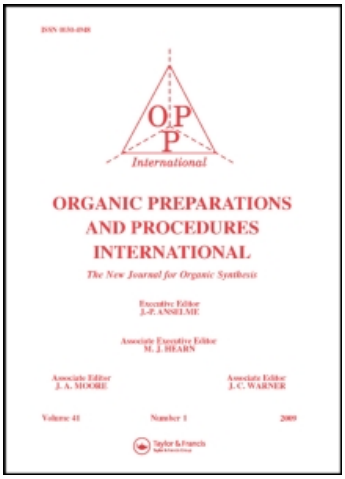

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MOLYBDENUM IN ORGANIC SYNTHESIS. A REVIEW

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INTRODUCTION

Molybdenum (atomic no. 42; atomic weight 95.94; mp. 2610°C; bp. 5560°C; electronic configuration [Kr] $4d^5 5s^1$) a chemical element belonging to group 6 of periodic table is a silvery white metal, tough but malleable and softer than glass. Its main mineral ores are molybdenite, powellite and wulfenite. It exists in common oxidation states of -4, -2, 0, +2, +4, +6. It is used to prepare a number of alloys because it imparts toughness, weldability and corrosion resistance and is capable of enduring high temperature *e.g.,* in the manufacture of parts of jet engines. Sodium molybdate is used in manufacture of paints. Mo compounds are also used as catalysts in various industrial processes. Mo is also present in enzymes of nitrogen fixing bacteria such as nitrate reductase and nitrogenase. Nitrogenase contains two proteins molybdoferredoxin and azoferridoxin. Molybdoferredoxin is a brown, air sensitive solid which contains two Mo atoms, 24 to 36 Fe atoms and 24 to 36 S atoms together with a protein and has a molecular weight of about 22500.

Recently there has been increased interest in various molybdenum compounds for uses in organic synthesis in the laboratory and in industry. Due to its variable oxidation states, there are many stable Mo compounds which have been employed recently in organic synthesis. The present review is a survey of the literature up to 2003 and covering various organic transformations reported with different molybdenum reagents so far. Many of these reagents are available commercially and others may be prepared in the laboratory. The review starts with reactions of $Mo(CO)_6$ which have been investigated in great details. Wherever available, the probable reaction paths have also been described.

I. MOLYBDENUM CARBONYLS

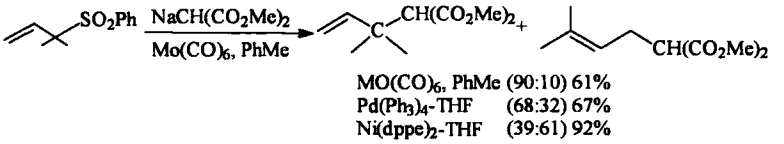
1. Molybdenum Hexacarbonyl: $Mo(CO)_6$

Molybdenum hexacarbonyl[1] is a colorless, odorless, air stable and diamagnetic solid that forms orthorhombic crystals (density 1.96 g cm^{-3}) and has an octahedral structure; the crystals are hydrophobic and decompose without melting at 150°C but melts reversibly under vacuum at 142-146°C. $Mo(CO)_6$ is very slightly soluble in non-polar organic solvents, slightly soluble in polar

organic solvents and insoluble in water. Solutions of $Mo(CO)_6$ are quite stable to oxidation and decompose only very slowly in air. It can be prepared from pyrophoric Mo and CO under high pressure. $Mo(CO)_6$ has found more applications in organic synthesis than any other Mo reagent. It is used to catalyze various reactions namely C-C bond formation, cyclization, ring cleavage of heterocyclic compounds, reductions, oxidations, heterocyclic ring formation etc.

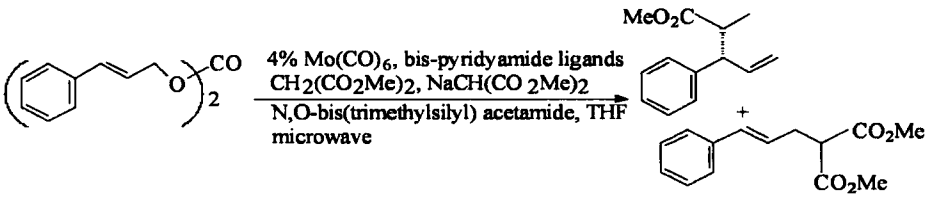
a. C-C Bond Formation

$Mo(CO)_6$ catalyzes alkylation at more substituted allylic site[2] in contrast to poor selectivity of Pd and Ni catalyzed reactions (*Eq. 1*). 4-Chloro- and 4-pyrrolidinyl substituted



(1)

ligand derivatives exhibited high regioselectivity in the asymmetric allylation of cinnamyl carbonate catalysed by $Mo(CO)_6$ (*Eq. 2*).[3] It is also a convenient catalyst for the allylic alkylation of carbon nucleophiles with allylic acetates and carbonates (*Eq. 3*).[4] Reductive coupling of



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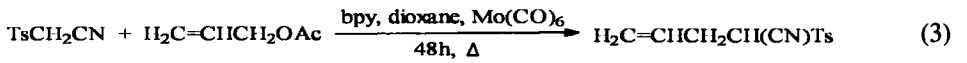
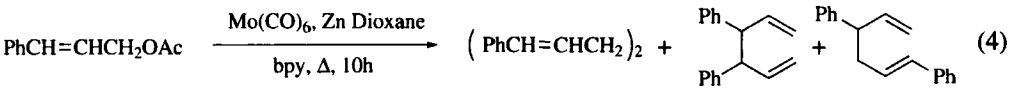


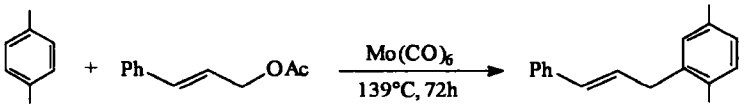
(3)

allylic acetates with Zn catalysed by hexacarbonyl molybdenum (0) (*Eq. 4*)[5] and allylation of



(4)

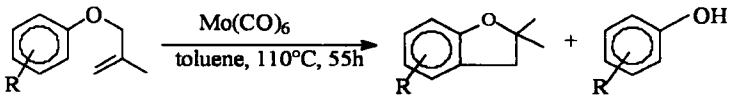
aromatic compounds with allylic esters and alcohols in presence of $Mo(CO)_6$ have also been reported (*Eq. 5*).[6]



(5)

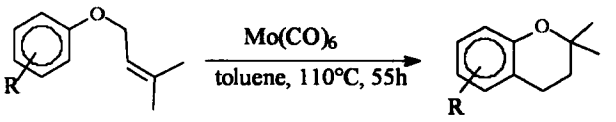
Molybdenum hexacarbonyl efficiently catalyzes Claisen rearrangement-cyclization reaction of

allyl aryl ethers[7] and allyl prenyl ethers[8] to give good yields of corresponding dihydrobenzofurans and 2,2-dimethylchromans respectively (*Eqs. 6 and 7*). Recently $Mo(CO)_6$ has been



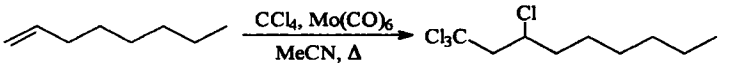
(6)

R = H, 4-Mem 4-OMe, 4-Br, 4-Et, 4-^{i}Pr, 4-^{t}Bu, 2-Me, 3-Me



(7)

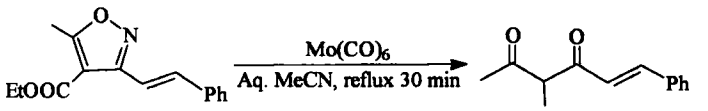
reported to catalyze addition of α-polyhalides to olefins (*Eq. 8*).[9]



(8)

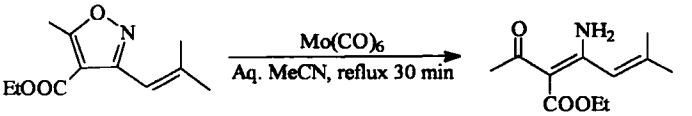
b. Ring Opening

3-Alkenylisoxazoles are cleaved by hexacarbonyl molybdenum to give β-diketones[10] (*Eq. 9*) whereas β-amino-α,β-unsaturated ketones are obtained under anhydrous conditions



(9)

(*Eq. 10*).[11-13] Isoxazole gives pyran-4-ones on cleavage (*Eq. 11*),[14] while isoxazoline rings give



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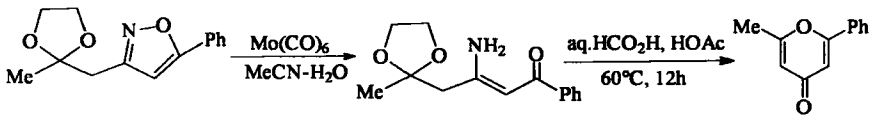
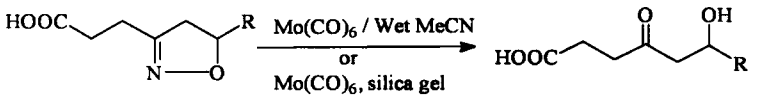


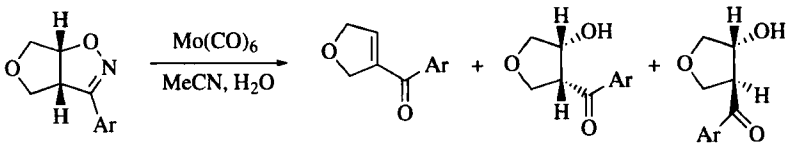
(11)

β-hydroxyketones[15,16] on ring opening (*Eq. 12*).



(12)

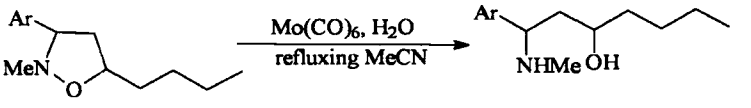
Different stereoisomeric β-hydroxyketones[17] are obtained from the ring opening of tetrahydrofuroisoxazoles (*Eq. 13*). 1,3-Aminoalcohols[18] are obtained by reductive cleavage of



(13)

Ar = *p*-C_6H_4X; X = H, Me, OMe, Ph, Cl, F

isoxazolidines with molybdenum hexacarbonyl (*Eq. 14*).



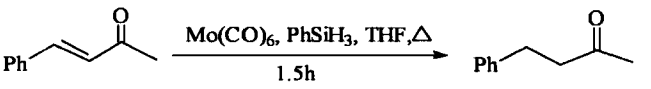
(14)

c. Reduction

Carboxylic acids are reduced to alcohols[19] in high yields by $Mo(CO)_6$ in presence of Rh and Al_2O_3 (*Eq. 15*) under high pressure of hydrogen. α,β-Unsaturated carbonyl compounds

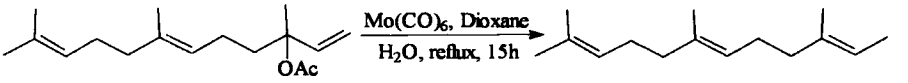
$$n\text{-}C_{14}H_{29}COOH \xrightarrow[5\%\ Rh/Al_2O_3,\ Mo(CO)_6,\ 150^\circ C]{H_2\ (100\ atm),\ DME} n\text{-}C_{14}H_{29}CH_2OH \qquad (15)$$

are selectively reduced at the double bond (*Eq. 16*) using phenylsilane and molybdenum



(16)

hexacarbonyl as a catalyst.[20] Allylic acetates are reductively deacetoxylated using $Mo(CO)_6$ with concurrent migration of double bond (*Eq. 17*).[21] Reductive desulfurization of thiols[22,23]



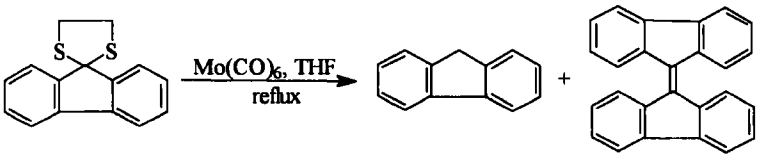
(17)

and thiomethyl ethers[22] has been reported with $Mo(CO)_6$ in THF or acetic acid (*Eq. 18*).

$$RSR' \xrightarrow[12\text{-}16h]{Mo(CO)_6,\ THF,\ reflux} RH \qquad (18)$$

R= alkyl. aryl, benzyl; R'=H, Me

Desulfurization and reductive coupling of thioketals[24] has also been reported (*Eq. 19*).



(19)

The reaction of alkyl or aryl sulfonyl chloride with $Mo(CO)_6$ in anhydrous tetramethylurea at 70°C[25] provides a convenient synthesis of disulfides (*Eq. 20*). $Mo(CO)_6$ reacts

$$RSO_2Cl \xrightarrow{Mo(CO)_6} \underset{55\text{-}75\%}{RSSR} \qquad (20)$$

with α-bromosulfoxides in DMF to form thioacetals (*Eq. 21*). It is evidently functioning both as a reagent and catalyst. Deoxygenation of the sulfoxides to sulfides which require an equimolar quantity of $Mo(CO)_6$ is the first step in thioacetalization.[26]

$$R^1SOCHR^2Br \xrightarrow[DMF]{Mo(CO)_6} [R^1SCHR^2Br] \xrightarrow{Mo(CO)_6} (SR^1)_2CHR^2 \qquad (21)$$

The reductive dehalogenation of α-haloketones[27-29] has been reported under different conditions. Dehalogenation of α-haloesters is also efficiently achieved with a novel reducing system consisting of phenylsilane, catalytic amounts of $Mo(CO)_6$ and Ph_3P (*Eq. 22*).[29]

$$R^1R^2CXCOR \xrightarrow[THF,\ C_6H_6,\ Toluene\ or\ diglyme,\ 65\text{-}95°C,\ 1\text{-}24\ h]{Mo(CO)_6,\ PhSiMe_3,\ Ph_3P,\ NaHCO_3} R^1R^2CHCOR \qquad (22)$$

R^1, R^2 = H, alkyl; R = alkyl, aryl, OEt; X = Cl, Br

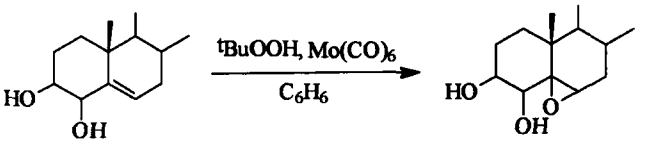
Aromatic *N*-nitrosamines are converted into secondary amines (*Eq. 23*) when refluxed in 1,2-dimethoxyethane for 15-18 h with a slight excess of molybdenum hexacarbonyl.[30]

$$\begin{matrix} Ar \\ R \end{matrix}\!\!>\!N\!-\!NO \xrightarrow{Mo(CO)_6} \begin{matrix} Ar \\ R \end{matrix}\!\!>\!NH \qquad (23)$$

d. Oxidations

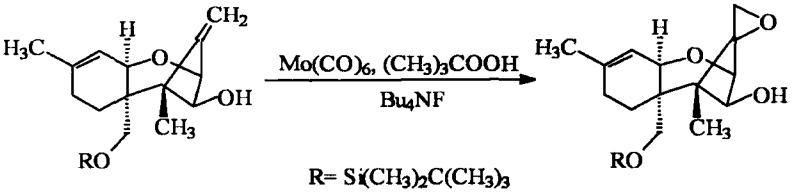
(i) Epoxidations of Olefins

Epoxidation of olefins,[31] unsaturated and allylic alcohols[32,33] has been reported with ^tBuOOH and $Mo(CO)_6$ (*Eq. 24*). This method has also found applications in the epoxidation of



(24)

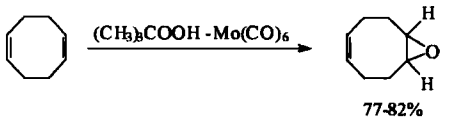
steroids[34] and the selective epoxidation of 2,2-disubstituted double bonds in presence of trisubstituted double bond by treatment with *t*-butylhydroperoxide and $Mo(CO)_6$[35] in presence of Bu_4NF (*Eq. 25*).



R= $Si(CH_3)_2C(CH_3)_3$

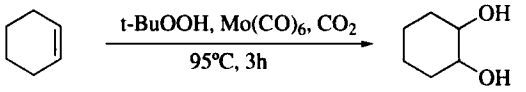
(25)

Monoepoxidation of 1,5-cyclooctadiene has been reported with *t*-butylhydroperoxide in presence of molybdenum hexacarbonyl at 80°C (*Eq. 26*).[36] Olefin oxidation to epoxide or diols using



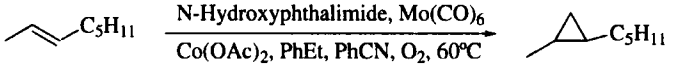
(26)

$Mo(CO)_6$ catalyst and ^tBuOOH as oxidant in supercritical CO_2, also proceeds in nearly quantitative yields (*Eq. 27*).[37]



(27)

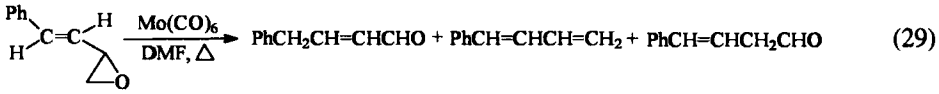
N-Hydroxyphthalimide (NHPI) and $Mo(CO)_6$ catalyst have been used to epoxidize olefins under oxygen atmosphere in presence of ethylbenzene or tetralin. It involves autoxidation of the hydrocarbon assisted by NHPI and epoxidation of olefins with the resulting hydroperoxide catalyzed by $Mo(CO)_6$ (*Eq. 28*).[38] *cis*-Alkenes were epoxidized in the stereospecific manner to form the corresponding *cis*-epoxide in high yields.



(28)

(ii) Deoxygenation and Rearrangement of Epoxides

$Mo(CO)_6$ is also used as a catalyst for the rearrangement of epoxides to aldehydes and for isomerization of β,γ- to α,β-unsaturated aldehydes.[39] The corresponding olefins are also obtained as a minor product (*Eqs. 29 and 30*). Quantitative deoxygenation of epoxides has also



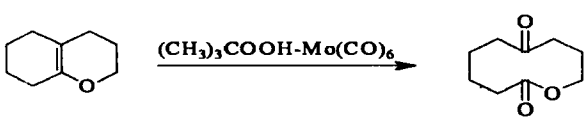
(29)

(30)

been obtained by using $Mo(CO)_6$.[40]

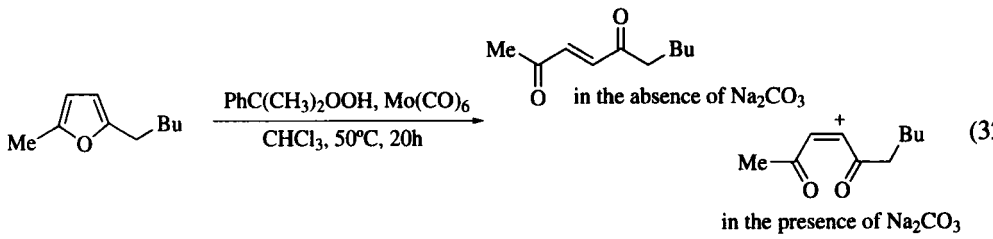
(iii) Oxidation of Enol Ethers, Furan Rings and Schiff Bases

Oxidation of 5,6,7,8-tetrahydrochroman led to cleavage of double bond to give 6-ketononanolide in 50% yield (*Eq. 31*) in presence of $(CH_3)_3COOH$ and $Mo(CO)_6$.[41] Oxidation of



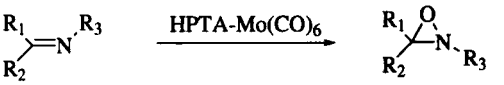
(31)

furan derivatives yielded *E*- and *Z*-enediones (*Eq. 32*) by cumene hydroperoxide and molybedenum hexacarbonyl[42] while oxidation of Schiff base with tert-amyl hydroperoxide (HPTA)



(32)

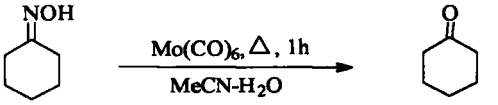
catalyzed by molybdenum hexacarbonyl or $MoCl_5$ in benzene solution gave oxaziridines in high yields (*Eq. 33*).[43]



(33)

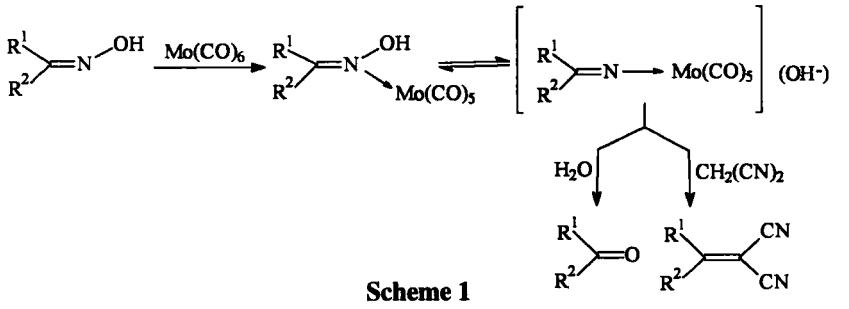
(iv) Oxidative Deoximation

The conversion of oximes to the corresponding carbonyl compounds[44] is carried out by reflux the oximes and $Mo(CO)_6$ in aqueous solvents (*Eq. 34*). The process involves initial formation of an oxime-molybdenum complex as the precursor of the subsequent nitrene complex



(34)

hydroxide which leads to carbonyl compound after hydrolysis in the medium and Knoevenagel type condensation if an anhydrous solvent is used (*Scheme 1*).

