IN THE NAME OF GOD

NEW APPLICATIONS OF MOLYBDENUM PENTACHLORIDE IN ORGANIC SYNTHESIS

BY

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Dedicated to:

My Father & Mother,

For leading their children into intellectual pursuits

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ABSTRACT

New Applications of Molybdenum Pentachloride ($MoCl_5$) in Organic Synthesis

BY

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In this study, we have presented that molybdenum pentachloride ($MoCl_5$) 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 tranformations.

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 $MoCl_5$ with NaI or zinc powder in dry CH_3CN 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 $MoCl_5$ in dry CH_2Cl_2. Intrestingly, it has been explored that $MoCl_5$ 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 $MoCl_5$-Zn system in dry CH_3CN in excellent yields.

Finally, $MoCl_5$ 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 ($MoCl_5$) in Organic Synthesis

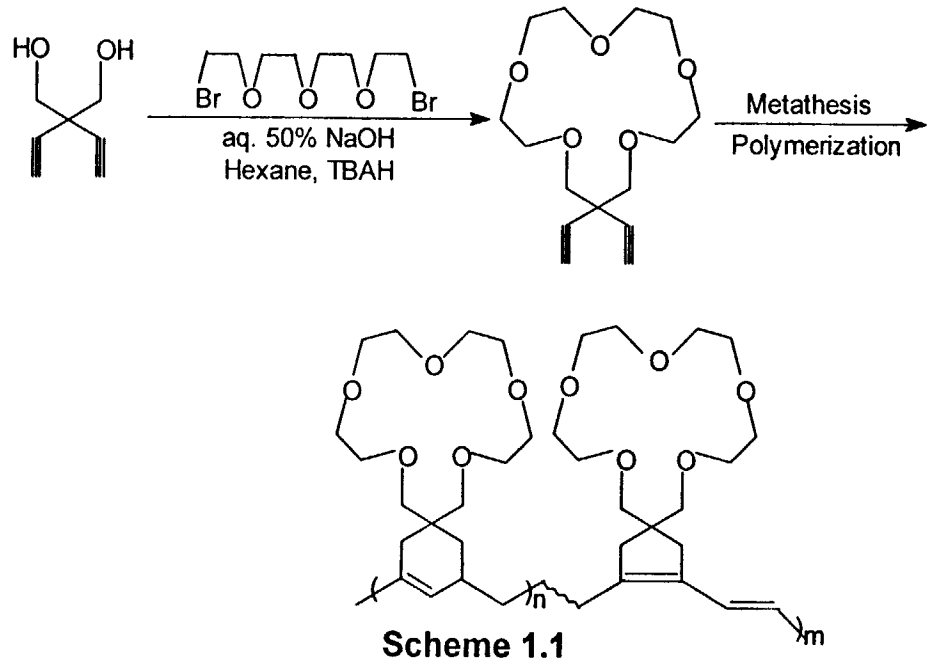
Molybdenum is one of the strong *d*-block oxophilic transition metals. This type of oxophilocity has given many virtual applications to the halides of molybdenum, especially $MoCl_5$, in organic and polymer chemistry. Replacement of hydroxyl group by chlorine in cyclohexanol has been carried out in the presence of $MoCl_5$ (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 $NbCl_5$,$TaCl_5$, $MoCl_5$ and WCl_6 appear to be efficient. A qualitative assessment of chlorination activity would suggest the order WCl_6> $TaCl_5$ >> $NbCl_5$> $MoCl_5$.[1]

$$ROH \xrightarrow[r.t.,\ 3days,\ 86\%]{MoCl_5/Et_2O} RCl \qquad (1.1)$$

$R=C_6H_{11}$

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_6- and $MoCl_5$- 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. $MoCl_5$ based catalysts were used because their catalytic activities were known to be greater than those of WCl_6- based catalysts for the polymerization of highly functionalized dipropargyl monomers.[2]



Scheme 1.1

Norbornadiene was also polymerized using a combined $MoCl_5/EtAlCl_2$ catalyst system with increased polymerization rate and polymer yields versus either catalyst component alone.[3]

Novel conjugated ionic polymers from propargylammonium-bromides having different ammonium cations were synthesized and characterized. $PdCl_2$ and $PtCl_2$ were found to be very effective catalysts, whereas most of the W- and Mo- based catalysts except $MoCl_5/EtAlCl_2$ failed to polymerize the ionic acetylene monomers.[4]

Selective oxidation of petroleum residues takes place in the presence of $MoCl_5$. Sulfone type compounds form from sulfides and thiophenes during liquid-phase oxidation of high S-petroleum residue with cumene hydroperoxide in the presence of $MoCl_5$ or $(NH_4)_2MoO_4$.[5]

Catalytic dihydroxylation of cyclohexene derivatives takes place in the presence of $MoOBr_3$ or $MoCl_5$ 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 HCO_2H or $EtCO_2H$ instead of AcOH.[6]

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. MoO_2(acetylacetonate)$_2$ and $MoCl_5$ were the most active and selective catalysts. The catalysts showed little tendency toward cleavage of the product epoxide rings.[7]

Regioselective opening of a cyclopropane ring is carried out by mercury (II) and transmetallation of the product with $MoCl_5$ (Scheme 1.2).[8]

Aminopropargyl group containing siloxanes were prepared and used as supports for Na_2PdCl_4-$MoCl_5$ catalysts for hydrogenation of olefines and $PhNO_2$. The catalytic activity at 40°C with EtOH as solvent was in the following order: styrene > aceyonitrile > cyclohexene > PhNO2, 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.[9]