

IN THE NAME OF GOD

**NEW APPLICATIONS OF MOLYBDENUM  
PENTACHLORIDE IN ORGANIC SYNTHESIS**

BY  
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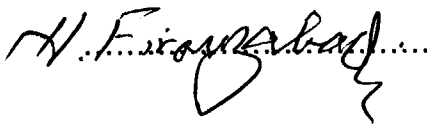
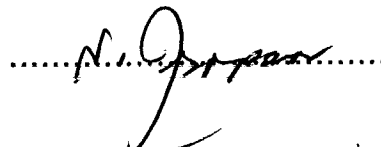

THESIS

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN  
PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE  
DEGREE OF MASTER OF SCIENCE (M.Sc)

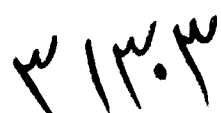
IN  
ORGANIC CHEMISTRY  
SHIRAZ UNIVERSITY  
SHIRAZ, IRAN

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October 2000



*Dedicated to:  
My Father & Mother,  
For leading their children into intellectual pursuits*

*M / M. M*

## **ACKNOWLEDGEMENT**

I heartily wish to discharge a pleasant duty and to acknowledge the benefit of constructive suggestions from and valuable discussions with my major supervisor, Professor Habib Firouzabadi that I received.

I would like to express my gratitude to Professor Nasser Iranpoor for his friendly advises throughout my education.

I also appreciate honorable members of my thesis committee, especially Professor Bahman Tamami, for their careful reading and correcting the manuscript.

Finally, my gratitude is also due to my family, especially my parents and my best friend, Mehrnaz, for their patience and encouragement during my education.

## ABSTRACT

### New Applications of Molybdenum Pentachloride ( $\text{MoCl}_5$ ) in Organic Synthesis

BY

Arezu Jamalian

In this study, we have presented that molybdenum pentachloride ( $\text{MoCl}_5$ ) is a versatile and multi-purpose reagent that can be utilized as either an oxophilic reagent or a Lewis acid in a wide variety of functional group transformations.

Deoxygenation of various types of sulfoxides and also reductive coupling of different sulfonyl chlorides are efficiently performed by means of low valent molybdenum species derived by *in situ* reaction of  $\text{MoCl}_5$  with NaI or zinc powder in dry  $\text{CH}_3\text{CN}$  or THF.

Deprotection of masked functional groups is of especial practical importance in organic syntheses. Along this line, it is shown that acylals (1,1-diacetates) are converted to their parent carbonyl compounds by using catalytic amount of  $\text{MoCl}_5$  in dry  $\text{CH}_2\text{Cl}_2$ . Interestingly, it has been explored that  $\text{MoCl}_5$  can be used in several reaction cycles with different acylals in one-pot reaction mixture. Oximes are also deprotected to their corresponding carbonyl compounds in the presence of  $\text{MoCl}_5$ -Zn system in dry  $\text{CH}_3\text{CN}$  in excellent yields.

Finally,  $\text{MoCl}_5$  is introduced as an efficient reagent for dehydration of tertiary benzylic alcohols to their alkenes.

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## ABBREVIATIONS

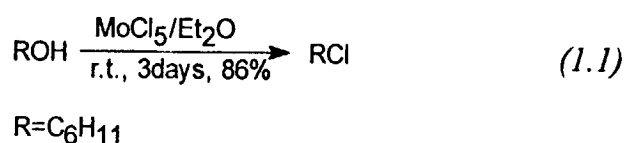
CAN	ceric ammonium nitrate
DMAC	dimethylacetamide
DME	1,2-dimethoxyethane
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
HMPA	hexamethylphosphoramide
HMPT	hexamethylphosphoric triamide
IBX	1-hydroxy-1,2-benziodoxol-3(1H)-one-1-oxide
MTO	methylrhenium trioxide
5-NFDA	5-nitro-2-furfural diacetyl acetal
PDC	pyridinium dichromate
TBAH	tetrabutylammonium hydrogen sulfate
TEACC	triethyl ammonium chlorochromate
THF	tetrahydrofuran
TS	titanium silicate

## CHAPTER ONE

### Introduction and Literature Review

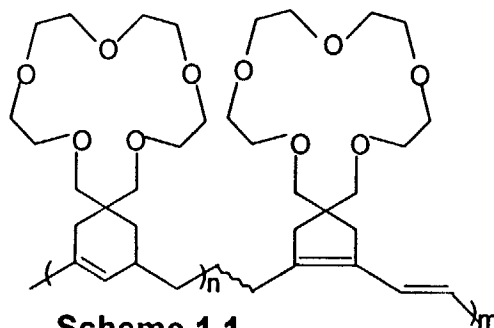
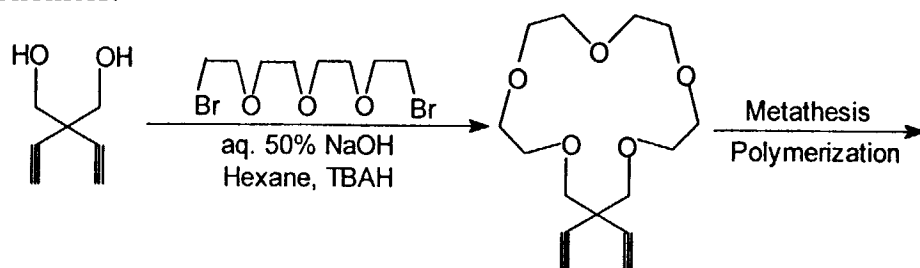
#### 1.1. A Brief Literature Review on the New Applications of Molybdenum Pentachloride (MoCl<sub>5</sub>) in Organic Synthesis