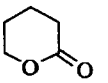


Scheme 1

e. Carbonylation Reactions

Alkyl iodides are carbonylated by molybdenum hexacarbonyl to esters in presence of fluoride ions (*Eq. 35*) and diiodides lead to high yields of corresponding lactones (*Eq. 36*).[45] Reactions also proceed with bromides. An unusual feature of this reaction is that both R groups of the ester molecule are furnished by an electrophilic reagent, while the oxygen atom appears to

$$RI \xrightarrow[THF, \Delta, 20h]{Mo(CO)_6,\ Bu_4NF,\ 3H_2O} RCOOR \tag{35}$$

$$I(CH_2)_4I \xrightarrow[THF, \Delta, 20h]{Mo(CO)_6,\ Bu_4NF,\ 3H_2O} \text{  } \tag{36}$$

come from a water molecule. In order to make reaction catalytic in Mo, methyl formate was added to the reaction medium so as to provide the stochiometric amount of carbon monoxide necessary for ester formation (*Eq. 37*). The mechanism of reaction is still not clear. Compounds

$$2RI + HCOOMe + H_2O \xrightarrow{Mo(CO)_6,\ F^-} RCOOR + 2HI + MeOH \tag{37}$$

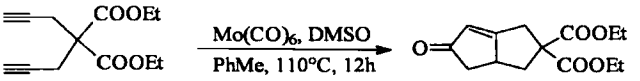
containing trichloromethyl group can be dehydrochlorinated[46] in presence of $Mo(CO)_6$ by refluxing at 140°C (*Eq. 38*).

$$Cl_3C\text{-}CH_2R \xrightarrow[140°C,\ 5h]{Mo(CO)_6,\ CHCl_3} Cl_2C{=}CHR \tag{38}$$

R = n-hexyl, $(CH_2)_3Cl$, CH_2Cl, $CHClC_5H_{11}$-n

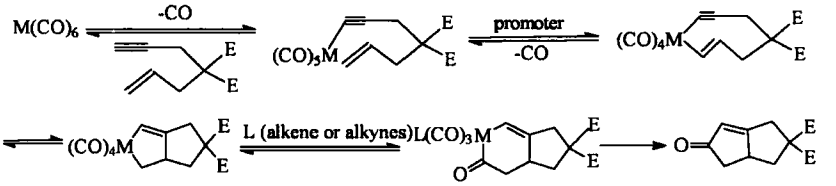
f. Pauson-Khand Reaction

The synthesis of cyclopentenones from alkynes and alkenes in either intramolecular or intermolecular manner employing dicobalt octacarbonyl is known as Pauson-Khand reaction.[47] Co-cyclization of alkynes, alkenes and CO in presence of stochiometric amount of $Mo(CO)_6$ and excess of dimethyl sulfoxide which acts as promoter is another version of Pauson-Khand reaction (*Eq. 39*). The yields of cyclopentenones are better than those obtained using $Cr(CO)_6$ or



(39)

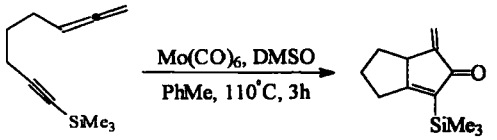
$W(CO)_6$. The reactions are believed to be proceeding by the mechanism shown in *Scheme 2*.



Scheme 2

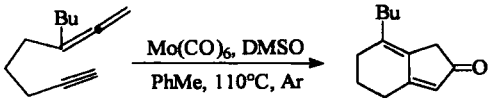
Reactions did not proceed in the absence of DMSO. Different metal carbonyls behave differently with DMSO. Chromium carbonyl did not work for this purpose and tungsten carbonyl, from which removal of CO has been difficult, yielded cyclopentenone in poor yield. $Mo(CO)_6$ provided a clean reaction to yield cyclopentenone in 76% yield. The reaction has been

extended to allenic trimethylsilyl alkynes[48] to give trimethylsilyl cyclopentenones (*Eq. 40*).



(40)

A further modification yielded the cyclopentenones fused with six membered ring (*Eqs. 41 and 42*).[49, 50]



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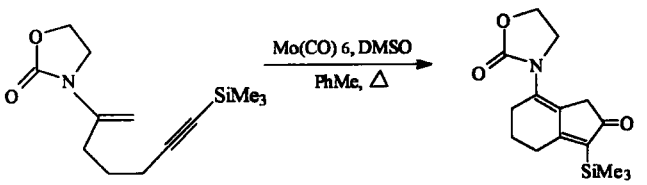
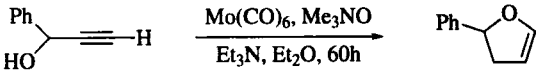


(42)

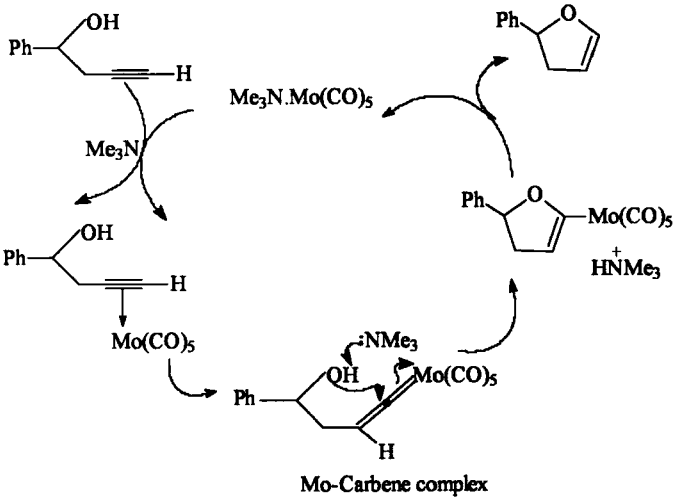
g. Synthesis of Heterocycles

Dihydrofurans (endocyclic enol ethers) have been prepared by cycloisomerization of alkynyl alcohols[57] in presence of $Mo(CO)_6$ and trimethylamine *N*-oxide (*Eq. 43*). The cyclization



(43)

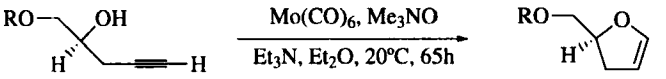
is believed to be proceeding by pathway shown in *Scheme 3*. Oxidative decarbonylation of



Scheme 3

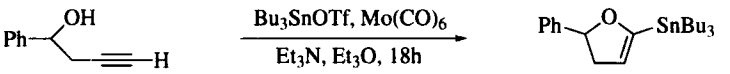
$Mo(CO)_6$ by trimethylamine *N*-oxide yields $Mo(CO)_5.Me_3N$ which carries on further reaction.

Displacement of trialkylamine ligand by the terminal alkyne group is followed by isomerization of η^2-molybdenum alkyne complex to the vinylidene carbene. The alcohol is deprotonated by Me_3N and induces cyclization to give molybdenum carbene anion. Protonation of the molybdenum carbon bond then provides the endocyclic enol ether. The method has been used to prepare chiral dihydrofurans starting from chiral alkynyl alcohols (*Eq. 44*).[52] The reaction of



(44)

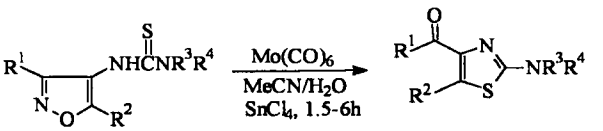
alkynols in presence of tributyltin triflate[53] gave the endocyclic α-stannyl dihydrofurans (*Eq. 45*).



(45)

h. Synthesis of Substituted 2-Aminothiazoles and Pyridines

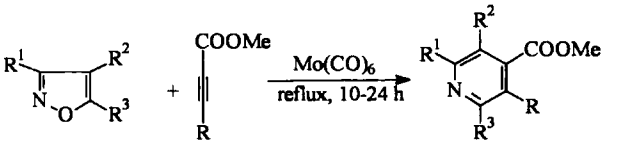
Substituted 2-aminothiazoles are synthesised by cleavage of isoxazoles at N-O bond followed by cyclization in presence of $Mo(CO)_6$ and $SnCl_4$ in aqueous acetonitrile (*Eq. 46*).[54]



(46)

R^1, R^2, R^3 = alkyl, aryl; R^4 = H, Me

Substituted isoxazoles undergo cycloaddition with acetylene derivatives across the C-4-C-5 bond in presence of hexacarbonyl molybdenum and subsequent elimination of an oxygen atom to give pyridine derivatives (*Eq. 47*).[55]

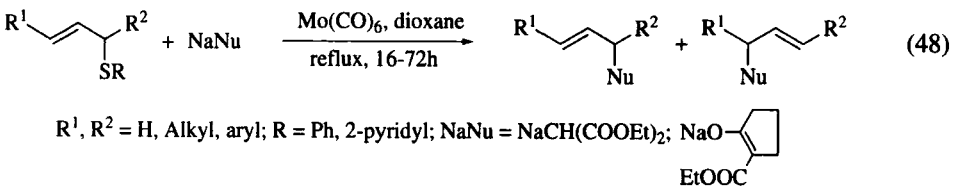


(47)

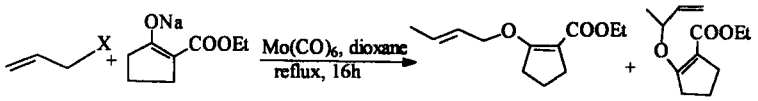
R = H, COOMe; R^1-R^3 = H, alkyl, aryl

i. Substitution Reactions

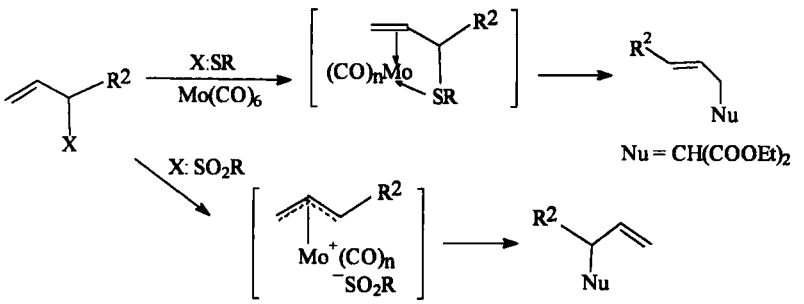
Molybdenum hexacarbonyl is a useful reagent for desulfenylative allylation of carbon nucleophiles with allylic sulfides.[56] $Mo(CO)_6$ serves as a thiophilic metal reagent for developing a new type of three-carbon homologation namely desulfenylative allylation of carbon nucleophiles with allylic sulfides. (*Eq. 48*). The ratio of the two positional isomers depends on the substituents in the allyl sulfides. The method has been extended to the displacement of sulfides, sulfones and



selenides by other nucleophiles[57] also (*Eq. 49*).

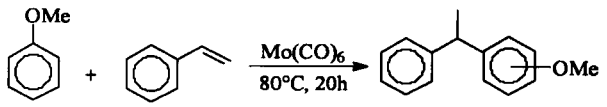


The reactivity of sulfonyl and selenenyl groups with $Mo(CO)_6$ seems to be higher than that of sulfenyl groups. The regiochemistry in nucleophilic substitution of allylic sulfones was different from both allylic sulfides and selenides. Attack of diethyl sodiomalonate on allylic sulfides and selenides occurred preferentially at the γ-position and occurred preferentially at the more substituted end of allyl unit of allylic sulfones after the desulfonylation. Nucleophilic substitution of allylic sulfones proceeded *via* allyl molybdenum complex whereas allylic sulfides and selenides did not form the corresponding π-allyl molybdenum intermediate since the coordination of sulfenyl and selenyl groups to molybdenum center was stronger than that of olefinic moiety (*Scheme 4*). Electrophilic aromatic substitution of ethers with olefins catalyzed by



Scheme 4

$Mo(CO)_6$ has also been reported in high yields (*Eq. 50*).[58]



j. Reactions of Ethers and Acid Halides

Acyclic ethers on refluxing with acid chloride in presence of $Mo(CO)_6$ in hexane,

isooctane or in absence of solvent gave esters and alkyl chloride or alkene (*Eq. 51*).[59] Cyclic

$$ROR + R'COCl \xrightarrow{Mo(CO)_6} RCl + R'COOR \quad (51)$$

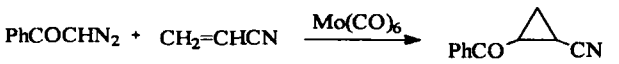
ethers under similar conditions gave halo esters and/or elimination products (*Eq. 52*) in presence

$$+ CH_3COCl \xrightarrow{Mo(CO)_6} CH_3COOCH_2CH_2CH_2CH_2Cl \quad (52)$$

of group VI metal carbonyls. The catalytic order of effectiveness is $Mo(CO)_6 > W(CO)_6 > Cr(CO)_6$. In case of unsymmetrical ethers, the alkyl chloride formed is the one derived from more highly substituted alkoxy carbon atom.

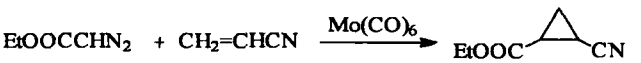
k. Cyclopropanation

$Mo(CO)_6$ catalyzes the cyclopropanation of α,β-unsaturated esters and nitriles by diazoketones and esters at 25°C (*Eqs. 53 and 54*). Molybdenum carbenes may be intermediates



$$PhCOCHN_2 + CH_2{=}CHCN \xrightarrow{Mo(CO)_6} PhCO\text{-}\triangle\text{-}CN \quad (53)$$

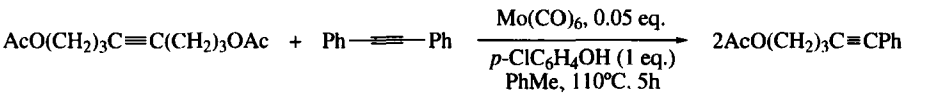
and carbene dimers are obtained in the absence of excess substrate.[60] *trans*-Substituted products are the predominant products.



$$EtOOCCHN_2 + CH_2{=}CHCN \xrightarrow{Mo(CO)_6} EtOOC\text{-}\triangle\text{-}CN \quad (54)$$

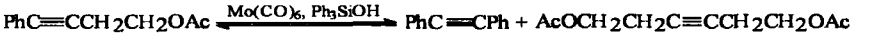
l. Metathesis

Disubstituted alkynes can be preapred[61] by using $Mo(CO)_6$ catalysed cross alkyne metathesis (*Eq. 55*). Silanol-molybdenum hexacarbonyl has been used as an efficient catalyst for



$$AcO(CH_2)_3C{\equiv}C(CH_2)_3OAc + Ph{-}{\equiv}{-}Ph \xrightarrow[\substack{p\text{-}ClC_6H_4OH\ (1\ eq.)\\ PhMe,\ 110°C,\ 5h}]{Mo(CO)_6,\ 0.05\ eq.} 2AcO(CH_2)_3C{\equiv}CPh \quad (55)$$

metathesis of functionalized alkynes under microwave irradiation (*Eq. 56*).[62]

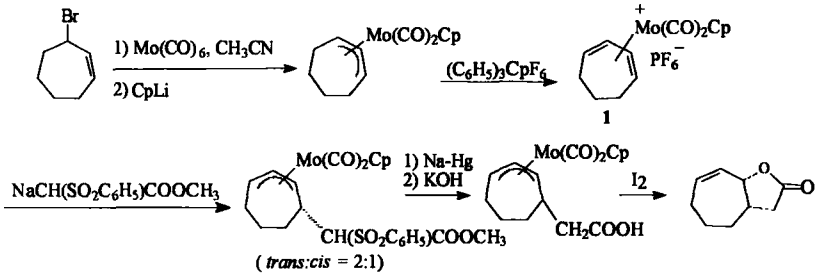


$$PhC{\equiv}CCH_2CH_2OAc \xrightleftharpoons{Mo(CO)_6,\ Ph_3SiOH} PhC{\equiv}CPh + AcOCH_2CH_2C{\equiv}CCH_2CH_2OAc \quad (56)$$

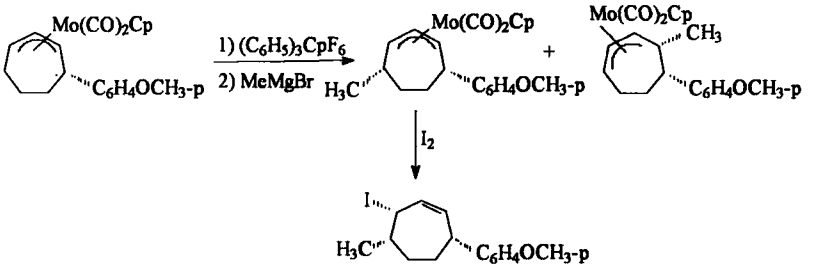
2. Preparation and Reactions of Cycloheptadienyl-Mo⁺(CO)₂CpPF₆⁻

The complex[63] is prepared by treatment of allylic cycloheptenyl bromide with $Mo(CO)_6$ followed by cyclopentadienyl lithium. This complex reacts with carbon nucleophiles to give

products of stereoselective allylic substitution as shown in *Scheme 5*. Reaction of a monosubstituted complex with a second nucleophile can also proceed stereo and regioselectively with preferential attack at the other allylic position to give *cis*-disubstituted complex (*Eq. 57*).



Scheme 5



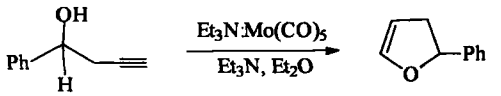
(57)

3. Et_3N:$Mo(CO)_5$

Et_3N:$Mo(CO)_5$[64] is prepared by photolysis of $Mo(CO)_6$ in a mixture of diethyl ether and triethylamine (Rayonet lamp, 350 nm, pyrex filter) (*Eq. 58*).

$$Mo(CO)_6 \xrightarrow[Et_3N,\ Et_2O]{hv\ (pyrex\ filter)} Et_3N{:}Mo(CO)_5 \qquad (58) \qquad (58)$$

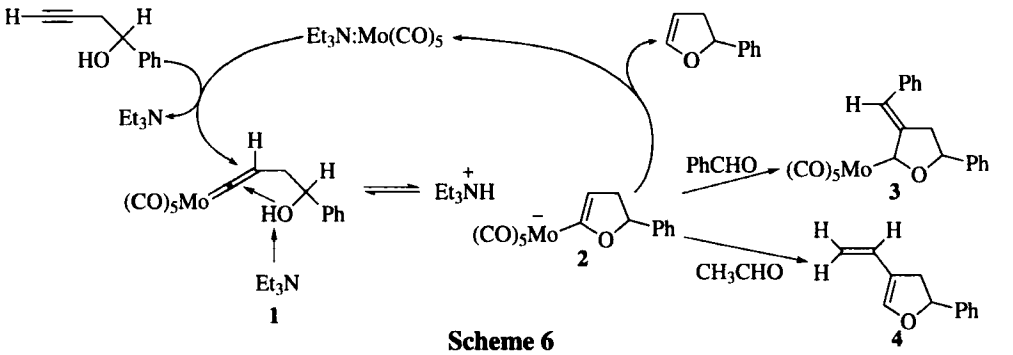
Addition of an alkynol (dark reaction) to Et_3N:$Mo(CO)_5$ in ether followed by stirring for 18 h gave a dihydrofuran.[65] The reaction requires the presence of a tertiary amine (*Eq. 59*).



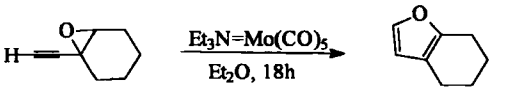
(59) (59)

The mechanism of formation of the dihydrofuran (*Scheme 6*) involves the formation of molybdenum carbene anion (**2**) as a catalytic intermediate which can be isolated as aldol condensation-dehydration products (**3**) and (**4**).

This reaction has been extended to epoxyalkynes to yield furans[64] (*Eq. 60*). Et_3N:$Mo(CO)_5$ catalyzed isomerization to furans proceeded by way of concerted rearrangement to epoxy vinylidenecarbenes to the cyclic α,β-alkenyloxacarbene intermediates. Vinylogous deprotonation of carbene intermediate and subsequent protonation of the molybdenum furan bond (possibly by reductive elimination of furyl molybdenum hydride) yielded substituted furans

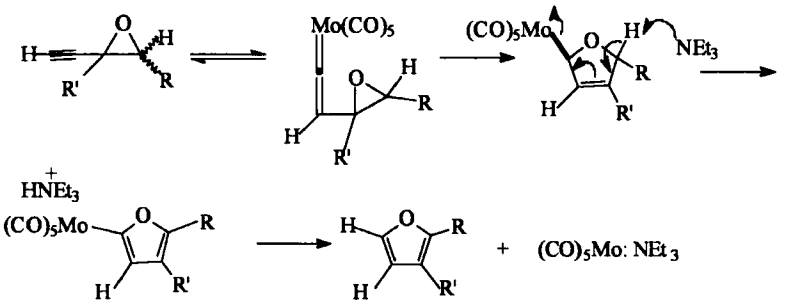


Scheme 6



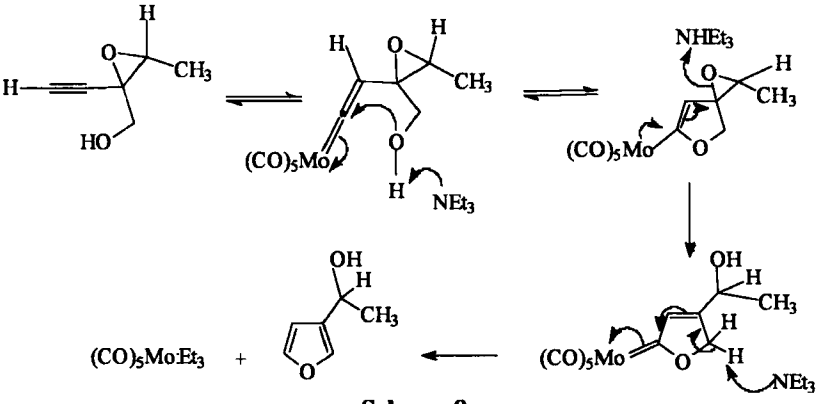
(60)

(*Scheme 7*). Primary homopropargylic alcohols such as 3-butyn-1-ol and enyol are generally



Scheme 7

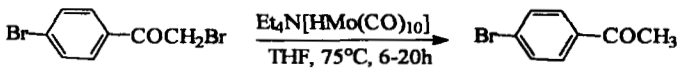
unreactive under Et_3N:$Mo(CO)_5$ catalysis but relief of strain energy gained by epoxide opening drives the formation of furan (*Scheme 8*).



Scheme 8

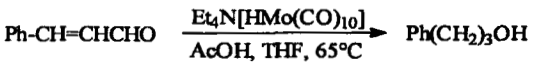
4. $Et_4N[\mu\text{-}HMo_2(CO)_{10}]$

Phenacyl halides are reduced by $Et_4N[\mu\text{-}HMo_2(CO)_{10}]$ in THF at 75°C to the corresponding acetophenones[66] in reasonably good yields (*Eq. 61*). Similarly aldehydes are reduced to



(61)

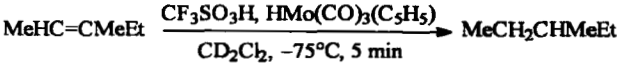
alcohols selectively in the presence of ketones, α,β-unsaturated esters. Ketones are reduced at the C-C bond only by $Et_4N[\mu\text{-}HMo_2(CO)_{10}]$ whereas α,β-unsaturated aldehydes[67] are reduced both at the double bond and the aldehyde to yield the alcohol (*Eq. 62*).



