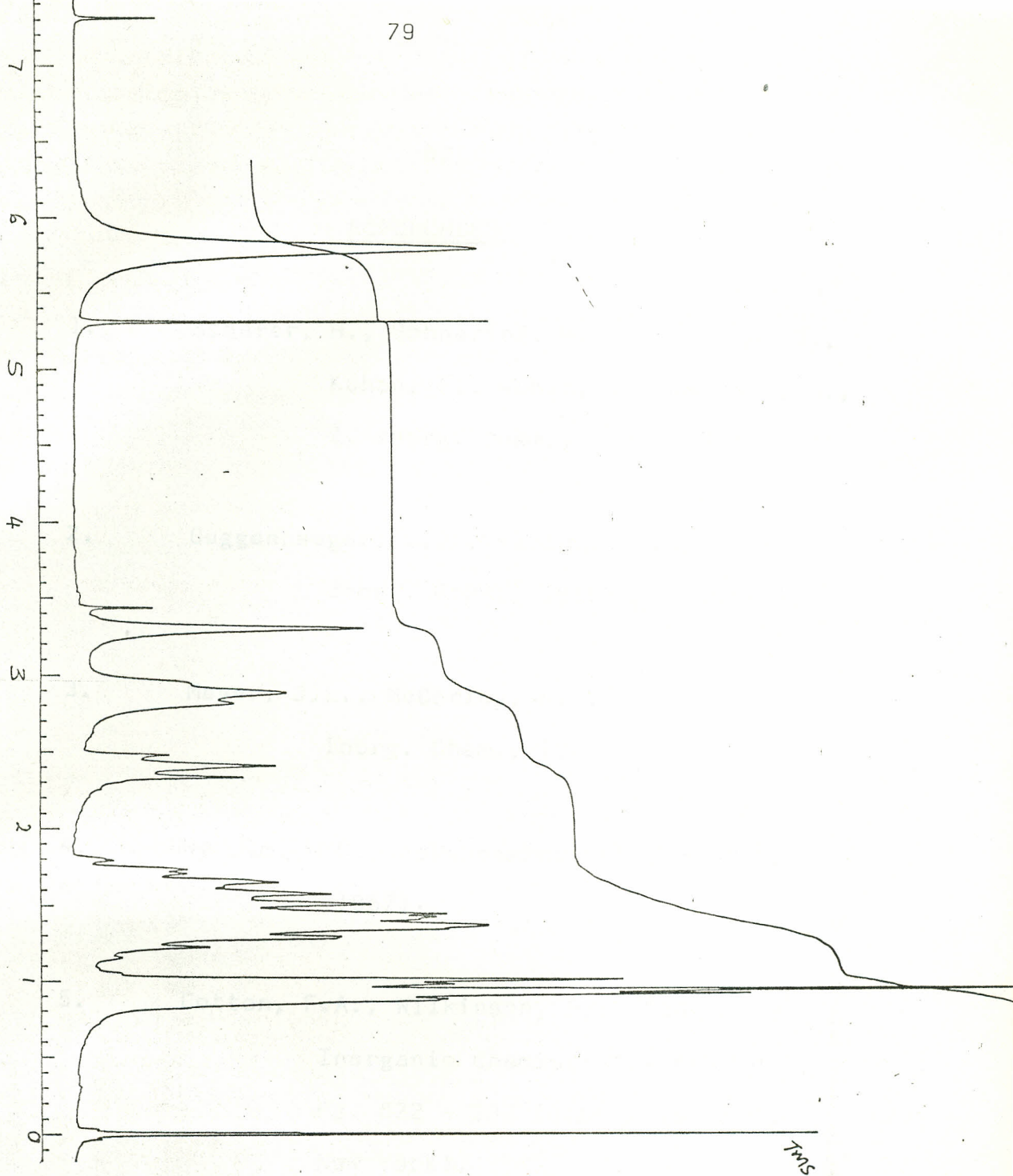


Fig. 19(b) NMR spectrum of distillate from the reaction of $\text{Mo}(\text{CO})_4\text{Br}_2$ with butylamine.

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