Molybdenum is one of the strong *d*-block oxophilic transition metals. This type of oxophilicity has given many virtual applications to the halides of molybdenum, especially MoCl<sub>5</sub>, in organic and polymer chemistry. Replacement of hydroxyl group by chlorine in cyclohexanol has been carried out in the presence of MoCl<sub>5</sub> (Equation 1.1). Since the chloride ion is a poor nucleophile and hydroxide ion is too basic to function as an effective leaving group, quite forcing conditions are usually needed to convert primary alcohols to alkyl chlorides. The chlorination reactions involving NbCl<sub>5</sub>, TaCl<sub>5</sub>, MoCl<sub>5</sub> and WCl<sub>6</sub> appear to be efficient. A qualitative assessment of chlorination activity would suggest the order WCl<sub>6</sub> > TaCl<sub>5</sub> >> NbCl<sub>5</sub> > MoCl<sub>5</sub>.<sup>1</sup>



A polyacetylene derivative, poly(dipropargyl-16-crown-5), is synthesized through the cyclopolymerization of the corresponding monomer by metathesis catalysts (Scheme 1.1). In general, it has been known that the classical metathesis catalyst systems such as WCl<sub>6</sub>- and MoCl<sub>5</sub>- based catalysts would not tolerate functionalities of monomers,

which resulted mostly in low molecular weight or insoluble polymers. However, the polymerization of the present monomer with a high concentration of oxygen proceeded well to give high molecular weight and soluble polymers.  $\text{MoCl}_5$  based catalysts were used because their catalytic activities were known to be greater than those of  $\text{WCl}_6$ - based catalysts for the polymerization of highly functionalized dipropargyl monomers.<sup>2</sup>



**Scheme 1.1**

Norbornadiene was also polymerized using a combined  $\text{MoCl}_5/\text{EtAlCl}_2$  catalyst system with increased polymerization rate and polymer yields versus either catalyst component alone.<sup>3</sup>

Novel conjugated ionic polymers from propargylammonium-bromides having different ammonium cations were synthesized and characterized.  $\text{PdCl}_2$  and  $\text{PtCl}_2$  were found to be very effective catalysts, whereas most of the W- and Mo- based catalysts except  $\text{MoCl}_5/\text{EtAlCl}_2$  failed to polymerize the ionic acetylene monomers.<sup>4</sup>

Selective oxidation of petroleum residues takes place in the presence of  $\text{MoCl}_5$ . Sulfone type compounds form from sulfides and thiophenes during liquid-phase oxidation of high S-petroleum residue with cumene hydroperoxide in the presence of  $\text{MoCl}_5$  or  $(\text{NH}_4)_2\text{MoO}_4$ .<sup>5</sup>

Catalytic dihydroxylation of cyclohexene derivatives takes place in the presence of  $\text{MoOBr}_3$  or  $\text{MoCl}_5$  catalysts, which gave the highest yields. The diol yield decreased and the epoxide yield increased with increasing acid concentration. Lower diol yields were obtained with  $\text{HCO}_2\text{H}$  or  $\text{EtCO}_2\text{H}$  instead of  $\text{AcOH}$ .<sup>6</sup>

Homogeneous liquid-phase epoxidation of allyl chlorides with *t*-butylhydroperoxide was carried out in the presence of various Mo catalysts in a batch reactor at 53-76°C and 1 atm. in 1,1,2,2-tetrachloroethane solution.  $\text{MoO}_2(\text{acetylacetonate})_2$  and  $\text{MoCl}_5$  were the most active and selective catalysts. The catalysts showed little tendency toward cleavage of the product epoxide rings.<sup>7</sup>

Regioselective opening of a cyclopropane ring is carried out by mercury (II) and transmetallation of the product with  $\text{MoCl}_5$  (Scheme 1.2).<sup>8</sup>

Aminopropargyl group containing siloxanes were prepared and used as supports for  $\text{Na}_2\text{PdCl}_4\text{-MoCl}_5$  catalysts for hydrogenation of olefines and  $\text{PhNO}_2$ . The catalytic activity at 40°C with EtOH as solvent was in the following order: styrene > acetonitrile > cyclohexene >  $\text{PhNO}_2$ , 1-decene and the effect of solvent on the catalytic activity was in the following order: EtOH > *iso*-PrOH > n-hexane. The activity of Pd-Mo catalyst was higher than that of the monometallic analogue.<sup>9</sup>