(62)

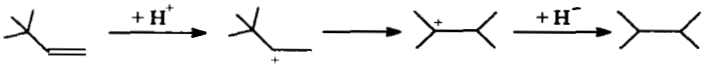
5. $HMo(CO)_3C_5H_5$

$HMo(CO)_3C_5H_5$ functions as a hydride donor in the stochiometric hydrogenation of hindered alkenes.[68] Therefore tetrasubstituted, trisubstituted and 1,1-disubstituted alkenes are rapidly hydrogenated in high yields at low temperature (–75°C) using $CF_3SO_3H/HMo(CO)_3C_5H_5$ (*Eq. 63*). The hydrogenation is believed to proceed (*Scheme 9*) by initial formation of a carbocation by protonation of the alkene, followed by trapping of the carbocation by the metal hydride to



(63)

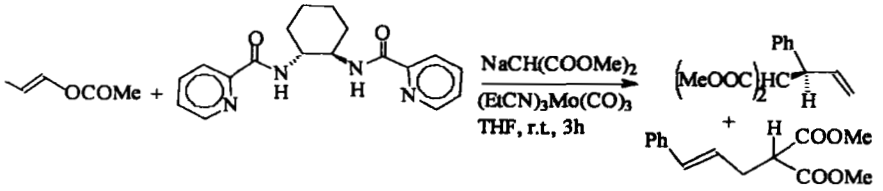
yield reduced product. Evidence for carbocation intermediate comes from characteristic rearrangement. Ionic hydrogenation of *t*-butyl ethylene produces 2,3-dimethylbutane since the initially formed secondary carbocation rearranges to a more stable tertiary carbocation by methyl migration. Only those alkenes which can form a tertiary carbocation (by protonation or protonation followed by rearrangement) have been successfully hydrogenated by this method.



Scheme 9

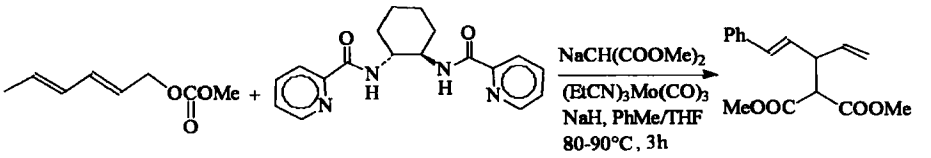
6. $(EtCN)_3Mo(CO)_3$

The catalyst,[69] generated by stirring a 1:15 mixture of $(EtCN)_3Mo(CO)_3$:ligand in THF at 60°C [where the ligand is *trans*-1,2-(2-pyridylcarboxamido)cyclohexane], induces asymmetric alkylation of methyl cinnamate with dimethyl sodiomalonate at room temperature (*Eq. 64*).



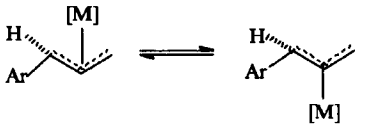
(64)

5-Phenylpentadienyl methyl carbonate and dimethyl sodiomalonate also yielded alkylation product at 80-90°C (*Eq. 65*).[70]



(65)

Methyl cinnamate is achiral and the catalyst may differentiate the enantiotopic faces leading preferentially to π-allyl molybdenum complex. The two diastereomeric π-allyl molybdenum complexes are in dynamic equilibrium in which the enantio-differentiation occurs by



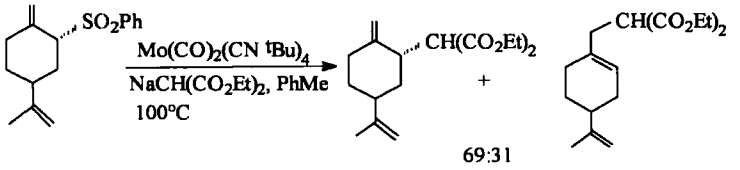
preferential nucleophilic attack on either complex. When a chiral substrate is used, it can differentiate between the two possibilities. Electron-deficient pyridine rings and bulkier naphthalene substrates gave good selectivities. Increasing the steric bulk of nucleophile led to very good results with both carbocyclic and heterocyclic substrates. Increasing the steric bulk further by using allyl malonate as the nucleophile did slow the reaction, but regio- and enantioselectivities were still excellent.

7. $Mo(CO)_2(CN^tBu)_4$

The molybdenum isonitrile complex[71] was prepared by treatment of $Mo(CO)_6$ with tert-butylisonitrile and cobalt chloride which promotes carbonyl substitution (*Eq. 66*). It is used as a

$$Mo(CO)_6 + {}^tC_4H_9NC \xrightarrow[\text{PhMe, 111°C}]{\text{0.1 eq } CoCl_2.2H_2O} Mo(CO)_6(CN\ {}^tBu)_{6-n} \quad n = 2\text{-}5 \qquad (66)$$

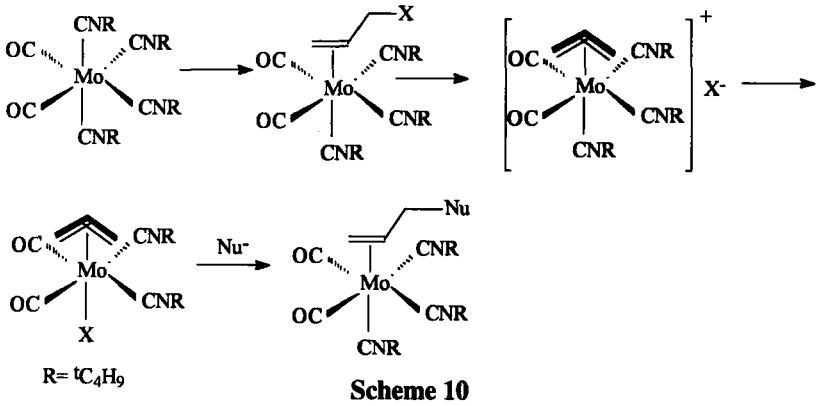
catalyst for alkylations of allyl sulfones with malonate anion at the more substituted allylic carbon (*Eq. 67*). The mechanism of the substitution is shown in *Scheme 10*.



(67)

8. $Mo(CO)_3(CN^tBu)_3$

$Mo(CO)_3(CNBu^t)_3$[72] has been used as catalyst for hydrostannation of propargylic esters of amino acids, for the regioselective synthesis of α-stannylated allylic esters which are suitable substrate for chelate Claisen rearrangements (*Eq. 68*).

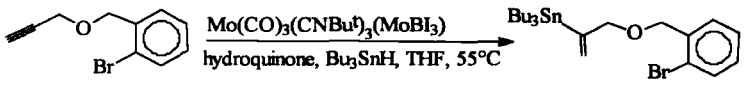


Scheme 10

$$ZNHCH_2COOCH_2C{\equiv}CH \xrightarrow[Bu_3SnH,\ PhMe,\ 50°C]{Mo(CO)_3(CNBu^t)} ZNHCH_2COOCH_2C(SnBu_3){=}CH_2 \qquad (68)$$

9. $Mo(CO)_3(CN^tBu)_3(MoBI_3)$

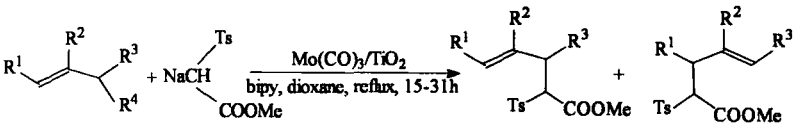
$Mo(CO)_3(CN^tBu)_3(MoBI_3)$[73] was also found to be a suitable catalyst for the regioselective hydrostannation of several types of alkynes in presence of hydroquinone and Bu_3SnH, preferentially giving rise to the α-stannylated products (*Eq. 69*).



(69)

10. $Mo(CO)_3/TiO_2$

Titanium oxide supported molybdenum carbonyl is used for selective monoallylation of methyl *p*-tolylsulfonylacetates[74] using allylic acetates or carbonates in refluxing dioxane (*Eq. 70*). The reaction required both 2,2'-bipyridyl as a ligand and sodium hydride as a base for preparation of the salt of methyl *p*-tolylsulfonylacetates.



(70)

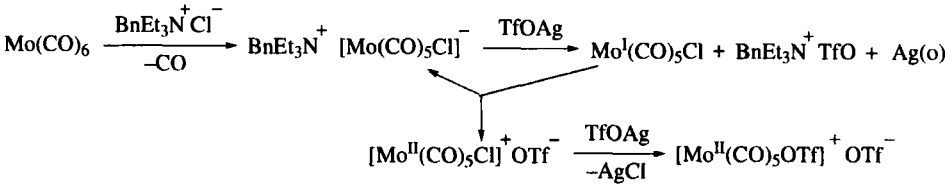
R^1–R^3 = H, alkyl, aryl; R^4 = OAc, OCOMe

The reactivity of the allylic acetates was less than that of the corresponding allylic carbonates. Monoallylation occurred selectively without diallylation. In substrates containing both an allylic acetate and an allylic carbonate moiety, allylation occurred chemoselectively at the carbonate moiety and regioselectively at the less substituted end of the allyl unit (*Eq. 71*).

$$\begin{array}{c} MeCOOCH_2CH{=}CHCH_2OCOOMe \\ NaCH(SO_2Me)(CO_2Me) \;\Big|\; \begin{array}{l} Mo(CO)_3/TiO_2,\ bpy \\ dioxane,\ 20\ h \end{array} \\ MeCOOCH_2CH{=}CHCH_2CH(SO_2Me)(CO_2Me) \end{array} \qquad (71)$$

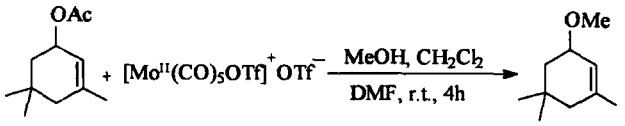
11. $[Mo(CO)_5OTf]^+OTf^-$

$[Mo(CO)_5OTf]^+OTf^-$ is generated *in situ* by treatment of $Mo(CO)_6$ with $PhCH_2(Et)_3N^+Cl^-$ and CF_3SO_3Ag (3 equiv.) as shown in *Scheme 11*.[75] It is used to catalyze the



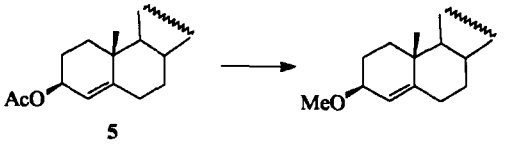
Scheme 11

substitution of allylic acetates with methanol in presence of CH_2Cl_2 and DMF at room temperature with overall retention of configuration (*Eq. 72*). The stereochemistry of this allylic

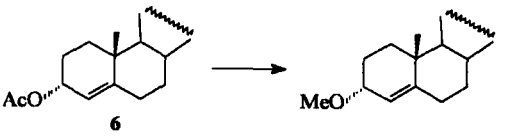


(72)

substitution was elucidated with the aid of epimeric acetates **5** and **6**. In both cases, predominant retention of configuration was observed (*Eqs. 73 and 74*).



(73)



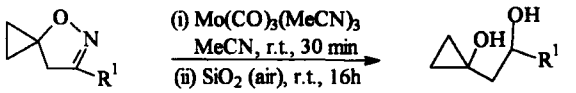
(74)

These results exclude a common intermediate such as an uncoordinated allylic carbocation and suggest that molybdenum is involved in a facially selective coordination. Retention of configuration occurs due to double inversion.

12. $(MeCN)_3Mo(CO)_3$

Tricarbonyltris(acetonitrile)molybdenum[76] is prepared by heating $Mo(CO)_6$ in anhydrous CH_3CN for 4 h (*Eq. 75*). *1*-(2-Oxoalkyl)cyclopropanols are efficiently synthesized from isoxazoline-5-spirocyclopropane by selective N-O cleavage in presence of silica gel at room temperature (*Eq. 76*).

(75)

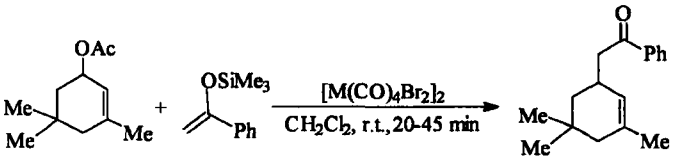


(76)

R^1 = Ph, $PhCH_2$, n-C_6H_{13}, $(MeOOC)_2CH(CH_2)_2$

13. $[Mo(CO)_4Br_2]_2$

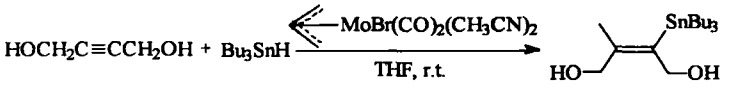
The molybdenum (II) complex $[Mo(CO)_4Br_2]_2$[77] has been found to catalyze the C-C bond-forming allylic substitution with silyl enol ethers derived from β-dicarbonyls or from simple ketones, aldehydes and esters under mild conditions (room temperature, 1-2 h) (*Eq. 77*).



(77)

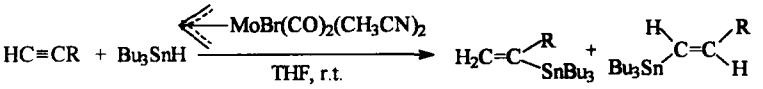
14. Bromo-π-allyl Complex of Molybdenum $\Leftarrow MoBr(CO)_2(CH_3CN)_2$

Tributyltin hydride adds instantaneously to various alkynes at room temperature in the presence of catalytic amount of bromo-π-allyl complex of molybdenum[78] to give the corresponding vinylstannanes in good yields (*Eq. 78*). Molybdenum-catalysed hydrostannation



(78)

reactions are *syn* additions, leading to vinylstannanes of exclusively *E*- configuration. Terminal acetylenes usually give a mixture of α- and β-regioisomers (*Eq. 79*).

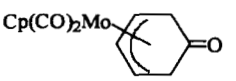


(79)

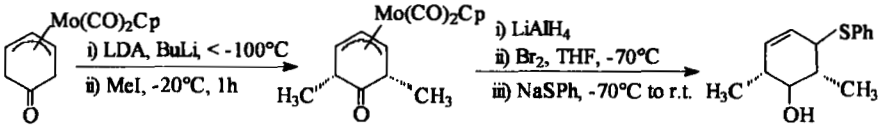
R = n-C_6H_{13}, n-C_4H_9, $CH(n\text{-}C_5H_{11})_2$

Branching at the C adjacent to a triple bond favors formation of the β-adduct. Total regioselectivity toward the formation of the β-regioisomer was achieved with 3-pentyl-1-octyne which bears a secondary substituent on the acetylenic bond. However, in the case of the secondary propargyl alcohol, *1*-octyn-3-ol, increasing the steric bulk of the substituent through *O*-tert-butyldimethyl silylation did not improve the regioselectivity.

15. (5-oxocyclohexenyl)Mo(CO)$_2$Cp

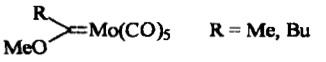


Stereospecifically substituted cyclohexane derivatives have been prepared by alkylation of (5-oxocyclohexenyl)Mo(CO)$_2$Cp.[79] (5-Oxocyclohexenyl)Mo(CO)$_2$Cp is used as a template to control stereochemistry and regiochemistry of alkylation (*Eq. 80*).

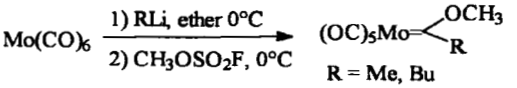


(80)

16. Molybdenum Carbene Complex

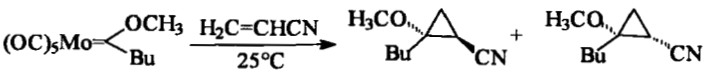


The molybdenum carbene complex[80] is prepared by reaction of alkyllithium with Mo(CO)$_6$ followed by methylation with CH_3OSO_2F at 0°C (*Eq. 81*). These carbenes are useful



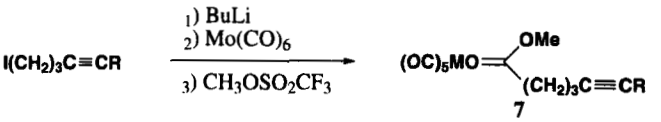
(81)

for the cyclopropanation of the electron-poor olefins.[80] The reaction occurs under mild conditions and at a faster rate with molybdenum carbene than with Cr or W derived complexes (*Eq. 82*). This cyclopropanation has been used to trap a molybdenum vinyl carbene generated by



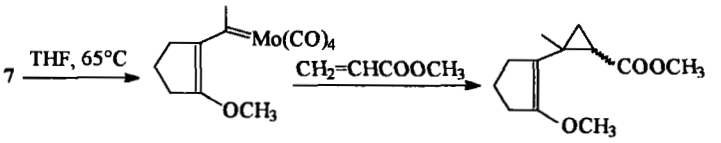
(82)

intramolecular cyclization of the carbene complex (**7**) of the alkyne (*Eq. 83*). The reaction of



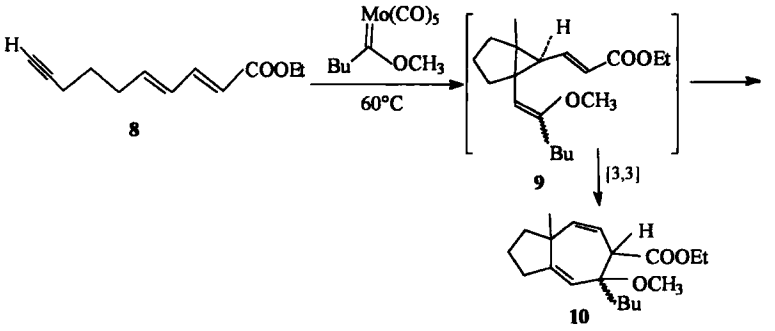
(83)

carbene **7** with methyl acrylate in THF at 65°C provided vinylcyclopropane in 71% yield (*Eq. 84*).[81] This reaction has been extended to dienyne **8**. Reaction of **8** with butylmethoxymolybdenum carbene at 60°C resulted in the formation of divinylcyclopropane **9** which by a



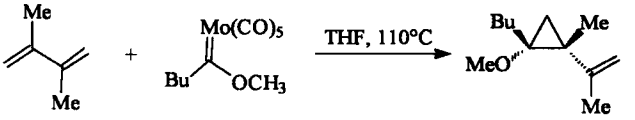
(84)

[3,3]-sigmatropic rearrangement, yielded hexahydroazulene **10** (*Eq. 85*).[82] The reaction has also been extended to unactivated 1,3-dienes.[83] The reaction was relatively slow for substituted



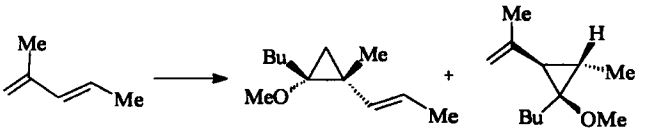
(85)

dienes (*Eq. 86*). High degrees of both regio- and diastereoselectivity were observed for this

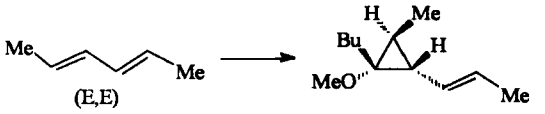


(86)

process (*Eq. 87*). Chemoselectivity was observed for the *E,E* isomer of 2,4-hexadiene to vinylcyclopropane but with the *E,Z* isomer, no reaction was observed (*Eq. 88*).

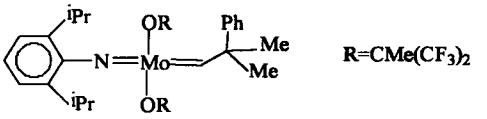


(87)



(88)

II. SCHROCK'S CATALYST:Mo(CHCMe$_2$Ph)(NAr)[OCMe(CF$_3$)]$_2$



Schrock's catalyst is air and moisture sensitive and is prepared as shown in the following equation (*Eq. 89*).[84]

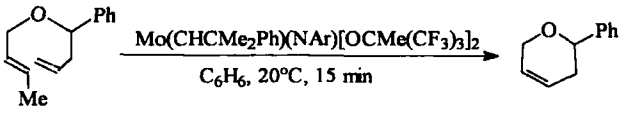
$$Mo(CHCMe_2Ph)(NAr)(OTf)_2(dme) + 2\ LiOR \xrightarrow[-30°C]{ether} Mo(CHCMe_2Ph)(NAr)(OR)_2 \quad (89)$$

Ar = 2,6-(^{i}Pr)$_2$C$_6$H$_5$; OR = OCMe(CF$_3$)$_2$

1. Cyclizations-Olefin Metathesis

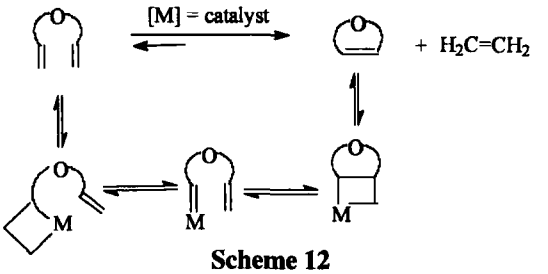
a. Synthesis of Unsaturated Oxygen Heterocycles

Schrock's catalyst has been employed in the synthesis of unsaturated oxygen heterocycles involving ring closing metathesis of a diene-ether[85] to generate a cyclic and a acyclic olefin (*Eq. 90*). The reaction is believed to proceed by molybdenum carbene complex as shown in



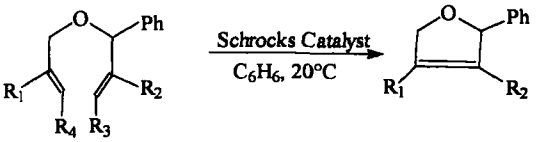
(90)

Scheme 12. Trisubstituted and tetrasubstituted alkenes have also been prepared (*Eq. 91*).



