SYNLETT Spotlight 119

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Molybdenum Hexacarbonyl [$Mo(CO)_6$]

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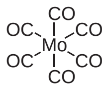
Introduction

Molybdenum hexacarbonyl [$Mo(CO)_6$] is a stable crystalline solid with an octahedral geometry (Figure 1). It is generally prepared by reductive carbonylation of molybdenum halides, or is obtained from commercial sources. $Mo(CO)_6$ finds use as catalyst or reagent in several processes, by itself or tuning its reactivity by ligand exchange.[1] Replacement of the carbonyl ligands by both p and s donors affords a large number of different molybdenum complexes which have found use in organic synthesis. The use of chiral ligands allows high levels of regio- and enantioselectivity to be attained.[2]

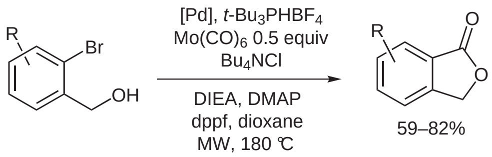


Molybdenum hexacarbonyl
1

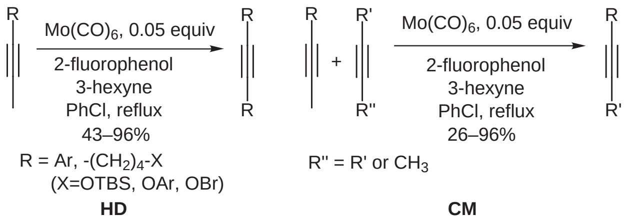
Figure 1

Abstracts

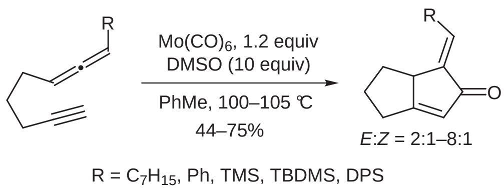
(A) The use of a thermostable catalytic system in combination with $Mo(CO)_6$ allowed the synthesis of benzofuranones starting from bromobenzyl alcohols.[3a] Indanones were obtained under similar conditions using *ortho*-bromo(chloro)styrenes.[3b] A variant was performed by using polymer-supported amines for the synthesis of amides from aryl halides.[3c] A convenient synthesis of α-methylene-γ-butyrolactones from allenyl carbonyls was performed by a DMSO-promoted carbonylation.[3d] These reactions enlighten the role of $Mo(CO)_6$ as a source of CO.



(B) 'Instant' catalysts formed from $Mo(CO)_6$ and phenols have been developed for alkyne metathesis.[4a,b] Pre-heating activation of catalytic systems consisting of $Mo(CO)_6$ and 4-chlorophenol has increased the yields of productive enyne metathesis.[4c,d] This procedure was used to dimerize *ortho*-alkoxypropynylbenzenes and to afford ring-closing alkyne metathesis (RCAM) products from dipropynyls. The use of 2-fluorophenol in place of 4-chlorophenol led to a more reactive and friendly catalyst, which has been employed not only in RCAM, but also in alkyne homodimerizations (HD) and cross metatheses (CM).[4e,f]



(C) $Mo(CO)_6$ was reported to effect Pauson–Khand reactions of enynes to afford cyclopentenones.[5a,b] Chiral alkynyl allenes afforded enantioenriched α-alkylidene cyclopentenones.[5c,d] Under the same conditions, functionalized difluoroallenes underwent intramolecular [2+2] cycloaddition to afford *gem*-difluoro bicyclo [4.2.0] systems, instead of the expected Pauson–Khand products.[5e] A tandem Pauson–Khand reaction of bisyne-bisallenes to [5.5.5.5] tetracycles has been reported by Cook, who used a saturated solution of $Mo(CO)_6$.[5f]



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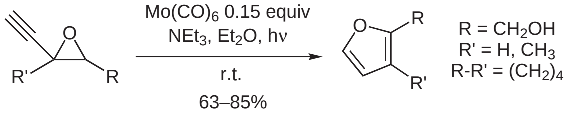
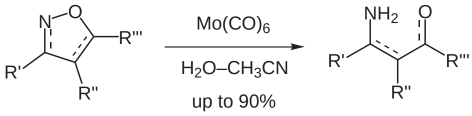
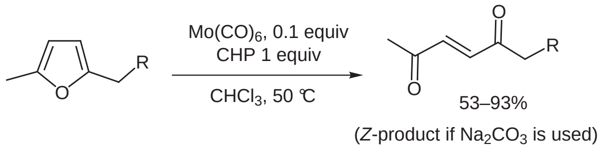
(D) $Mo(CO)_6$ has catalyzed the cycloisomerization of 1-alkyn-4-ols to 2,3-dihydrofurans and the isomerization of epoxyalkynes to furans.[6a] Cyclizations of allylphenylethers with skeletal rearrangement to benzopyrans have also been performed.[6b,c] Friedel–Crafts alkylations have been reported, too.[6d]



(E) $Mo(CO)_6$ has been used to reduce the N–O bonds of isoxazoles,[7a,b] isoxazolines,[7c–e] isoxazolidines[7f] and 1,2-oxazines.[7g,h] Variants employed sub-stoichiometric amounts of $Mo(CO)_6$ in the presence of $NaBH_4$,[7h] or a decomplexing work-up on silica gel.[7j] The selective reduction of azides,[7k] nitro compounds[7k] and hydroxylamines[7i] to amines and deoxygenation of epoxides[7l] have also been accomplished.



(F) $Mo(CO)_6$ behaved as a catalyst for the mild oxidation of 2,5-dialkylfurans to *E* or *Z* (depending on the use of a base) enediones using cumyl hydroperoxide (CHP).[8a] Diones gave peroxipyranones in moderate yields, irrespective of the C=C bond configuration, when *t*-butylhydroperoxide (TBHP) was used.[8a,b] This indicates that $Mo(CO)_6$ can be employed not only in reduction processes, but also in oxidations.



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