IN THE NAME OF GOD

NEW APPLICATIONS OF TUNGSTEN HEXACHLORIDE, MOLYBDENUM PENTACHLORIDE, ZIRCONIUM TETRACHLORIDE AND LITHIUM BROMIDE IN ORGANIC SYNTHESIS

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To the Memory of:

Khosrow

(My Honorable Martyr Brother)

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ABSTRACT

New Applications of Tungsten Hexachloride, Molybdenum Pentachloride, Zirconium Tetrachloride, and Lithium Bromide in Organic Synthesis

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In this study, we have presented that tungsten hexachloride (WCl_6) is a versatile and multi purpose reagent that can be utilized as either an oxophilic reagent or a Lewis acid in a wide variety of functional group transformations.

Deoxygenation of various types of sulfoxides and also reductive coupling of different sulfonyl chlorides are efficiently performed by means of low valent tungsten species derived by *in situ* reaction of WCl_6 with NaI or Zn in dry CH_3CN or THF.

Protection of different types of carbonyl compounds as diethyl acetals, 1,3-dioxanes, 1,3-dithiolanes and 1,3-dithianes are effectively catalyzed by WCl_6.

Deprotection of masked functional groups is of especial practical importance in organic syntheses. Along this line, we have shown that acetals, thioacetals and oximes are converted to the corresponding carbonyl compounds by using WCl_6 in dry CH_2Cl_2 or CH_3CN WCl_6/DMSO in dry CH_2Cl_2, and WCl_6/Zn in dry CH_3CN, respectively, in excellent yields.

An interesting feature of this study is that, WCl_6 in the presence of DMSO promotes facile and efficient one-pot ring expansion-

chlorination reactions of 1,3-dithiolanes and 1,3-dithianes derived from the corresponding substituted acetophenones in dry CH_2Cl_2. Chemoselective and efficient ring enlargement reaction of 1,3-dithiolanes and 1,3-dithianes is also achieved by this method in dry CH_3CN. To the best of our knowledge, at the present time, no reports are available for these transformations in the literature.

These encouraging results prompted us to extend our studies to other oxophilic metal chlorides, namely, molybdenum pentachloride ($MoCl_5$) and zirconium tetrachloride ($ZrCl_4$). Our findings show that they can also act as effective catalysts for acetalization, transacetalization, thioacetalization and transthioacetalization reactions. $MoCl_5$ shows very good ability for deprotection of acetals and dithioacetals and one-pot ring expansion-chlorination of 1,3-dithiolanes and 1,3-dithianes.

Finally, an exceptional chemoselective and efficient dithioacetalization of α,β-unsaturated and aromatic aldehydes in the presence of the other carbonyl compounds and acetals under solvent-free and neutral reaction conditions with lithium bromide (LiBr) as catalyst is also introduced.

TABLE OF CONTENT

CONTENT **PAGE**