Scheme 12

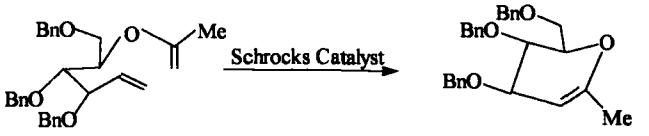
Schrock's catalyst has relatively low acidity which prevents the decomposition of allylic ethers. Schrock's catalyst has also been used for the synthesis of C-1 glycosides by an olefin enol ether



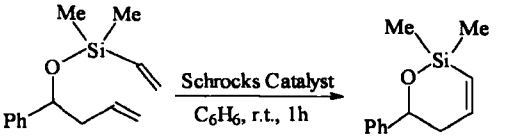
(91)

$R_2 = R_3 = R_4 = Me, R_1 = H;\quad R_1 = R_2 = R_3 = Me, R_4 = H$

metathetical coupling approach[86] and silicon assisted cross-coupling reaction *via* sequential ring closing metathesis[87] (*Eqs. 92 and 93.*). Substituted azetidinones also undergo alkene metathesis

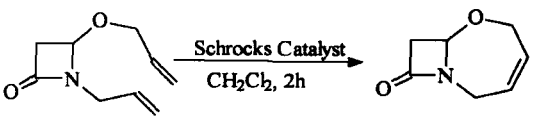


(92)



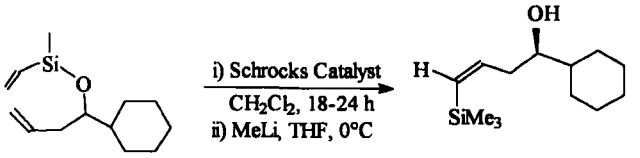
(93)

in presence of Schrock's catalyst to give β-lactams (*Eq. 94*).[88] It has also been used for *in situ*



(94)

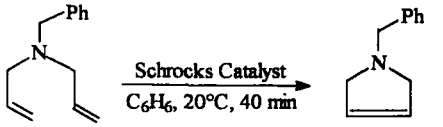
ring opening protocol for the regiospecific generation of functionalized (E)-disubstituted homoallylic alcohol (*Eq. 95*).[89]



(95)

b. Synthesis of *N*-Heterocycles

Unsaturated nitrogen heterocycles have also been synthesised by ring-closing metathesis of acyclic diene amines in the presence of Schrock's catalyst (*Eq. 96*).[90] The reaction

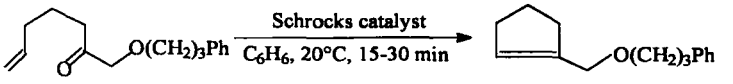


(96)

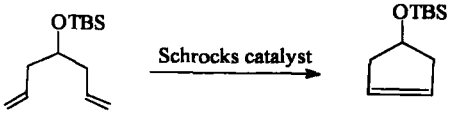
takes place *via* molybdenum carbenoids as shown in *Scheme 12*. Metathesis of monosubstituted olefins by Schrock's catalyst is faster than that of disubstituted olefins.

c. Synthesis of Cycloalkenes

Molybdenum alkylidene complexes catalyze olefin metathesis-carbonyl olefination reactions of ketones to yield cycloalkenes in good yields and this olefination strategy has been useful to synthesise unsaturated five-, six- and seven-membered rings (*Eqs. 97 and 98*).[91] The

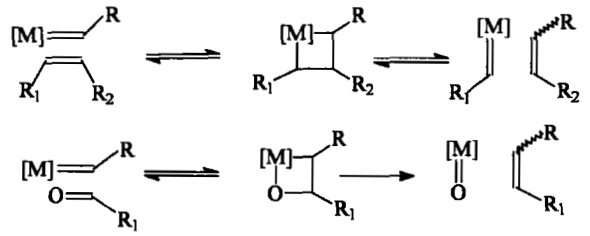


(97)

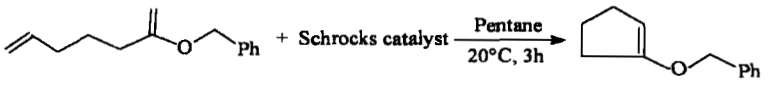


(98)

possible reaction pathways are shown in *Scheme 13*. Even acyclic enol ethers have been converted into five- or six-membered cyclic enol ethers with molybdenum alkylidene complex (*Eq. 99*).[92]



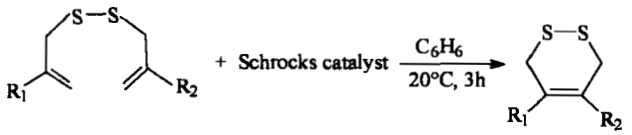
Scheme 13



(99)

d. Unsaturated Cyclic Disulfides

Ring closing metathesis of disulfide[93] containing substrates gives poor yields of products (*Eq. 100*) as compared to oxygen containing substrate due to two factors: (a) the additional

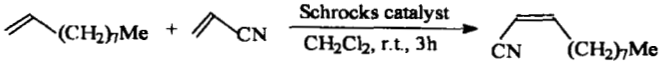


(100)

torsional strain imposed in the heterocyclic ring by the dihedral angle of the disulfide moiety (90°) and (b) poisoning of catalyst by the disulfide moiety. Substitution at the β-position to the sulfur atom inhibits the ring closing metathesis reaction much more than substitution at the position γ to S atom. In case of substitution at the β-position to both S atoms, no ring closing metathesis takes place. These results show that there is difficulty in forming tri- and tetra-substituted double bonds. Since more highly substituted olefins are generally more thermodynamically stable than less substituted olefins, the observed trend is influenced by kinetic parameters.

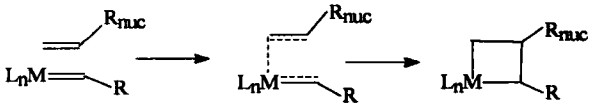
2. Acrylonitrile Cross-Metathesis

Cross metathesis of acrylonitrile and a second olefin[94] with Schrock's molybdenum catalyst gave a new substituted acrylonitrile and alkene (*Eq. 101*). Acrylonitrile does not undergo



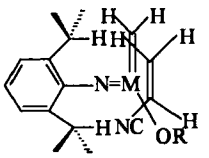
(101)

self-metathesis due to its low nucleophilicity. This cross-metathesis requires the olefin to be electron rich. Selectivity and yields are lower for olefins bearing electron-withdrawing substituents. This is consistent with the idea that the alkyl substituted olefin is reacting as a nucleophile with an electrophilic molybdenum centre (*Scheme 14*). High cross-metathesis selectivity arises when



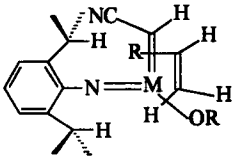
Scheme 14

one olefin in a reacting pair possesses a π substituent and the other olefin bears a small, electron-rich non-conjugated substituent. The incoming olefin adds to the CNO face of iminoalkylidene intermediate and the *syn*-cyano substituted alkylidene is formed in the alkylidene donation state of the catalytic process. A *cis*-olefin results from the reaction of $RCH{=}CH_2$ with *syn*-Mo=CHCN which minimizes steric interactions with the equatorial alkoxide or with *anti*-Mo=CHCN in a manner which minimizes steric interactions with the imido ligand.



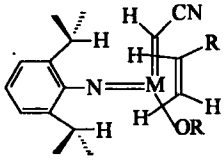
methylene-*syn* rotomer

11



syn rotomer-*cis* olefin

12

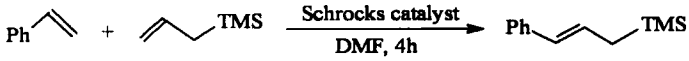


anti rotomer-*cis* olefin

13

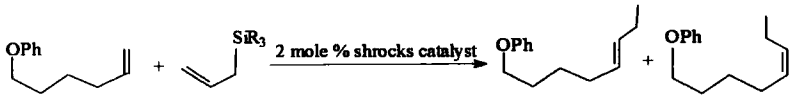
3. Preparation of Allyl Silanes

Allyltrimethylsilanes coupling with π-substituted terminal olefins[95] proceeds in excellent yields and with high selectivity in the presence of Schrock's molybdenum catalyst (*Eq. 102*).



(102)

Metathetical coupling of allyltrimethylsilane with small alkyl-substituted olefin is not highly selective since the olefin does not possess good alkylidene-stabilizing substituents, and, with bulky substituents, still smaller level of selectivity is observed. Increasing the size of the alkyl groups on the allyltrialkylsilane reagent can increase *trans* selectivity (*Eq. 103*).

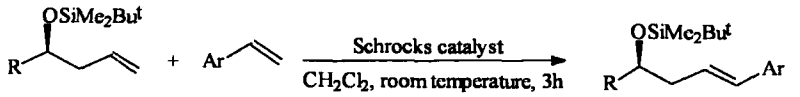


(103)

R = Me 2.6:1; R = ^{i}Pr 7.6:1

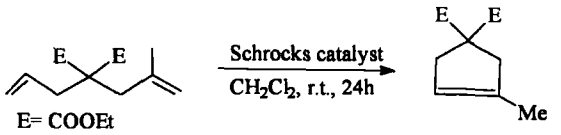
Hyperconjugative C-Si electron donation from the CH_2SiMe_3 substituent of allyl- trimethylsilane should enhance the nucleophilicity but have little or no effect on alkylidene stability. Thus allyltrimethylsilanes undergo selective cross metathesis with π-substituted olefins such as styrene or acrylonitrile. Cross metathesis of homoallylic silyl ethers with a variety of para substituted

styrenes at room temperature using 1 mol % of catalyst[96] yielded *trans* disubstituted homoallylic alcohols exclusively (*Eq. 104*).



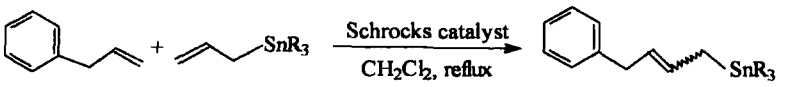
(104)

Mo carbene complex-Schrock's catalyst system has been used in the formation of trisubstituted and tetrasubstituted olefins[97] *via* ring closing metathesis of *gem*-disubstituted olefins (*Eq. 105*). Other examples of cross metathesis include reactions of olefins with stannyl



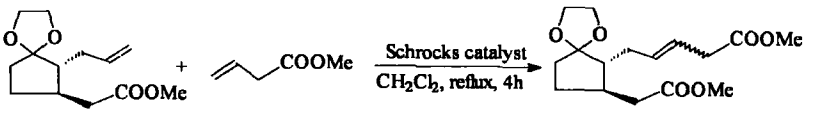
(105)

olefins (*Eq. 106*)[98] and allyl esters (*Eq. 107*).[99]



(106)

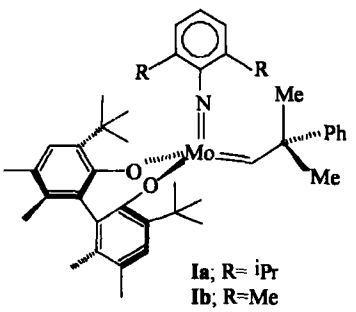
R= Ph, 74% E/Z 1:2; R=Bu 55% E/Z 1:4



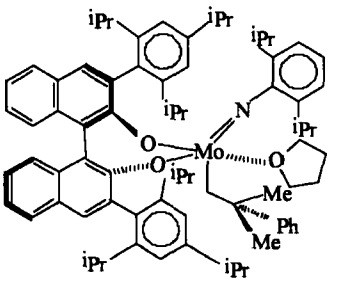
(107)

E/Z 2:1

4. Asymmetric Ring Closing Olefin Metathesis by Ia, Ib, II

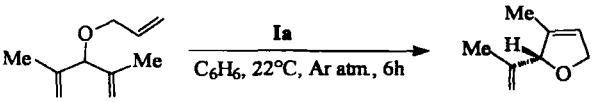


Ia; R= ^{i}Pr
Ib; R=Me



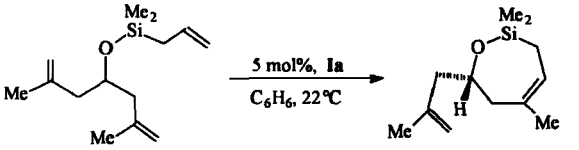
II

Ia and polymer-supported, recyclable chiral analog of **Ia** have been used for efficient and enantioselective desymmetrization reactions that lead to the formation of chiral furans with high degrees of optical purity by ring-closing olefin metathesis (*Eq. 108*).[100,101] Enantioselective



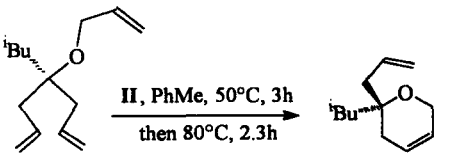
(108)

synthesis of seven-membered ring oxygen-containing unsaturated heterocycles has also been achieved by Mo-catalysed (**Ia**) asymmetric ring closing metathesis of trienes (*Eq. 109*).[102]

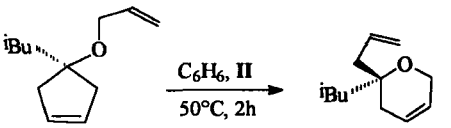


(109)

Mo-catalyst **II** has been also used for the enantioselective synthesis of unsaturated cyclic tertiary ethers by olefin metathesis (*Eqs. 110 and 111*)[103].



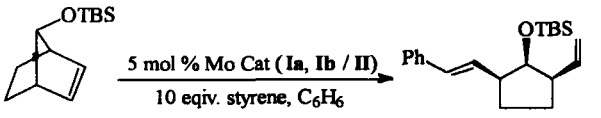
(110)



(111)

5. Asymmetric Ring Opening/Cross Metathesis by Ia, Ib, II

Mo-catalyzed asymmetric ring opening/cross metathesis with norbornene and styrene in the presence of **Ia**, **Ib** and **II** resulted in the formation of functionalized cyclopentyl diene in > 98% ee apart from substantial amounts of poly(norbornene), even in the presence of excess styrene. The enantioselective cleavage of norbornyl alkenes is followed by an intermolecular cross metathesis (*Eq. 112*) with a terminal olefin partner.[104,105]



(112)

III. BENZYLTRIETHYLAMMONIUM TETRATHIOMOLYBDATE: $(PhCH_2NEt_3)_2MoS_4$

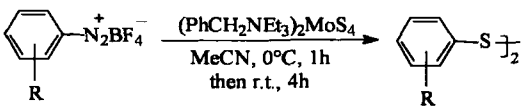
This reagent, which is soluble in organic solvents, has found many applications in organic synthesis. It is a useful reagent for sulfur transfer and also acts as a reducing agent.

1. Reactions of Halides

Benzyltriethylammonium tetrathiomolybdate is a useful reagent which readily reacts with variety of alkyl halides in CH_2Cl_2 at room temperature to afford the corresponding alkyl disulfides in high yields (*Eq. 113*).[106] Aryl disulfides can be prepared from aromatic precursors

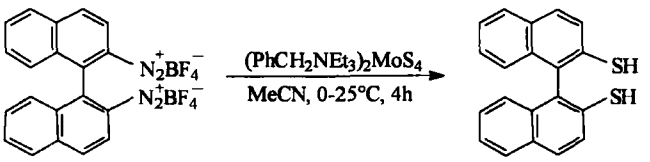
$$PhCH_2Cl \xrightarrow[CHCl_3,\ 8h]{(PhCH_2NEt_3)_2MoS_4} PhCH_2SSCH_2Ph \qquad (113)$$

without going through the intermediacy of thiols; from relatively stable aryl-diazonium fluoroborate[107] under anhydrous conditions with one equivalent of benzyl-triethylammonium tetrathiomolybdate in acetonitrile at 0-25°C (*Eq. 114*). Diazonium fluoroborate derived from



(114)

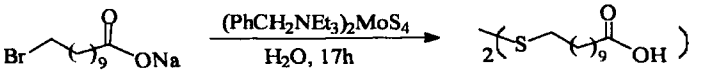
binaphthylamine reacted to yield 1,1'-binaphthalene 2,2'-dithiol as the only product (*Eq. 115*); no



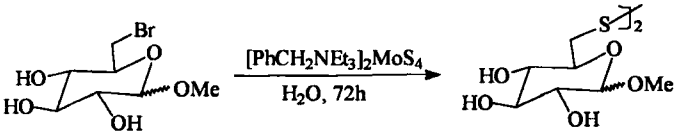
(115)

dimerization was observed. The mechanism of sulfur transfer reactions remains unclear.

Reactions of a number of alkyl halides with tetrathiomolybdate in water also afforded the corresponding disulfides in good yields. Substrates containing carboxyl group posed problems wherein the decomposition of the reagent is predominant. In order to overcome this problem, the reactions were carried in aqueous medium (*Eqs. 116 and 117*).[108]

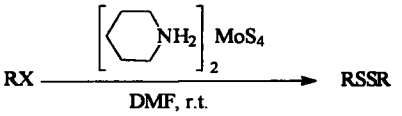


(116)



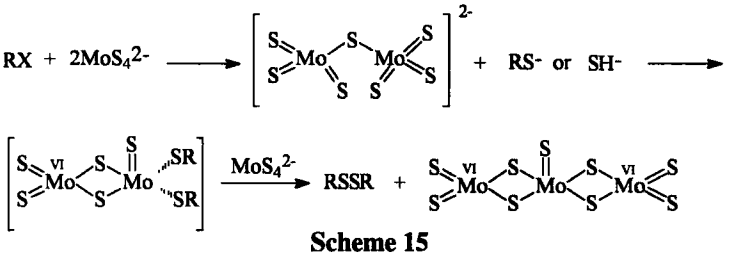
(117)

Reactions of alkyl halides with piperidinium tetrathiomolybdate in DMF at room temperature also yielded the corresponding disulfide in good yields (*Eq. 118*).[109] Benzyl bromide



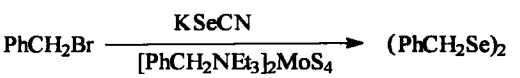
(118)

and benzyl chloride gave the same mercaptan whereas benzyl iodide afforded the disulfide as the exclusive product in high yield. Reactions are proposed to proceed as shown in *Scheme 15*.



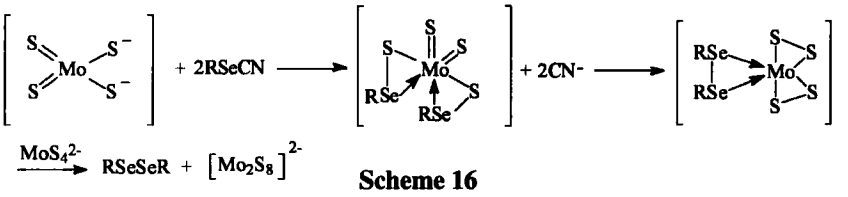
Scheme 15

A variety of benzylic halides have been reported to undergo reductive coupling to diselenides in presence of KSeCN and benzyltriethylammonium tetrathiomolybdate under mild conditions.[110] The coupling was suggested to be proceed *via* benzylselenocyanates generated *in situ* (*Eq. 119*). Reducible groups like nitro, cyano, keto and esters are not affected. The following



(119)

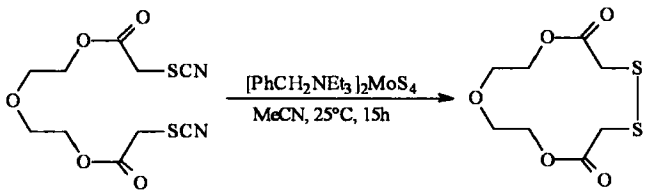
pathway (*Scheme 16*) has been proposed.



Scheme 16

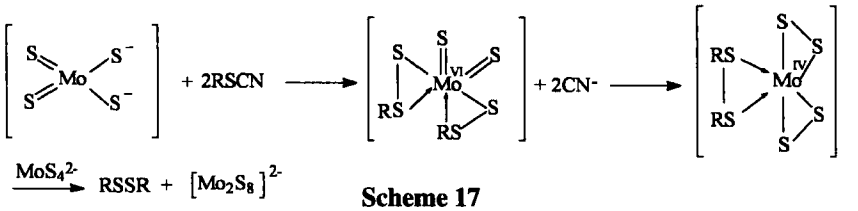
Attack of MoS_4^{2-} on selenium of selenocyanate lead to a mononuclear molydenum complex. This is followed by electron transfer from a sulfur ligand to Mo^{VI} to produce Mo^{IV} species. Further reaction with MoS_4^{2-} results in the formation of alkyl diselenides and $Mo_2S_8^{2-}$.

Reductive dimerization of organic thiocyanates assisted by benzyltriethylammonium tetrathiomolybdate led to the formation of corresponding disulfides in high yields (*Eq. 120*).[111]



(120)

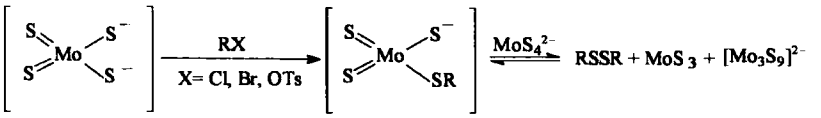
The method was employed to prepare macrocyclic rings. In the reaction of organic thiocyanates, tetrathiomolybdate does not act as sulfur transfer agent but rather as a reagent which mediates reductive dimerization as shown in *Scheme 17*.



Scheme 17

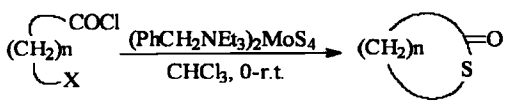
The attack of $[MoS_4]^{2-}$ on the sulfur of thiocyanate yields mononuclear molybdenum species with two disulfide ligands. Subsequently there is induced electron transfer from S^{2-} to Mo(VI) to produce Mo(IV) species. Further reaction of Mo(IV) species with MoS_4^{2-} leads to the formation of organic disulfide and $[Mo_2S_8]^{2-}$. This process involves a net two electron oxidation. Reaction of thiocyanate with tetrathiomolybdate does not involve the formation of thiol and its subsequent oxidation to disulfide.

In contrast, the mechanism of sulfur transfer in the reactions of alkyl halides and tosylates with tetrathiomolybdate is not fully understood. It is believed that alkylation of Mo-S bond is the key step which triggers an internal redox reaction with sulfur transfer leading to the formation of alkyl disulfide (*Eq. 121*).



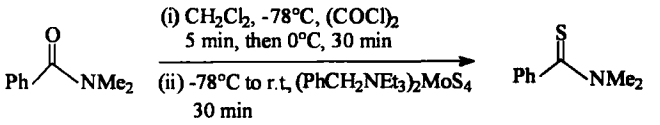
(121)

Intramolecular thiolactonization mediated by tetrathiomolybdate has been reported in the reactions of ω-haloacid chlorides (*Eq. 122*).[112] It is not a useful method to synthesize macrocyclic thiolactones due to large difference in reactivity of the two functional groups namely, halo



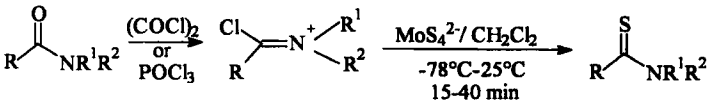
(122)

and acid chloride with tetrathiomolybdate. Tetrathiomolybdate has been reported as a thionating reagent for the conversion of amides and lactams to thioamides and thiolactams (*Eq. 123*).[113]



(123)

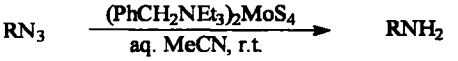
Since the electrophilicity of the carbonyl carbon in amides is low, they do not react with tetrathiomolybdate. The reaction of tetrathiomolybdate with amides and lactams in the presence of Lewis acid such as $CoCl_2$, $BF_3 \cdot Et_2O$ led to the decomposition of the reagent. When the amides and lactams were treated with $(COCl)_2$ or $POCl_3$ in CH_2Cl_2 to generate the chloroiminium salts *in situ*, they reacted readily with tetrathiomolybdate (*Scheme 18*) to afford the corresponding thioamides and thiolactams in excellent yields.



Scheme 18

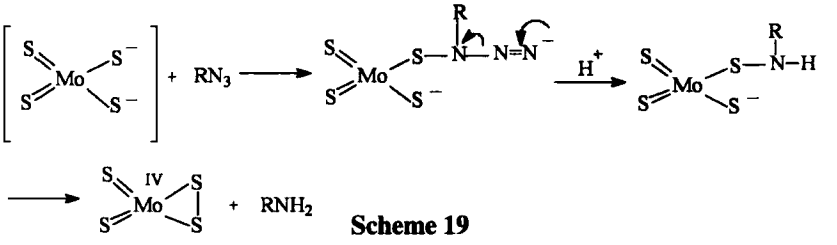
2. Reduction of Azides, Acyl Azides and N-Oxides

Aryl azides react with tetrathiomolybdate in CH_3CN-water at room temperature to give primary amines (*Eq. 124*). The acyl azides give the corresponding amides and sulfonyl azides



(124)

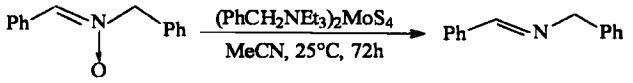
give the sulfonamides.[114] However treatment of alkyl azides with tetrathiomolybdate gave amines exclusively. The reductions are chemoselective as NO_2 and CHO groups are unaffected. The probable mechanism for these reactions is given in *Scheme 19*.



Scheme 19

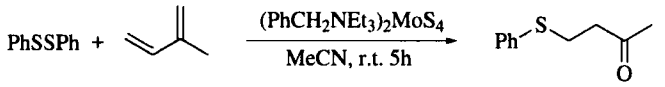
There is no sulfur transfer to the organic substrate. MoS_4^{2-} attacks the α-nitrogen of the azide to produce *N*-sulfenylamine, following nitrogen extrusion. This intermediate can then undergo internal electron transfer from S_2^{2-} to Mo(VI) resulting in the cleavage of the sulfur-nitrogen bond to form the amine. The difference in reactivity of alkyl azides may be due to the fact that alkylamine is a poorer leaving group than aniline, amide or sulfonamide at neutral pH.

Treatment of nitrones and N-oxides[115] with benzyltriethylammonium tetrathiomolybdate in acetonitrile yielded the corresponding imines and amines in good yields (*Eq. 125*). The



(125)

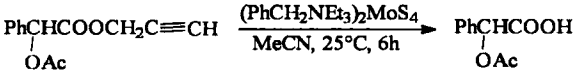
deoxygenations are chemoselective. However, sulfoxides and azoxy benzene are not deoxygenated under these conditions with tetrathiomolybdate. Benzyltriethylammonium tetrathiomolybdate has also been used for reduction/Michael addition (*Eq. 126*).[116]



(126)

3. Reactions of Propargyl Esters and Ethers

Prop-2-ynyl esters are selectively deprotected with tetrathiomolybdate in acetonitrile and gave the corresponding carboxylic acid in high yields (*Eq. 127*).[117] Acetyl, benzyl, ^{t}butyl and

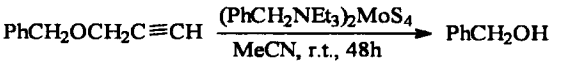


(127)

allyl esters remain unaffected under these conditions. The deprotection is believed to be restricted to terminal acetylenic compounds from which the proton may be abstracted by sulfur anion in tetrathiomolybdate followed by migration of the electron pair and subsequent C-O bond cleavage to give the carboxylic acid as shown in *Scheme 20*.

Scheme 20

The inertness of *1*-hexynyl benzoate to the reagent is in accordance with the above mechanism. An extension of the above method is the selective deprotection of propargyl ethers with tetrathiomolybdate to yield the corresponding alcohols (*Eq. 128*).[118]

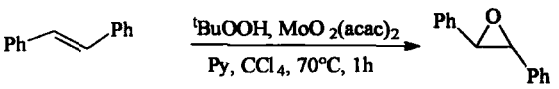


(128)

IV. DIOXOBIS(2,4-PENTANEDIONATO)MOLYBDENUM(VI); $MoO_2(acac)_2$

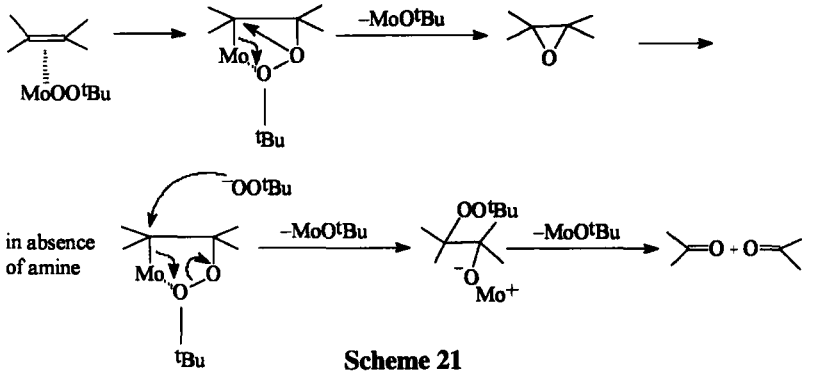
1. Epoxidation of Olefins

Aliphatic and aromatic olefins are converted to the corresponding epoxides by oxidation with *tert*-butyl hydroperoxide and $MoO_2(acac)_2$ in CCl_4 in the presence of catalytic amounts of an amine (*Eq. 129*).[119] Hydroxy group in the substrate remains unaffected by this reagent. The



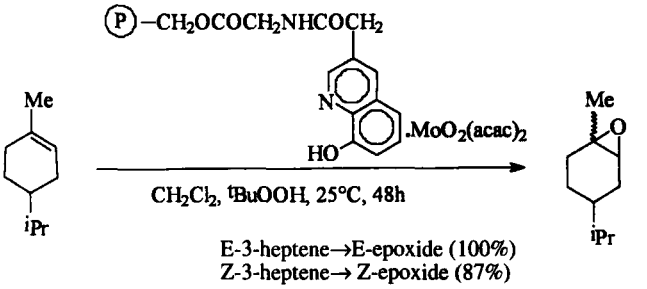
(129)

yield of epoxides is dependent on the structure of amine employed. For example, in the reaction of *1*-dodecene, epoxidation did not occur in the presence of imidazole but gave a 40% yield with pyridine and 68% yield with *N,N*-dimethylethylenediamine; epoxidation of *E*-stilbene was 46% in the presence of imidazole, 74% with *N,N*-dimethylethylenediamine and 93% with pyridine. In the absence of amines, aliphatic olefins did not undergo epoxidation whereas aromatic olefins gave the carbonyl compounds in high yields. The probable mechanism for epoxidation and C-C bond cleavage is given in *Scheme 21*.



Scheme 21

The role of added amines in assisting the selective epoxidation is not clear. The epoxidation of olefins (*Eq. 130*) has also been carried out in presence of a polystyrene supported

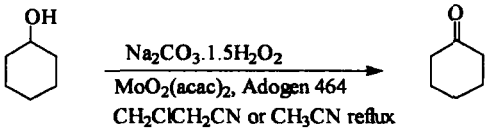


(130)

peptide linked epoxidation catalyst.[120] The hydroxyquinoline moiety of the catalyst is used for binding the epoxidant molybdenum. It was confirmed that polymer bound glycine alone did not yield an active epoxidant on treatment with $MoO_2(acac)_2$ and ^tBuOOH.

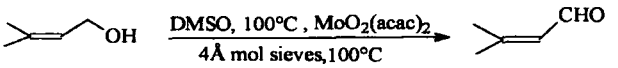
2. Oxidation

Alcohols can be oxidized to ketones with $MoO_2(acac)_2$, Adogen 464 and sodium percarbonate by refluxing in acetonitrile or 1,2-dichloroethane (*Eq. 131*).[121,122] Fair to high yields



(131)

have been obtained from various primary and secondary alcohols. Catalytic amounts of *cis*-dioxo molybdenum (VI) complex in association with sulfoxides can be used to oxidize alcohols into carbonyl compounds.[123] Primary alcohols are selectively oxidized to aldehydes and no further oxidation to carboxylic acids was observed. The oxidation is most effective for benzylic and allylic alcohols (*Eq. 132*).

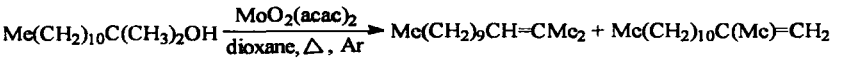


(132)

The mechanism probably involves a hydride transfer from a coordinated alkoxide to an oxo ligand on the Mo(VI) thereby forming aldehyde and an Mo(IV) species. The latter being reoxidized to Mo(VI) by the sulfoxide in an oxygen atom transfer step.

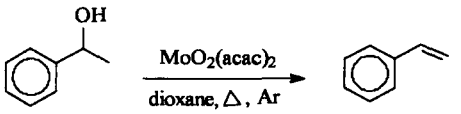
3. Dehydration

Molybdenum (VI) acetylacetonate is an effective catalyst for dehydration of tertiary alcohols to the corresponding olefins in high yields in the absence of other additives (*Eq. 133*).[124]



(133)

Secondary alcohols have also been reported to give olefins in some cases (*Eq. 134*).

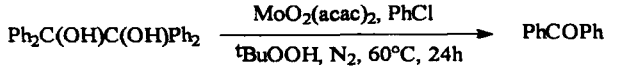


(134)

$MoO_2(acac)_2$-^{t}BuOOH system has high activity for oxidative cleavage of tertiary and secondary *vic*-diols.[125] $MoO_2(acac)_2$ itself cleaves the diol to give carbonyl compound in the absence of ^{t}BuOOH.

4. Cleavage of Diols

tert-1,2-Diols undergo cleavage to give ketones (*Eq. 135*). Diols with primary hydroxy



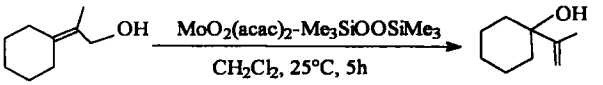
(135)

group give low yields of expected carboxylic acids because of overoxidation. High reactivity of *tert*- and *sec*-diols might be due to facile formation of molybdenum alkoxides from these diols.

The stoichiometric reaction of styrene glycol with $MoO_2(acac)_2$ in the absence of ^tBuOOH gave 78% of benzaldehyde in contrast to 93% of benzoic acid in presence of ^tBuOOH suggesting that a Mo(VI) species reacts with the diols to give carbonyl compounds and Mo(IV) species and, in a catalytic reaction, the Mo(IV) is oxidized to Mo(VI) by ^tBuOOH.

5. Isomerization of Allylic Alcohols

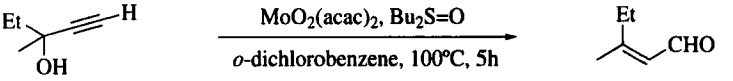
Isomerization of primary allylic alcohols has also been reported in presence of catalyst prepared *in situ* from $MoO_2(acac)_2$ and $Me_3SiOOSiMe_3$ to give isomeric alcohols in good yields (*Eq. 136*). This catalyst is also effective for rearrangement of secondary allylic alcohols[126] to *tert*-allylic alcohols.



(136)

6. Meyer-Schuster Rearrangement

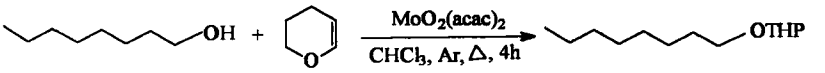
Rearrangement of 3-methyl pent-1-yn-3-ol to the α,β-unsaturated aldehyde is also catalyzed by *cis*-dioxomolybdenum (VI) complex[127] (*Eq. 137*).



(137)

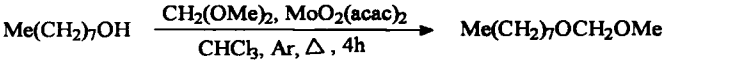
7. Protection and Deprotection

Tetrahydropyranylation of alcohols and phenols[128] is catalyzed by $MoO_2(acac)_2$ (2 mole %) by refluxing under an argon atmosphere (*Eq. 138*). Alcohols can also be protected as



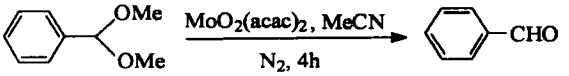
(138)

methoxymethyl derivatives with $CH_2(OCH_3)_2$, $MoO_2(acac)_2$ and $CHCl_3$ by refluxing under an argon atmosphere (*Eq. 139*).[129]



(139)

Molybdenyl(VI)acetylacetonate is an effective catalyst for deprotection of acetals to give corresponding aldehydes and ketones (*Eq. 140*).[130] The aromatic acetals are easily deprotected in high yields while aliphatic acetals give lower yields. *t*-Butyldimethylsilyl (TBDMS)



(140)

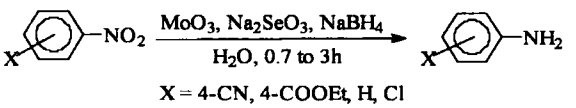
ethers are efficiently cleaved by *t*-butyl hydroperoxide and $MoO_2(acac)_2$ to regenerate the corresponding alcohols (*Eq. 141*).[131] Deprotection of *1-t*-butyldimethylsiloxy octane yielded *n*-octyl acetate under the reaction conditions.

$$ROSiMe_2Bu\text{-}t \xrightarrow[{}^tBuOOH,\ 24h]{MoO_2(acac)_2,\ CH_2Cl_2} ROH \qquad (141)$$

The reaction of TBDMS ethers derived from secondary alcohols with MeOH-$MoO_2(acac)_2$ was slow and with TBHP-$MoO_2(acac)_2$ gave alcohols in good yields, and only small amount of acetates was formed. The acid-labile β-hydroxy esters were unaffected under the conditions. Since the TBHP-$MoO_2(acac)_2$ is known to be unreactive to functionalities such as esters, THP ethers and cyclic acetals, this method is an efficient and mild deprotection method in presence of these functionalities.

V. $NaBH_4$-MoO_3

Molybdenum trioxide-sodium borohydride has been used for reduction of nitro groups, oximes and also ring opening of unsaturated pyranosides. Nitroarenes are reduced to anilines with molybdenum trioxide-sodium borohydride in presence of sodium selenite.[132] The reductions can be carried out in aqueous medium (*Eq. 142*). Water-ethanol mixture has also been used as

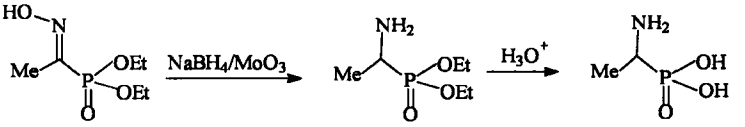


(142)

solvent. The reductions are accelerated by electron-withdrawing group and retarded by electron-donating groups.

When Na_2SeO_3 or MoO_3 were used as catalysts alone, the reduction occurred only to a small degree except for 4-nitrobenzonitrile and ethyl 4-nitrobenzoate. Reduction of both these nitroarenes in the presence of Na_2SeO_3 catalyst mainly gave *N*-arylhydroxylamines. When the black-brown precipitate isolated (by filtration) was used as catalyst, its behavior was similar to that of MoO_3-Na_2SeO_3.

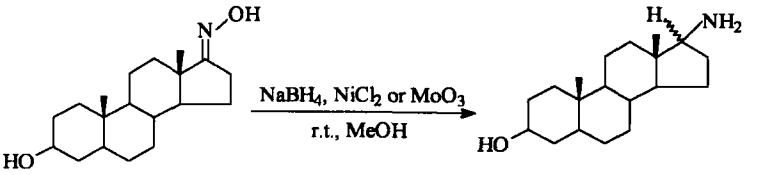
Hydroxyiminophosphonates can be reduced with $NaBH_4$ in the presence of MoO_3 in MeOH at ambient temperature to give *1*-aminophosphonates, which can be hydrolysed to give *1*-aminophosphoric acids in good yield (*Eq. 143*).[133] The optimum yield was obtained by using a



(143)

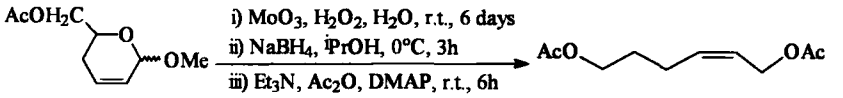
ratio of 1:1.5:5 of substrate:$NaBH_4$:MoO_3. It is uncertain whether this reaction involves complexation with transition metal followed by hydride transfer or *in situ* formed transition metal hydride.

Aminosteroids can be prepared by the reduction of corresponding hydroxyiminosteroid with MoO_3 and $NaBH_4$ in MeOH at ambient temperature (*Eq. 144*).[134,135] Carbon-carbon double



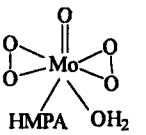
(144)

bond is not affected under these conditions. Unsaturated aldopyranosides can be reductively cleaved by stirring with MoO_3-H_2O_2 at room temperature followed by addition of $NaBH_4$ in ^{i}PrOH at 0°C and finally addition of Et_3N, Ac_2O and DMAP at room temperature (*Eq. 145*).[136]



(145)

VI. DIPEROXO-OXAHEXAMETHYLPHOSPHORAMIDO MOLYBDENUM (VI): MoO_5•HMPA

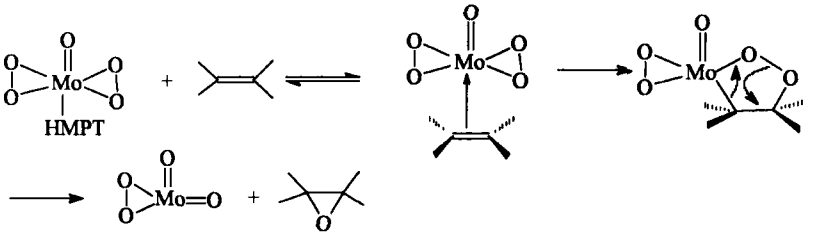


14

MoO_5•HMPA[137] can be prepared by dissolving molybdenum trioxide at 40°C in 30% H_2O_2. The yellow solution so obtained is cooled to 10°C and HMPA is added with efficient stirring. A yellow precipitate is formed immediately, filtered at pump and washed with ether. The dried material is crystallized from methanol to afford yellow crystals in high yield. The water-free complex MoO_5•HMPA can be obtained by dehydration of **14** with phosphorus pentoxide *in vacuo*.

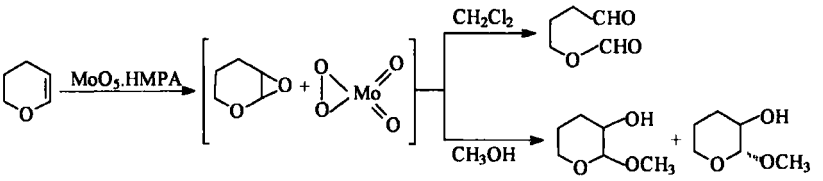
1. Oxidations

cis-2-Butene is converted into *cis*-2,3-epoxybutane and *trans*-2-butene into *trans*-2,3-epoxybutane when epoxidation is carried out with MoO_5•HMPA in aprotic solvents such as CH_2Cl_2. The epoxidation is stereospecific with retention of configuration of olefin as shown in *Scheme 22*.[138]



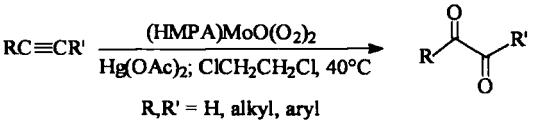
Scheme 22

Oxidation of dihydropyran with MoO_5•HMPA in CH_2Cl_2 gave the cleavage product while reaction in methanol gave *cis*- and *trans*-2-methoxy-3-hydroxytetrahydropyran (*Eq. 146*).[139] Oxidation of diaryl- and aralkyl alkynes in presence of mercuric acetate and



(146)

MoO_5•HMPA in dichloroethane afforded the corresponding α-diketones in good yields.[140] Terminal alkynes are converted into α-ketoaldehydes in excellent yields (*Eq. 147*). The presence

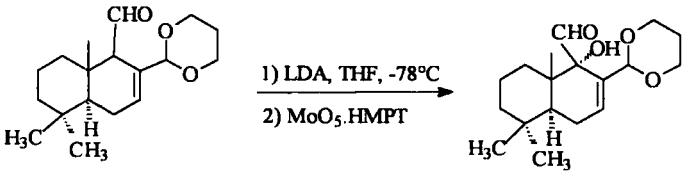


(147)

of the mercuric salt catalyst is required to promote the oxidation because the alkynes are totally inert as such towards oxodiperoxomolybdenum (VI) complex. Low alkyne to $Hg(OAc)_2$ ratios are adopted to obtain high alkyne conversions in reasonable reaction times.

2. Hydroxylation

Treatment of **13** with LDA in THF at -78°C followed by treatment with MoO_5•HMPA (1.5 equiv) led to aldehyde enolate hydroxylation in high yield (*Eq. 148*).[141]

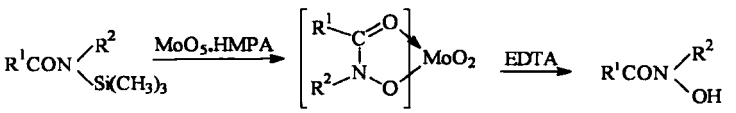


13

(148)

3. Reactions of Amides and Esters

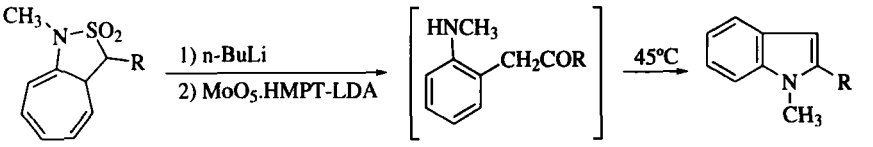
Oxidation of *N*-trimethylsilylamides with MoO_5•HMPA complex in methylene chloride at room temperature for several hours to several days afforded dioxomolybdemun complexes in moderate yield from which free hydroxamic acids were liberated (*Eq. 149*)[142] by treatment with



(149)

EDTA. 8-Azaheptafulvenes rearrange on oxidation of the anion with MoO_5•HMPA-LDA to 1,2-

disubstituted indoles (*Eq. 150*).[143] The tropone sulfene cycloadduct is converted to 2-phenylbenzofuran under same conditions (*Eq. 151*).



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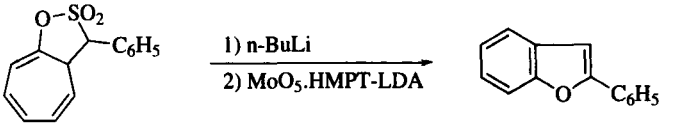


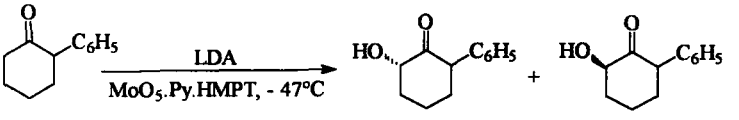
(151)

VII. OXODIPEROXYMOLYBDENUM(PYRIDINE)(HEXAMETHYLPHOSPHORAMIDE):MoO_5•Py•HMPA or $Mo(O_2)_2$Opy•HMPA or MoOPH

MoOPH[144] was prepared by stirring a solution of MoO_5•HMPA in dry THF and adding pyridine dropwise at 20°C. The yellow crystalline precipitate was collected, washed with THF, anhydrous ether and dried under vacuum. Molybdenum peroxide is light sensitive and decomposes to a significant extent after several days of storage in a clear glass container at room temperature. The smell of HMPA and pyridine is apparent and crystals become "sticky". They are not hazardous in contact with typical organic solvents. MoOPH decomposes with copious gas evolution. No hazards exist if the reagent is refrigerated. Molybdenum peroxide behaves as electrophilic oxygen donor and resembles organic peracids in some of their chemical properties. Anionic species such as alkyllithium reagents or nitrile stabilized carbanions are attacked rapidly by MoO_5•Py•HMPA below 0°C resulting in C-O bonds formations. Electron-rich neutral substrates including sulfides, N-silylamides or oximes are oxidized slowly at ambient temperature.

1. α-Hydroxylation

MoO_5•Py•HMPA is used to hydroxylate ketones, esters and lactones having enolizable α-methine or methylene group (*Eqs. 152-154*).[144-146] One stereoisomer is produced predominantly. α,β-Unsaturated ketones also give rise to α-hydroxylation.[147] The method has been



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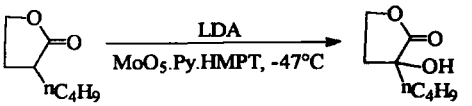

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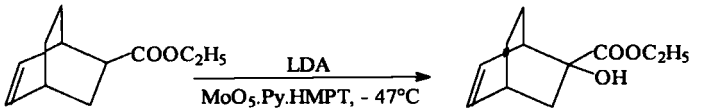
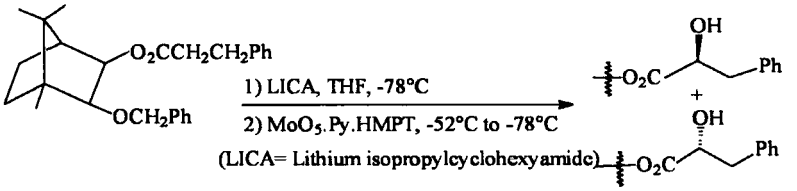


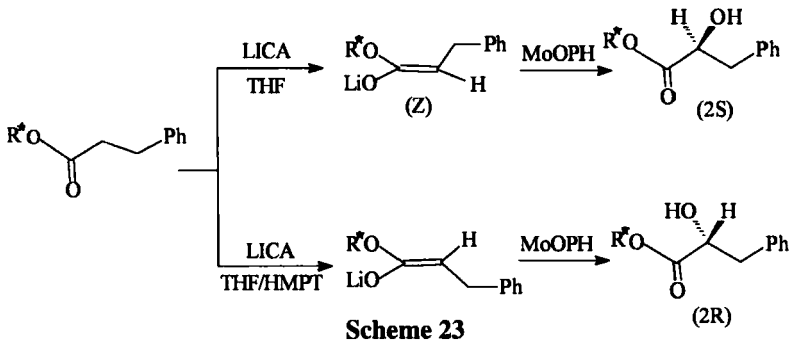
(154)

further extended for the diastereoselective hydroxylation of chiral ester enolates by MoO_5•Py•HMPA, for example 3-phenylpropionates of chiral alcohols derived from (+)-camphor are oxidized by MoOPH with high diastereoselectivity (*Eq. 155*).[148] The deprotonation was



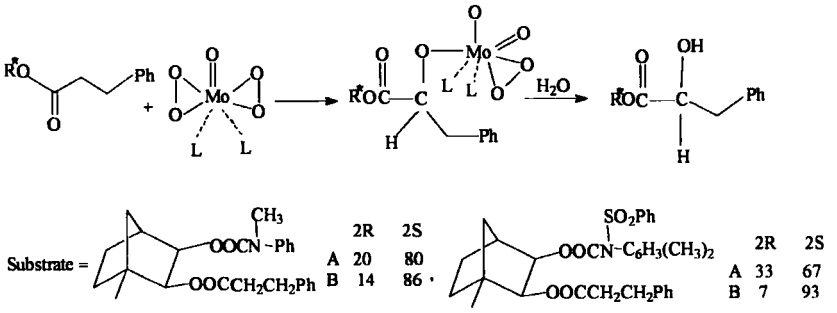
(155)

performed using LICA (lithium isopropylcyclohexamide) or LICA/HMPA as the base in THF, because under these conditions both *Z* and *E* isomers of the enolate are accessible (*Scheme 23*).



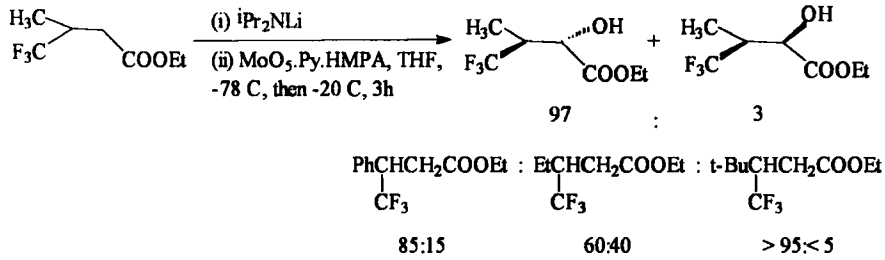
Scheme 23

Enolate hydroxylation of esters was performed with MoOPH. Most esters were hydrolyzed with excellent diastereoselection to yield products which are formed by the attack from the less hindered side of (*E*) enolate (*Scheme 24*). The stereoselective α-hydroxylation of



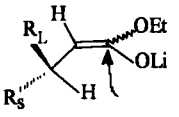
Scheme 24

esters induced by trifluoromethyl groups with MoO_5•Py•HMPA has also been reported (*Eq. 156*)[149]



(156)

The selectivity of hydroxylation in the case of non-fluorinated compound is due to steric effect of the substituent (R_L, R_S). Attack by MoOPH takes place *anti* to the R_L group to produce hydroxy ester as major isomer (**15**). Hydroxylation of β-fluoromethyl ester or ketone is not fully understood. The electronic factor of trifluoromethyl group plays an important role in this system. One possibility is that lithium is chelated to trifluoromethyl group (**16**). The lithium enolate was trapped with chlorotrimethylsilane giving one isomer exclusively and the bulky electrophile, MoOPH attacks on the less hindered side.



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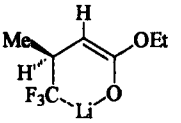
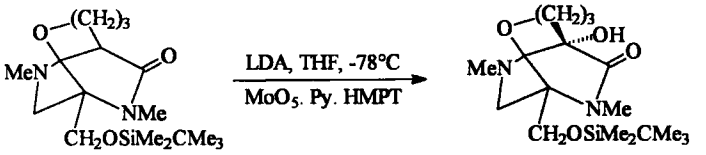


16

MoOPH has also been reported for the angular hydroxylation of cyclic amides (*Eq. 157*)[150] and the α-hydroxylation of nitriles to give cyanohydrins (*Eq. 158*).[151] Oxodiperoxymolybdenum pyridine dimethyltetrahydropyrimidone (MoO5•Py•DMPU)[152] is a safer alternative



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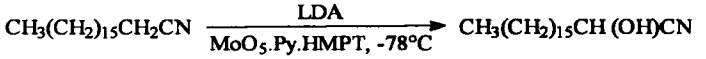
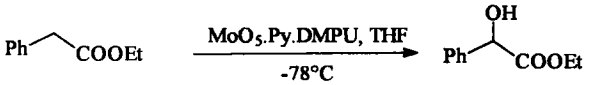


(158)

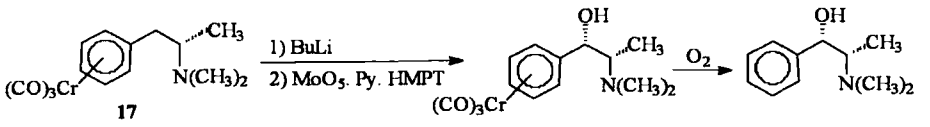
to MoOPH for the α-hydroxylation of carbonyl compounds (*Eq. 159*).



(159)

2. Stereospecific Benzylic Hydroxylation

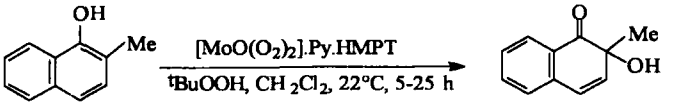
The anion of the chromium tricarbonyl complex of (+)-*N,N*-dimethylamphetamine (**17**) is hydroxylated by MoOPH to give optically pure (+)-*N*-methylpseudoephedrine (*Eq. 160*).[153]



(160)

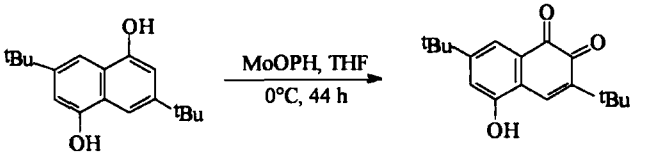
3. *Oxidation*

$MoO(O_2)_2$•Py•HMPA has been used as a catalyst in the oxygenation of *o*-alkylated α- and β-naphthols to α-ketols in presence of ^tBuOOH (*Eq. 161*).[154] Similarly *o*-quinones have been



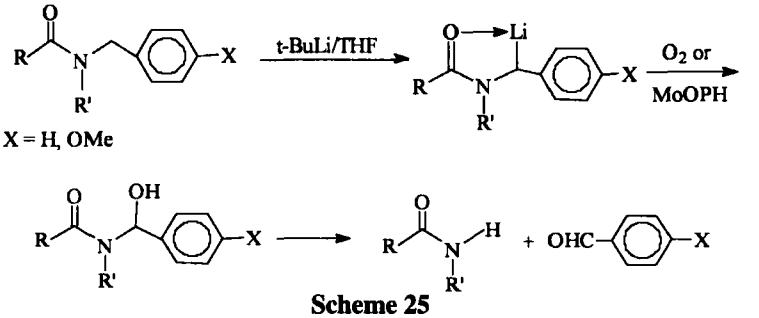
(161)

synthesized (*Eq. 162*) by oxygenation of phenols in presence of MoOPH at 0°C.[155]



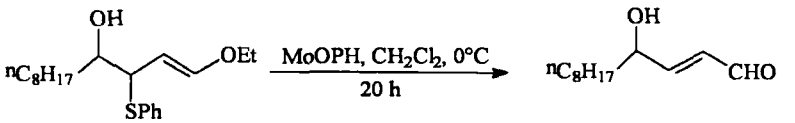
(162)

Treatment of non-enolizable *N*-benzyl or *N*-*p*-methoxybenzyl amides with BuLi generates carbanions which can be oxidised with molecular O_2 or MoOPH. The resulting hemiaminals undergo cleavage to give the debenzylated amides (*Scheme 25*).[156]



Scheme 25

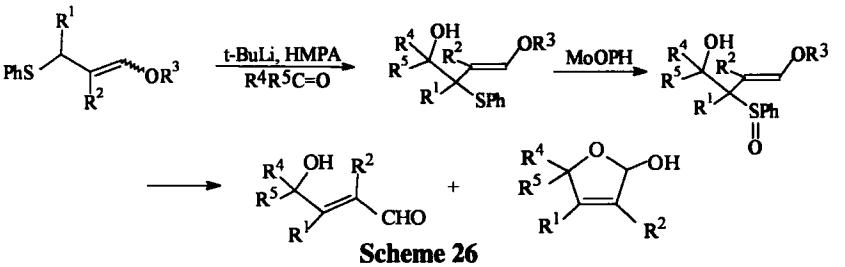
Carbonyl adducts of 3-alkoxysulfides are converted into (E)-4-hydroxy-2-alkenals in a highly stereoselective manner by oxidation of allylic sulfides to allylic sulfoxides by MoO_5•Py•HMPA followed by [2,3] sigmatropic rearrangement of allylic sulfoxide (*Eq. 163*).[157]



(163)

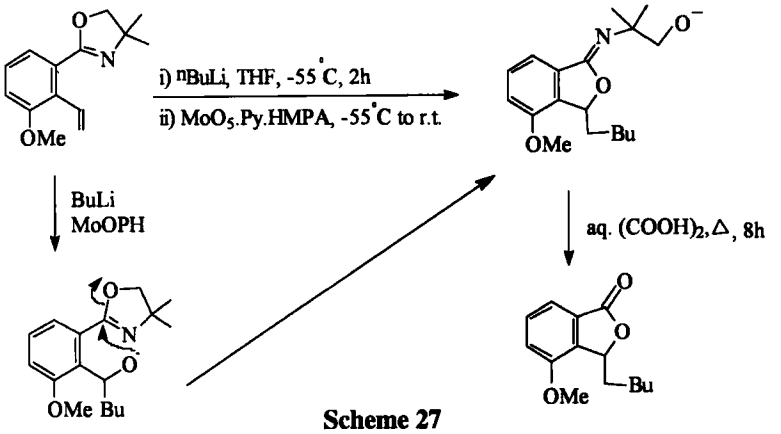
The complete sequence of reactions is shown in *Scheme 26*. Substitution and bulkiness of the

substituent at the position β- to phenylthio group plays an important role in controlling the stereochemistry of the subsequent [2,3] sigmatropic rearrangement to give high E-preference.



Scheme 26

Imidolactones can be prepared by the intramolecular ring opening of the oxazoline ring by the hydroxyl group introduced by the MoOPH (*Scheme 27*).[158] Addition of LiBr to the oxazoline improves the yield in the presence of the methoxy group (67%) whereas in the absence of

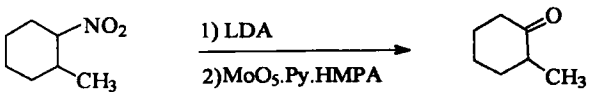


Scheme 27

LiBr yield was 34%. When freshly prepared BuLi was used, the yield was 71%. It is the methoxy group which is now coordinated to LiBr and not the nitrogen or the oxygen of the oxazoline ring because in the absence of 3-methoxy group, no significant improvement of yield was observed.

4. Oxidative Denitration

Nitrocycloalkanes can be converted to cycloalkanones by treatment with base to generate the nitronate anion followed by oxidation with MoO_5•Py•HMPA. Primary nitro compounds are converted to corresponding carboxylic acids under these conditions *via* an aldehyde (*Eq 164 and 165*).[159]

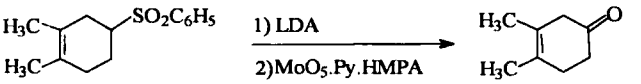


(164)

$$C_6H_5CH_2NO_2 \xrightarrow[2)MoO_5.Py.HMPA]{1)\ N(C_2H_5)_3} C_6H_5COOH \qquad (165)$$

5. Oxidative Desulfonylation

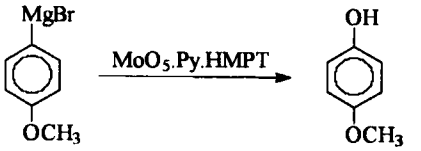
Aryl sulfones are converted to ketones by oxidation of α-carbanion with MoO_5•Py•HMPA in THF at –70°C in good yields (*Eq. 166*).[160]



(166)

6. Reaction of Grignard Reagents

Reaction of arylmagnesium bromides with MoO_5•Py•HMPA in THF at –78°C to 10°C gave the corresponding phenols (*Eq.167*).[161]

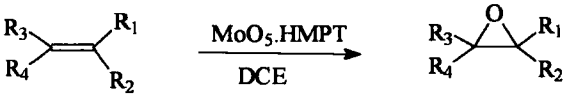


(167)

VIII. EPOXIDATION WITH OXODIPEROXYMOLYBDENUM (AQUO) (HEXAMETHYLPHOSPHORAMIDE):$MoO(O_2)_2(H_2O)$(HMPA)

$MoO(O_2)_2(H_2O)$ (HMPA)[137] is prepared by vigorous stirring of a mixture of MoO_3 and 30% H_2O_2 and maintaining the reaction temperature at 35-40°C. After the intial exothermic period, the mixture was heated at 40°C for 3.5 h with stirring. After cooling to 20°C, the reaction mixture was filtered to remove solids and yellow solution was cooled to 10°C. HMPA was added with stirring and a crystalline precipitate was obtained as yellow needles (67%). It is light sensitive and decomposes to a significant extent after several days of storage in a clear glass container at room temperature.

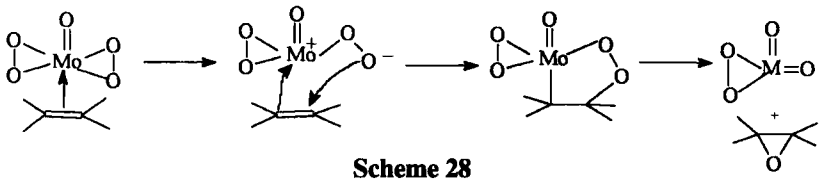
Reaction of olefins with $MoO(O_2)_2(H_2O)$ (HMPA) gives epoxides in high yields (*Eq. 168*)[162] The epoxidation is proposed to proceed *via* a the metal complex-olefin intermediate



(168)

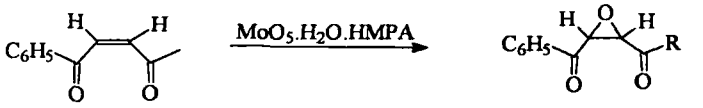
R_1 = Ph, $^nC_6H_{13}$, Et, Me ; R_2 = H, CH_3 ; R_3 = H, Me ; R_4 = H, Me

and an aprotic 1,3-dipolar mechanism (*Scheme 28*).



Scheme 28

Enediones that can adopt an *s-cis* conformations are oxidized by molybdenum peroxo complex $MoO_5 \cdot H_2O \cdot HMPA$ stereospecifically to *cis*-2,3-epoxybutane-1,4-dione (*Eq. 169*).[163]



(169)

The *trans* isomer of the enedione as well as naphthaquinones do not react with the reagent.

$MoO_5 \cdot H_2O \cdot HMPA$ catalyses the oxidation of primary aromatic amines to the corresponding nitroso derivatives in varying yields in the presence of H_2O_2 as oxidant (*Eq. 170*).[164]

$$R\text{-}C_6H_4NH_2 \xrightarrow[H_2O_2,\ CH_2Cl_2,\ r.t.]{MoO(O_2)_2(H_2O)(HMPA)} R\text{-}C_6H_4NO \qquad (170)$$

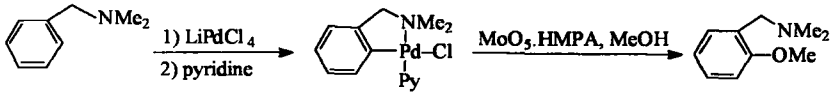
under a nitrogen atmosphere. Aromatic amines bearing electron-withdrawing substituents such as *p*-NO_2 or *m*-CF_3 do not react; similarly, no reaction occurred in the absence of catalyst. High yields of nitroso compounds are obtained by preventing their subsequent oxidation to the corresponding nitro derivatives through monitoring the progress of the reaction and quenching it immediately after disappearance of the amine. The oxidations are believed to be proceeding *via* the hydroxylamines. The oxygenation of nitrogen is due to the molybdenum complex.

The stoichiometric reaction of amines with $MoO_5 \cdot H_2O \cdot HMPA$ formed a *cis*-dioxoperoxo complex, $Mo(O)_2O_2(RNH_2)_2$, which yielded the corresponding oximes or Schiff bases (*Eq. 171*). $Mo(O)_2(O_2)(C_6H_5NH_2)_2$ catalyzes the oxidation of benzylamine to benzaldehyde oxime in the presence of H_2O_2 as oxidant.[165]

$$RNH_2 + MoO(O_2)_2H_2O.HMPA \xrightarrow{H_2O_2} RCH{=}NOH \text{ or } RCH{=}NCH_2R \qquad (171)$$

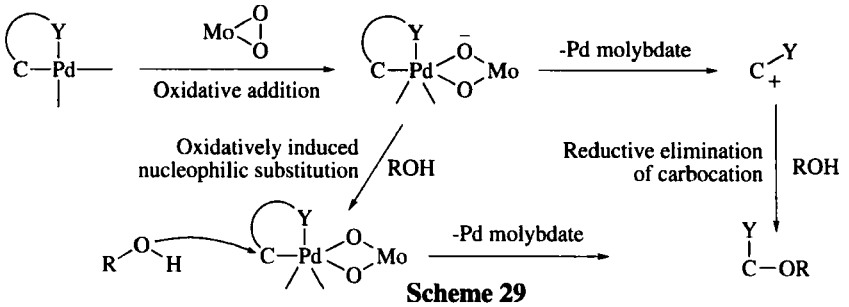
$R = C_6H_5CH_2,\ 2,4\text{-}Cl_2C_6H_3CH_2,\ 3,4\text{-}(MeO)_2C_6H_3CH_2,\ 2\text{-}ClC_6H_4CH_2$

$MoO_5 \cdot H_2O \cdot HMPA$ reacts with organopalladium compounds in alcoholic solvents to form alkoxylated products (*Eq. 172*).[166] The probable pathway of alkoxylation is shown in



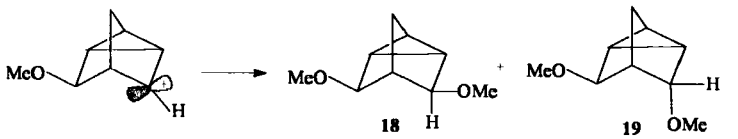
(172)

Scheme 29. The O-O bond of the molybdenum peroxide complex first adds oxidatively to the organopalladium compound and, subsequently, the organopalladium(IV) intermediate eliminates a carbocation which reacts with alcoholic solvents to give alkoxylated products. This view was



Scheme 29

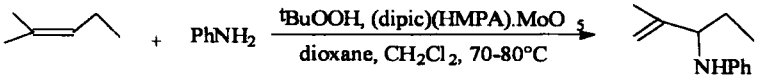
supported by the observation that the carbocation generated electrochemically from norbornadiene reacts with the methanolic solution of the reagent to give a mixture of **18** and **19** in the same ratio (*Eq. 173*) as that obtained in the above reaction.



(173)

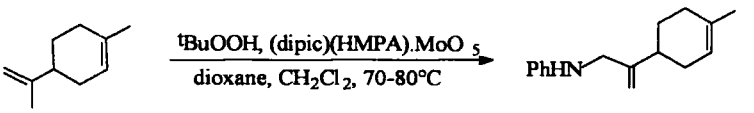
IX. MoO_5•HMPA•(dipic), (Dipic = pyridine 2,6-dicarboxylate)

Molybdenum peroxo complexes catalyze the regioselective allylic amination of alkenes by arylamines with *tert*-butyl hydroperoxide as the oxidant in dioxane-CH_2Cl_2 at 70-80°C (*Eq. 174*).[167] Along with *N*-phenyl-*N*-allylamine, azobenzene, azoxybenzene and polyaniline



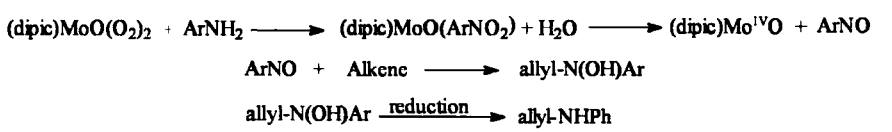
(174)

were also produced. The best yields were obtained with highly substituted alkenes. Single regioisomers were produced from substrates with unsymmetrical double bonds. Selectivity was low for *p*-chloroaniline. Chemoselective amination at the exocyclic allylic double bond (*Eq. 175*) was



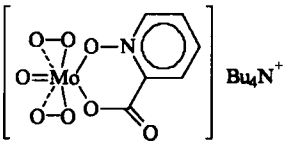
(175)

also observed. The reaction was believed to proceed by the pathway shown in *Scheme 30*.



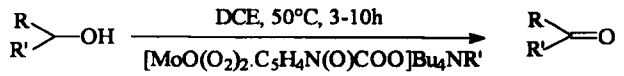
Scheme 30

X. Oxidation with Anionic Molybdenum-Picolinate N-oxido-Peroxo Complex MoO_5•PICO



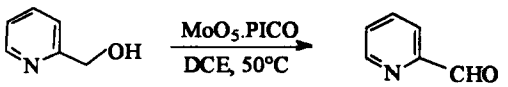
Na_2MoO_4•$2H_2O$ (14 mmol) was dissolved in 10 mL of water and the acidity of the solution was adjusted at pH 2 with 50% H_2SO_4. Then 7mL of H_2O_2 (36%, w/v) was added and resultant solution was diluted to 20 mL with water *(solution A)*. Picolinic acid *N*-oxide (15 mmol) was dissolved in 10 mL of an aqueous solution of tetra-*n*-butylammonium hydroxide (1.5 M) and resultant mixture was diluted to 20 mL with water (*solution B*). To 18 mL of *solution B* in an ice-cold bath and under vigorous stirring, was added 20 mL of *solution A* while the acidity was maintained at pH 2 by addition of 50% H_2SO_4. After 30 min, the formation of bright yellow precipitate (10 mmol) was observed. The solid was collected and washed with ether and recrystallized from dichloroethane. The water molecule may be removed by keeping the complex overnight in the dark under vacuum over P_2O_5. The dehydrated complex is very stable and may be stored for several weeks. Due to presence of lipophilic cation Bu_4N^+, it is highly soluble in non-polar solvents such as dichloroethane and oxidations are faster in non-polar solvents than in protic media.

Alcohols are oxidized to carbonyl compounds in non-polar solvents in the presence of anionic molybdenum picolinate *N*-oxido peroxo complex at 50°C (*Eq. 176*).[168] Further oxidation

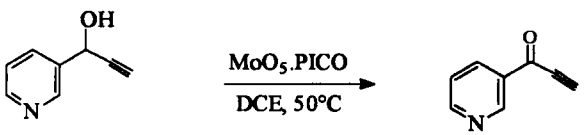


(176)

of the aldehydes to the carboxylic acids does not occur and there is very little difference in the reactivity between primary and secondary alcohols. The pyridine nitrogen and the C-C triple bond also do not compete with oxidation of the OH group (*Eqs. 177 and 178*).[169] The presence of

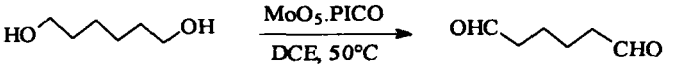


(177)



(178)

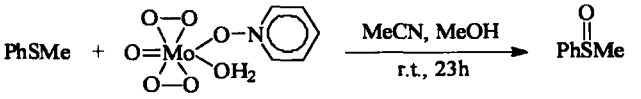
basic group greatly diminishes the yield of the carbonyl product because of the ability of the substrate to displace the picolinate-*N*-oxido ligand of the reagent. α,ω-Diols have also been reported to give the corresponding dialdehydes (*Eq. 179*) in good yields.



(179)

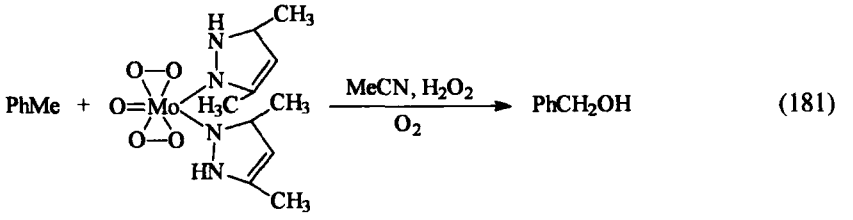
XI. $MoO(O_2)_2(Opyr)(H_2O)$ and $MoO(O_2)_2(dmpy)_2$

Aliphatic and aromatic sulfides, ketosulfides, sulfinic acids, esters and olefinic sulfides are oxidized to sulfoxides using oxodiperoxo complex of molybdenum coated on silica gel (150 Å pore size). Complete chemoselectivety was observed for oxidation of all functional sulfides (*Eq. 180*).[170] Molybdenum(VI)perxo *bis*(3,5-dimethylpyrazole)complex has been reported for the



(180)

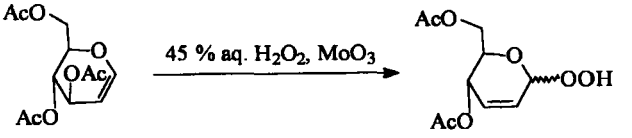
catalytic oxidation of allybenzenes with hydrogen peroxide (*Eq. 181*).[171]



(181)

XII. MoO_3 and 45% aq. H_2O_2

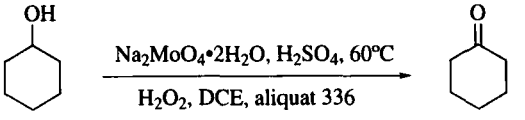
Glycals can be oxidized with MoO_3 and 45% aq. H_2O_2 to corresponding hydroperoxides (*Eq. 182*).[172]



(182)

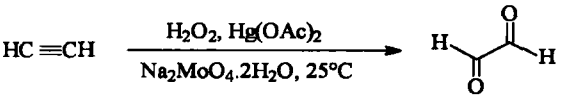
XIII. OXIDATIONS WITH SODIUM MOLYBDATE DIHYDRATE:Na_2MoO_4, $2H_2O$

Primary and secondary alcohols are oxidized to carbonyl compounds (*Eq. 183*)[173] under



(183)

phase-transfer conditions in presence of H_2O_2 and sodium molybdate dihydrate. The oxidation of primary alcohols proceeds more slowly than that of secondary alcohols. Acetylene is oxidized to glyoxal (*Eq. 184*)[174] by dilute H_2O_2 in the presence of sodium molybdate as catalyst and mercuric acetate as co-catalyst.



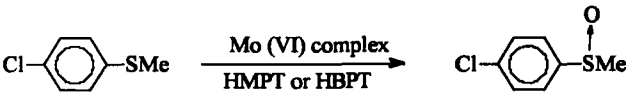
(184)

Subsequent oxidation of the glyoxal formed in the reaction gives formic acid (*Eq. 185*). Since this reaction occurs at slower or comparable rate to that of acetylene oxidation during

(185)

given time, it might be reasonable to propose that this might also be the route leading to formic acid formation in process of acetylene oxidation.

Sulfides are oxidized to sulfoxides and alkenes are epoxidized by dil. H_2O_2 catalyzed by sodium molybdate dihydrate (*Eqs. 186 and 187*).[175]



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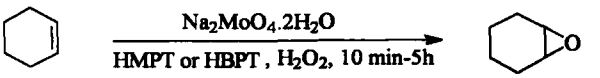


(187)

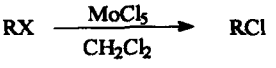
XIV. MOLYBDENUM HALIDES

1. Molybdemun (V) Chloride ($MoCl_5$)

Molybdenum pentachloride is dark-colored solid soluble in water and undergoes hydrolysis. It is slightly soluble in $TiCl_4$ and diethyl ether. It is moisture sensitive and is stored under nitrogen. It can be prepared by the reaction of molybdenum(VI) oxide and carbon tetrachloride or CCl_2=CCl(CCl_3). It can be prepared by reaction of refluxing thionyl chloride and MoO_3. Industrially, it is prepared by direct chlorination of molybdenum metal.

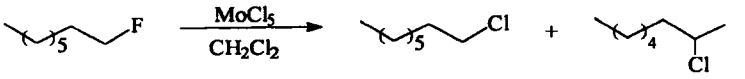
a. Chlorination of Alkyl Halides

Secondary alkyl iodides, bromides and fluorides are converted to alkyl chlorides in fair to good yields by reaction with $MoCl_5$ in CH_2Cl_2 at room temperature (*Eq. 188*).[176] $MoCl_5$ also



(188)

effect halogen exchange with alkyl fluorides and iodides but not with primary alkyl bromides. The conversion of *1*-fluorooctane to *1*-chlorooctane is accompanied by rearrangement producing 2-chloroöctane (*Eq. 189*).

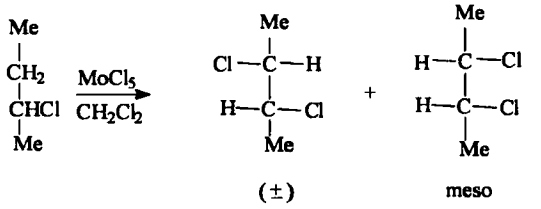


(189)

A Lewis acid-assisted ionization of the carbon–halogen bond followed by conversion of the carbonium ion to chlorohydrocarbon by reaction with halo-metalloate complex is a likely mechanism for this transformation.

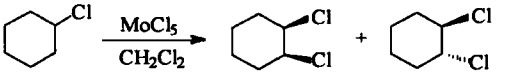
b. Vicinal Chlorination

The reaction of alkyl chlorides with an excess of $MoCl_5$ leads to *vic*-dichlorides in fair to excellent yields. 2-Chlorobutane is converted to a mixture of (±)2,3-dichlorobutane and *meso* 2,3-dichlorobutane (*Eq. 190*).[177] The reaction sequence has been applied to chlorination of alkyl



(190)

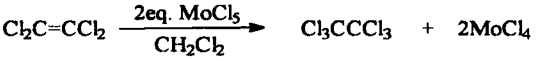
halides containing either a secondary or tertiary *vicinal* carbon (*Eq. 191*).



(191)

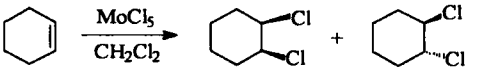
c. Chlorination of Alkenes and Alkynes

Tetrachloroethylene reacts with molybdenum(V) chloride under irradiation to form hexachloroethane and molybdenum(IV) chloride (*Eq. 192*).[178] Molybdenum(V) chloride reacts



(192)

with disubstituted alkenes and internal alkynes to produce dichloroalkanes and dichloroalkenes in fair to good yields (*Eqs. 193 and 194*).[179] *vic*-Chlorination may not be proceeding *via* the ionic



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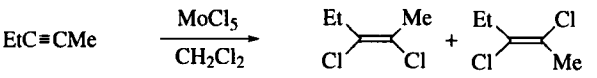
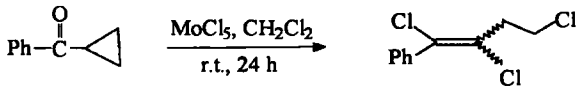


(194)

or radical pathway observed in the reactions of alkenes with molecular chlorine. Chlorination of alkenes gave *cis*- and *trans*-addition products. Yields are lower with terminal, tri- and tetrasubsti-

tuted olefins and terminal alkynes. Dichloromethane and chloroform are the preferred solvents.

Cyclopropyl aryl ketones react with $MoCl_5$ in CH_2Cl_2 at room temperature to yield chloro-substituted olefins (*Eq. 195*).[180] Aromatic compounds are benzylated by trimethylbenzylsilane in



(195)

presence of molybdenum pentachloride at 20°C (*Eq. 196*).[181] The aryl-aryl coupling of substituted aryl derivatives has also been reported with $MoCl_5$.[182]

$$PhH + Me_3SiCH_2Ph \xrightarrow[1\ h,\ 20°C]{MoCl_5,\ MeNO_2} PhCH_2Ph \qquad (196)$$

d. Acylative Cleavage of Acyclic Ethers Catalyzed by $MoCl_5$

$MoCl_5$ is an efficient catalyst for acylative cleavage of the C-O bond of ethers (*Eq. 197*).[183] Reactivity of the R-O bond cleavage between alkyl, allyl, benzyl, trimetylsilyl and *tert*-butyl groups was found to be in the order: trimethyl silyl > *tert*-Bu > benzyl > allyl > alkyl.

$$Bu_2O + PhCOCl \xrightarrow[80°C,\ 6h]{MoCl_5,\ ClCH_2CH_2Cl} PhCO_2Bu \qquad (197)$$

2. $MoCl_5$-PPh_3

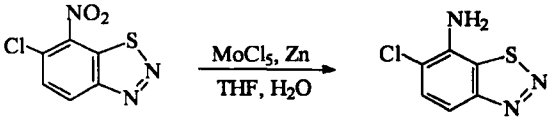
Molybdenum(V) chloride–triphenylphosphine catalyzes the insertion of CO_2 into methyloxirane to give the cyclic carbonate of propane-1,2-diol in high yield. The reaction proceeds at room temperature under 1 atm CO_2 pressure (*Eq. 198*).[184] Other Lewis acid/acids can be used in place of $MoCl_5$, though the molybdenum reagent is most efficient.

(198)

3. $MoCl_5$-Zn

a. Deoxygenation of Pyridine and Pyridazine *N*- Oxides

Molybdenum(V) chloride-Zn is a mild selective reagent for the deoxygenation of pyridine and pyridazine-*N*-oxides and for the reduction of aromatic and heteroaromatic nitro groups to amines (*Eqs. 199 and 200*).[185] It has also been used recently for the reductive deoximation in



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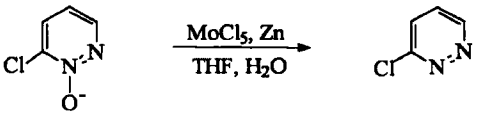
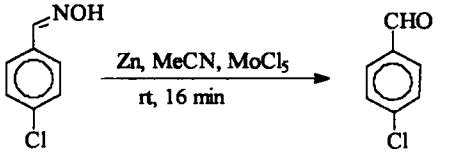


(200)

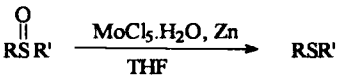
acetonitrile (*Eq. 201*).[186]



(201)

b. Sulfoxide Reduction by Low-valent Molybdenum Species

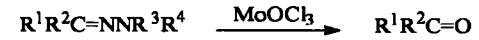
Treatment of THF solution of $MoCl_5$ with water followed by Zn metal produces a low valent molybdenum species which effectively converts sulfoxides to sulfides at room temperature in high yields (*Eq. 202*).[187] The active deoxygenating species in solution is believed to be Mo^{III}.



(202)

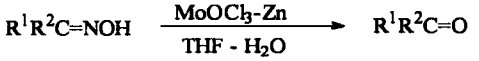
4. Molybdenum (V) Trichloride:$MoOCl_3$ and $MoOCl_3$-Zn

Hydrazones, dimethylhydrazones and tosylhydrazones are reductively converted to corresponding carbonyl compound by $MoOCl_3$ in reasonably high yields (*Eq. 203*).[188] Regeneration of



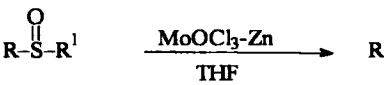
(203)

carbonyl compounds from oximes in H_2O-THF (*Eq. 204*)[187] and deoxygenation of sulfoxides to



(204)

sulfides has been reported by $MoOCl_3$-Zn (*Eq. 205*).[188]

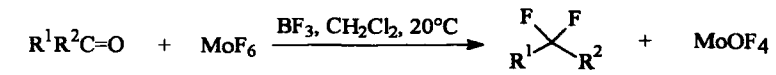


(205)

5. Molybdenum Hexafluoride:MoF_6

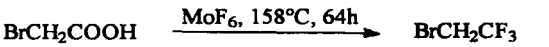
MoF_6 is a colorless liquid, soluble in saturated hydrocarbons, chlorinated and fluorinated hydrocarbons. The rate of decomposition of the solution of MoF_6 in *n*-hexane is 1% h^{-1}. The reaction of MoF_6 with CCl_4 takes place at 150°C. MoF_6 reacts violently with water and

protic solvents. Carbonyl compounds are converted into *gem*-difluoro derivatives with MoF_6 and BF_3 in CH_2Cl_2 at room temperature (*Eq. 206*).[189] The transformation is compatible with organic



(206)

functionalities such as Cl, Br, COOR, $C(O)NR_2$, CN, NO_2 and $P(O)R_2$. Alcohols, amines, ethers and double bonds are attacked. MoF_6 is able to convert aliphatic and aromatic carboxylic acids into trifluoro derivatives at high temperature in the absence of a catalyst (*Eqs. 207 and 208*).[189]



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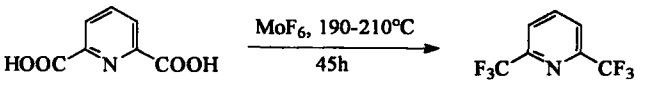
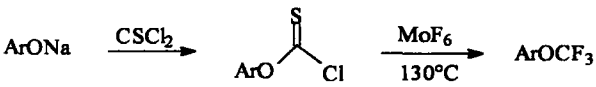


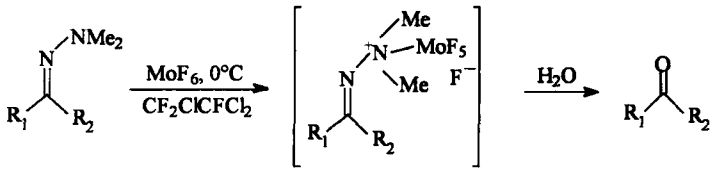
(208)

Aryl trifluoromethyl ethers can be conveniently prepared by treatment of the sodium salt of a phenol with $CSCl_2$ to form the chlorothioformate, which is treated with MoF_6 at –25°C and then heated gradually (*Eq. 209*).[190] Chloroformates do not undergo this reaction.



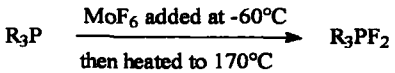
(209)

MoF_6 has been used for the oxidative cleavage of hydrazones at 0°C in presence of $CF_2ClCFCl_2$ to give carbonyl compounds (*Eq. 210*).[190] Fluorination of phosphines to give the



(210)

fluorophosphoranes has also been achieved by MoF_6 (*Eqs. 211 and 212*).[191]



(211)

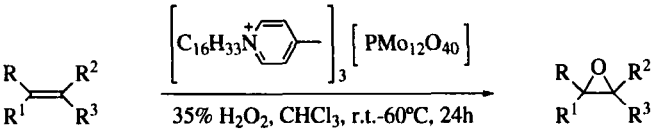
(212)

XV. HETERO-POLY-MOLYBDENUM COMPLEXES

1. MPCP:$[PMo_{12}O_{40}]^{3+}[C_5H_5N^+(CH_2)_{15}Me]_3$

MPCP is prepared from 12-molybdatophosphoric acid ($H_3PMO_{12}O_{40}$) and cetyl pyridinium chloride [$C_5H_5N^+(CH_2)_{15}CH_3Cl^-$]. Alkenes and allyl alcohols are epoxidized with H_2O_2 in

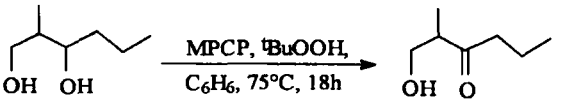
presence of $[PMo_{12}O_{40}]^{3+}[C_5H_5N^+(CH_2)_{15}Me]_3$ at room temperature to 60°C (*Eq. 213*)[192]. With alkadienes, the epoxidation occurs regioselectively with 98% selectivity. The high regioselectivity of epoxidation by MPCP-H_2O_2 system is comparable to Sharpless epoxidation using ^{t}BuOOH as oxidant.



(213)

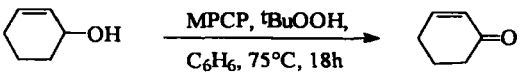
$R\text{-}R^3$ = alkyl; $R\text{-}R^2$ = alkyl; R^3 = hydroxyalkyl

The primary hydroxyl group could not be oxidized while secondary alcohols[193] were smoothly oxidized to corresponding ketones by MPCP-^{t}BuOOH. The oxidation of cyclic alcohols was strongly dependent on the steric factors. Sterically hindered cyclohexanols could not be converted to cyclohexanones in good yield and *l*-menthol was hardly oxidized to menthone. The oxidation of diols (*Eq. 214*) involving both primary and secondary hydroxy functions in a molecule



(214)

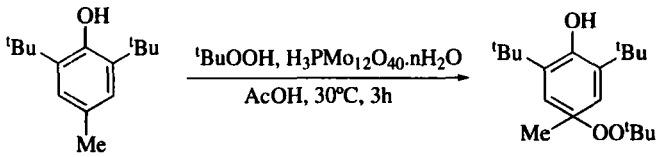
afforded ketoalcohols with high chemoselectivity. Allylic alcohols were also oxidized to α,β-unsaturated ketones (*Eq. 215*).



(215)

2. $H_3PMo_{12}O_{40}nH_2O$

p-Substituted phenols are oxidized in presence of $H_3PMo_{12}O_{40}\cdot nH_2O$ and *t*-butylhydroperoxide at 30°C to enones (*Eq. 216*).[194]



(216)

3. $Na_5PMo_2V_2O_{40}$

Alcohols and amines undergo selective aerobic oxidative dehydrogenation in presence of molybdenum-vanadium hetero polyanion salt $Na_5PMo_2V_2O_{40}$, impregnated over activated carbon in toluene at 100°C to yield aldehydes and imines in reasonably good yield (*Eqs. 217 and 218*).[195]

$$PhCH_2OH \xrightarrow[\text{activated C, PhMe, 100°C}]{Na_5PMo_2V_2O_{40}} PhCHO \qquad (217)$$

$$PhCH_2NH_2 \xrightarrow[\text{activated C, PhMe, 100°C}]{Na_5PMo_2V_2O_{40}} \underset{\text{after 0.5 h}}{PhCH{=}NCH_2Ph} \quad \text{or} \quad \underset{\text{after 20 h}}{PhCHO} \qquad (218)$$

Selective dehydrogenation of benzylic and secondary alcohols to benzaldehyde and ketone took place without subsequent oxidation of benzaldehyde to carboxylic acid (*Scheme 31*).

$$ArCH_2OH + PMo_{10}V^{V}_{2}O_{40}^{5-} \xrightarrow{-2H^+,\,-2e^-} ArCHO + H_2PMo_{10}V^{IV}_{2}O_{40}^{5-} \xrightarrow{+0.5O_2} PMo_{10}V^{V}_{2}O_{40}^{5-} + H_2O$$

Scheme 31

Benzylamines are also quantitatively and selectively dehydrogenated in two stages to corresponding aldehydes *via* a Schiff base intermediates (*Scheme 32*).

$$ArCH_2NH_2 \xrightarrow{PVMo} [ArCH{=}NH] \xrightarrow[-NH_3]{+H_2O} ArCHO \xrightarrow[-H_2O]{ArCH_2NH_2} ArCH{=}NCH_2Ar \xrightarrow[-ArCHO]{+H_2O}$$

$$ArCH_2NH_2 \xrightarrow{PVMo} [ArCH{=}NH] \xrightarrow[-NH_3]{+H_2O} ArCHO$$

Scheme 32

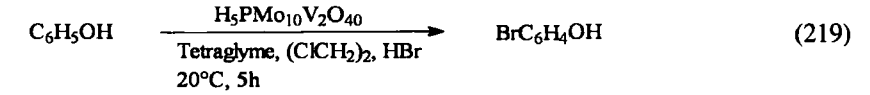
Secondary alcohols are only slightly but selectively dehydrogenated to ketones with following relative reactivities *1*-phenylethanol >> 2-octanol ~ 3-heptanol > cyclohexanol, whereas tertiary alcohols are inert. Secondary benzylamines such as dibenzylamine and *N*-methylbenzylamine underwent the same reaction although initial formation of the Schiff base is much slower. The α-substituted α-methylbenzylamine reacts rapidly to yield imine $PhC(CH_3){=}NCH(CH_3)Ph$ which gives acetophenone only in limited amount due to higher stability of Schiff base. Tribenzylamine is inert due to absence of a hydrogen at nitrogen.

Primary aliphatic amines are effectively dehydrogenated *e.g.*, cyclohexylamine to cyclohexanone, octylamine to octaldehyde and octanoic acid. Significant amount of acids are formed with primary cyclic amines because aliphatic aldehydes undergo oxidation much more easily than their aromatic counterparts. Simple secondary aliphatic amines such as di-*n*-butylamine are inert as is aniline. For aliphatic amines, no Schiff base intermediates were formed, thus the overall reaction to carbonyl compound is faster, although oxidative dehydrogenation reaction itself is slower than for benzylamine.

4. $H_5PMo_{10}V_2O_{40}$

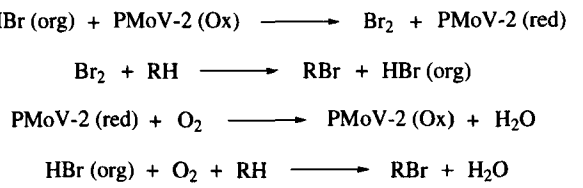
Selective bromination of phenol and its derivatives has been achieved by bromination at ambient conditions catalyzed by heteropolyanion compound $H_5PMo_{10}V_2O_{40}$ dissolved in 1,2-dichloroethane by complexation with tetraglyme (*Eq. 219*).[196] *para*-Bromination of phenol, *o*-cresol, *p*-cresol, *1*-naphthol and *N,N*-diethylaniline is reported to proceed in reasonably good

yields. No bromination of toluene was observed under these conditions.



(219)

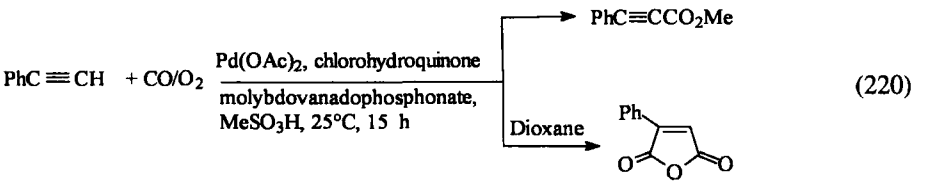
Tetraglyme, 18-crown ether and low molecular weight polyethers dissolve PMoV-2 and promote catalytic oxidation. High molecular weight polyethers do not complex with hetero polyanion compounds and no reaction takes place. The sequence of reaction is shown in *Scheme 33*.



Scheme 33

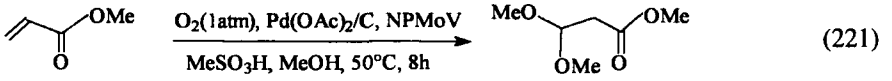
5. Molybdovanadophosphate

Carbonylation of terminal alkynes can be efficiently achieved *via* a muti-catalytic system, Pd(II)-chlorohydroquinone-NPMoV under carbon monoxide and oxygen (*Eq. 220*).[197]



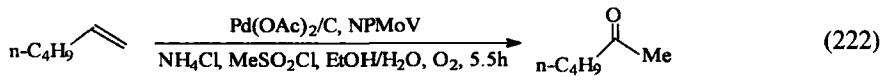
(220)

$Pd(OAc)_2$/NPMoV supported on activated carbon is reported to catalyze acetalization of alkenes under oxygen almosphere (*Eq. 221*).[198] Terminal alkenes and dienes also have been found to



(221)

undergo selective Wacker type oxidation by $Pd(OAc)_2$/NPMoV (*Eq. 222*).[199] Direct coupling of benzene with olefins has also been reported.[200]



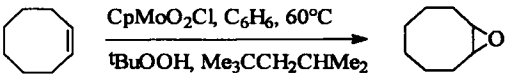
(222)

XVI. MISCELLANEOUS MOLYBDENUM COMPLEXES

1. C_pMoO_2Cl Cp = pentamethyl cyclopentadienyl

Olefins are epoxidized in presence of C_pMoO_2Cl, *t*-BuOOH and $Me_3CCH_2CHMe_2$ at 60°C in good yields (*Eq. 223*).[201] Relative rate of epoxidation of cyclohexene, *1*-methylcyclohexene and 1,2-dimethylcyclohexene with various alkyl hydroperoxides demonstrates that the

rate depends on the structure of the alkyl group of the alkylhydroperoxide.

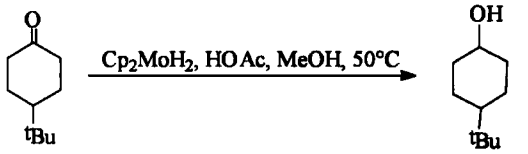


(223)

2. $(\eta^5\text{-}C_5H_5)_2MoH_2$

Molybdenum(IV) dihydride $(C_p)_2MoH_2$[202] ($C_p = \eta^5\text{-}C_5H_5$) has basic character and is easily protonated to give $[(C_p)_2MoH_3]^+$ having oxidation number 6. Therefore a system consisting of $(\eta^5\text{-}C_5H_5)_2MoH_2$ and protonic acids such as RCOOH, HCl and *p*-$MeC_6H_4SO_3H$ reduces aldehydes and ketones under mild conditions chemoselectively. Acetaldehyde and acetone are easily reduced by this system at room temperature while ethyl acetate was not reduced. The system also reduces allylic alcohol but it was inert to unsubstituted alkenes. α,β-Unsaturated ketones were converted to saturated ketones and alcohols indicating that 1,4-reduction is taking place.

The stereochemistry of the carbonyl reduction was examined by using substituted cyclohexanones. The reduction of 4-*t*-butylcyclohexanone afforded mainly *cis*-4-*t*-butyl- cyclohexanol when two equivalents or more of acid RCOOH (R = CF_3, Me, Et or ^{t}Bu), HCl or TsOH was used (*Eq. 224*).[202]

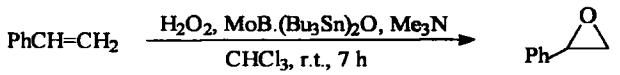


(224)

The diastereoselectivity was found to decrease with the increasing bulk of the alkyl group in the carboxylic acids and by reducing the amount of acid, *i. e*, use of 1 equiv. of TsOH, resulted in inversion of diastereoselectivity from excess of *cis*-isomer to excess of *trans*-isomer.

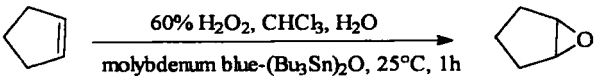
3. *Molybdenum Blue-$(Bu_3Sn)_2O$; MoB-$(Bu_3Sn)_2O$*

Molybdenum blue was produced by the reaction of molybdenum powder with an insufficient amount of 30% H_2O_2. The catalyst itself was prepared *in situ* by stirring molybdenum blue (MoB) and $(Bu_3Sn)_2O$ in $CHCl_3$ for 20 min at room temperature. The epoxidation of alkenes was carried out with H_2O_2 in presence of molybdenum oxide(VI)-$(Bu_3Sn)_2O$ in $CHCl_3$ at 25°C.[203] The oxidation of styrene gave poor yields of styrene oxide. However, addition of an equimolar amount of trimethylamine (TMA) enhanced the yield of styrene oxide significantly (*Eq. 225*). The presence of TMA is also indispensable in the reaction of cyclohexene and



(225)

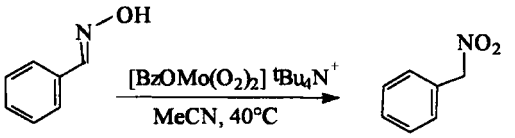
α-pinene (57 to 87%). The role of the amine is used to stabilize the epoxide. The epoxidation by MoB-$(Bu_3Sn)_2O$ has been extended to cyclopentene in presence of 60% H_2O_2 at room temperature (*Eq. 226*).[204]



(226)

4. $[BzOMo(O_2)_2]\ ^tBu_4N^+$

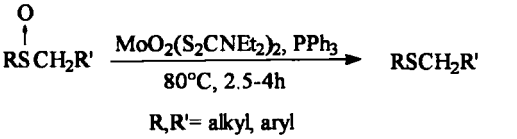
Oximes are oxidized to corresponding nitro compound in presence of $[BzOMo(O_2)_2]^tBu_4N^+$ in CH_3CN at 40°C in good yields (*Eq. 227*).[205]



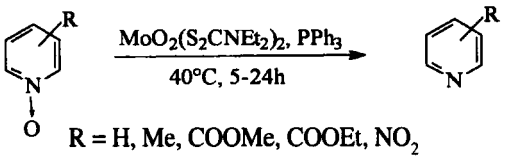
(227)

5. $MoO_2(S_2CNEt_2)_2$

Sulfoxides and pyridine *N*-oxides are deoxygenated to corresponding sulfides and pyridine in presence of $MoO_2(S_2CNEt_2)_2$ (*Eqs. 228 and 229*).[206]



(228)

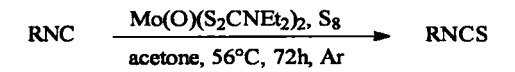


R = H, Me, COOMe, COOEt, NO_2

(229)

6. $Mo(O)(S_2CNEt_2)_2$

$Mo(O)(S_2CNEt_2)_2$ catalyzes the sulfurization of a variety of isonitriles with elemental sulfur or propene sulfide as sulfur donor to corresponding isothiocyanates in good yields under mild conditions (*Eq. 230*).[207]



(230)

7. $MoO_2Cl_2(DMSO)_2$

$MoO_2Cl_2(DMSO)_2$ has been used catalytically for the oxidation of variably substituted thiols to disulfides (*Eq. 231*).[208]

$$2RSH + DMSO \xrightarrow[rt,\ 20\ min]{MoO_2Cl_2(DMSO)_2} RSSR + H_2O + H_2S \qquad (231)$$

8. $(DME)Cl_2Mo(=N\ ^tBu)_2$

Imines are reported to undergo metathesis in presence of $(DME)Cl_2Mo(=N\ ^tBu)_2$ in benzene at 85-90°C (*Eq. 232*).[209]

$$\begin{matrix} PrN{=}CHPh \\ PrN{=}CH\ ^tBu \end{matrix} \xrightarrow[C_6H_6,\ 85\text{-}90°C,\ 3\ days]{(DME)Cl_2Mo(=N\ ^tBu)_2} \begin{matrix} PrN{=}CHPh \\ PhN{=}CH\ ^tBu \end{matrix} + \begin{matrix} PhN{=}CHPh \\ PrN{=}CH\ ^tBu \end{matrix} \qquad (232)$$

9. ZrO_2 and Mo-ZrO_2

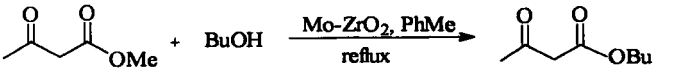
The esterification of various mono- and dicarboxylic acids by ZrO_2 and Mo-ZrO_2 solid acid catalyst (*Eq. 233 and 234*)[210] has been carried out at 85°C. The Mo-ZrO_2 mixed oxide catalyst exhibited higher acidity than ZrO_2 catalyst which is due to electron-deficient state formed by

$$MeCOOH + BuOH \xrightarrow[358\ K,\ 6h]{Mo\text{-}ZrO_2} MeCOOBu \qquad (233)$$

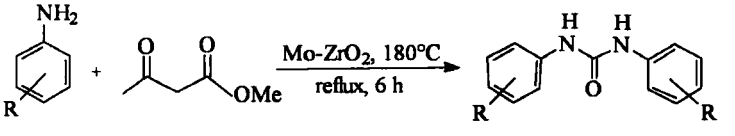
the introduction of Mo cations into the lattice of ZrO_2 solid. Acetic acid on esterification with BuOH and ^{i}BuOH gave 95% and 85% of esters respectively. No reaction occurred with cyclohexanol which suggests that bulky alcohols do not give esters.

$$HOOC(CH_2)_nCOOH + ROH \xrightarrow[358\ K,\ 6h]{Mo\text{-}ZrO_2} ROOC(CH_2)_nCOOR + H_2O \qquad (234)$$

Mo-ZrO_2 solid acid catalyst is also used for transesterification of β-keto esters (*Eq. 235*)[211] and for synthesis of diarylureas (*Eq. 236*).[212] Pt-Mo/ZrO_2 solid acid catalyst has been

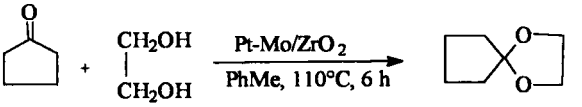


(235)



(236)

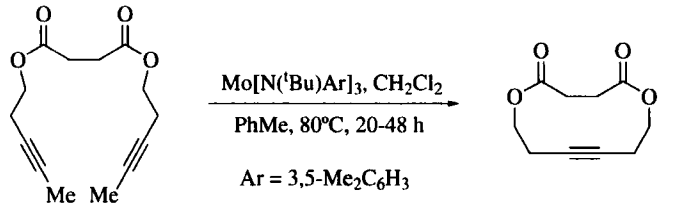
reported for selective protection of carbonyl compounds (*Eq. 237*).[213]



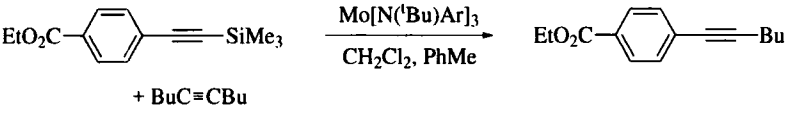
(237)

10. Mo[N(ᵗBu)Ar]₃, Ar = 3,5-Me₂C₆H₃

$Mo[N(^tBu)Ar]_3$ are catalyst precursors for *in situ* activation and for metathesis of alkynes (*Eq. 238*)[214] and cross metathesis of alkynes (*Eq. 239*).[215]



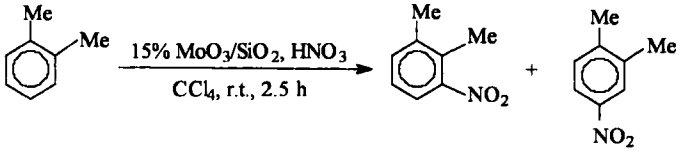
(238)



(239)

11. MoO_3/SiO_2

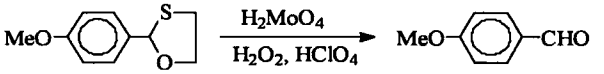
Nitration of aromatic compounds can be carried out on solid catalyst, MoO_3/SiO_2, WO_3/SiO_2, TiO_2/SiO_2 and TiO_2-WO_3/SiO_2 in high yield (*Eq. 240*).[216]



(240)

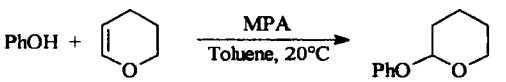
12. Molybdic Acid and Molybdophosphoric acid

Molybdic acid (H_2MoO_4) has been effective for the deprotection of 1,3-oxathiolanes to give the parent carbonyl compounds in high yields (*Eq. 241*).[217] Molydophosphoric acid



(241)

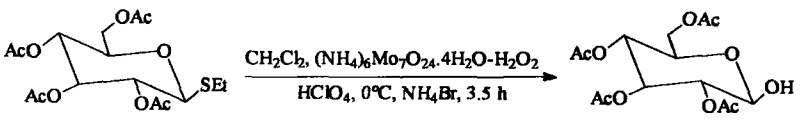
supported on silica has been used for efficient tetrahydropyranylation of phenols and alcohols (*Eq. 242*).[218]



(242)

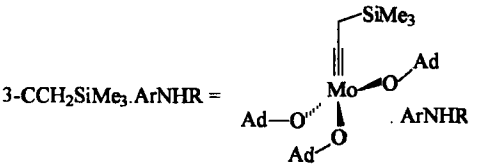
13. $(NH_4)_6Mo_7O_{24}•4H_2O - H_2O_2$

Hydrolysis of thioglycosides can be efficiently achieved by $(NH_4)_6Mo_7O_{24}•4H_2O$–H_2O_2 (*Eq. 243*).[219]

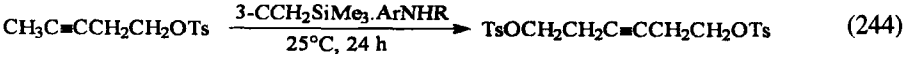


(243)

14. Trialkoxy Molybdenum (VI) Alkylidene Complex



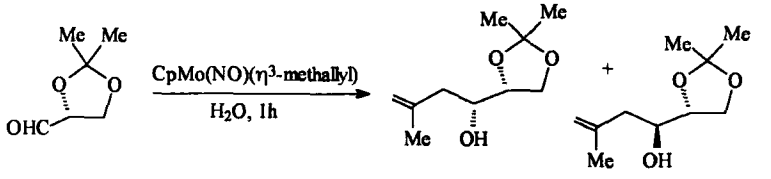
3-CCH_2SiMe_3•ArNHR has been used as a catalyst for facile alkyne metathesis (*Eq. 244*).[220]



(244)

15. $C_pMo(NO)(\eta^3$-methallyl)

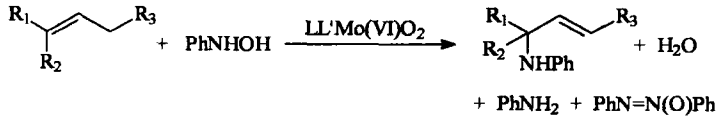
Allylic addition to chiral aldehydes can be carried out with $C_pMo(NO)(\eta^3$-methallyl)[221] with high enantiomeric purity (*Eq. 245*).



(245)

16. Mo(dipic)(HMPA)(η^2-PhNO)

Mo catalyzed process for olefin amination using *N*-phenylhydroxylamine as the stoichiometric aminating agent is shown in *Eq. 246*.[222] The initial step in the catalytic reaction

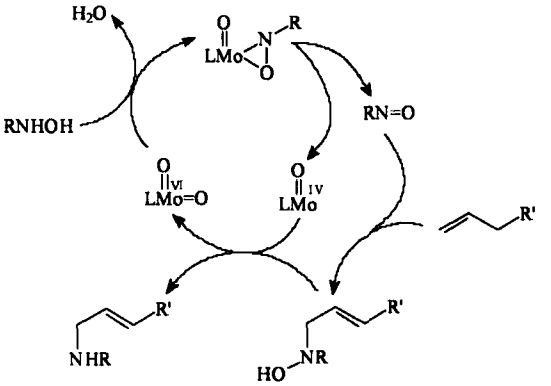


(246)

mechanism is the generation of complex **20** from reaction of LL'Mo(VI)O_2 (**21**) with PhNHOH (*Eq. 247*). The formation of molibdo-oxaziridines has already been reported by Sharpless

(247)

et al.[223] The complex (**20**) reacts with olefins and transfers NR group from Mo complex to olefin as shown in *Scheme 34*. A practical limitation of the stoichiometric and the catalytic reaction is the low to moderate yields which result from competing formation of other N-containing by-products, primarily aniline, azobenzene and azoxybenzene.



Scheme 34

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