**MgBr₂·OEt₂ – A Versatile Reagent in Organic Synthesis**

Compiled by Suresh Kumar Tipparaju

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**Introduction**

Use of magnesium(II) species as Lewis acid catalysts for various functional group transformations is well documented.\(^1\) Of these, magnesium halides are the most useful. Ready availability and ease of preparation prompted the frequent use of MgBr₂·OEt₂ in various organic transformations. The oxophilic and coordinating nature of MgBr₂·OEt₂ has been demonstrated through its use as a bidentate chelating Lewis acid in a number of chelation-controlled reactions such as cycloadditions,\(^2\) asymmetric aldol reactions,\(^3\) rearrangements,\(^4\) radical additions,\(^5\)\(^6\) hydrogen transfer reactions,\(^7\) stereoselective reductions,\(^8\) and anomerizations.\(^9\)

MgBr₂·OEt₂ is commercially available as a grey solid (mp >300 °C, fp 35 °C). It can be readily prepared by reacting a slight excess of magnesium turnings with 1,2-dibromoethane in anhydrous diethyl ether.\(^10\) The solution can be stored at room temperature for several months and the solid can be stored in a vacuum desiccator for indefinite periods without any loss of activity.

**Abstracts**

(A) Condensation of 2,5-dimethoxy-2,5-dihydrofuran with ethyl vinyl ether in the presence of a catalytic amount of MgBr₂·OEt₂ resulted in 2-furylacetaldehyde diethyl acetal in 50% yield. The reaction is a formal acetal and ethyl vinyl ether condensation followed by aromatization. The protocol has been employed in the synthesis of various 2-(2-furo)tetrahydrofuranic or -pyranic moieties in good yields.\(^11\)

(B) A mild and practical N-acylation of amides was possible by the dual activation of both amides and acid anhydrides with MgBr₂·OEt₂.\(^12\) The method was applicable to amides that can undergo O-acylation and are susceptible to racemization or O,N-acyl migrations.

(C) We have recently reported a mild method for the formation of cyclic siloxanes by the exchange of the Li counterion of an intermediate alkoxide with Mg, using excess MgBr₂·OEt₂.\(^13\) The reaction may formally be considered to be a semi-Brook rearrangement.

(D) MgBr₂·OEt₂, in combination with Bu₃SnH, was effective in a chelation-controlled reductive opening of methoxybenzylidene acetals.\(^14\) The reaction offers a mild and efficient method for selective mono-MPM ether protection of diols. High conversions, regioselectivity and tolerance to functional groups make this a very useful protocol in natural product synthesis.

(E) MgBr₂·OEt₂ effected deprotection of aliphatic SEM ethers under extremely mild and high yielding conditions in the presence of other sensitive groups like acetonides, TBS and TIPS ethers and O-silylated cyanohydrins.\(^15\) A variety of functionalities including alcohols, esters, benzyl groups, dithianes, and methoxy acetals are tolerated.

**SYNLETT** 2004, No. 5, pp 0912–0913
Advanced online publication: 10.03.2004
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(F) The MgBr₂·OEt₂–Me₆S system was used for a mild and chemoselective deprotection of p-methoxybenzyl (PMB) ethers in the presence of 1,3-diene, t-butylmethyl sulphonyl (TBDBS) ether, benzoate, benzyl ether, and acetonides. The method is especially effective for 1,3-diene systems that tend to isomerize rapidly when other protocols are employed.¹⁷

(G) A stereodivergent opening of the oxirane ring with MgBr₂·OEt₂ was recently demonstrated by us.¹⁸ While MgBr₂·OEt₂ alone resulted in the bromohydrin in high diastereomeric excess, use of MgBr₂·OEt₂/Amberlyst 15 gave the syn-product in high yields.

(H) The efficacy of MgBr₂·OEt₂ as a chelating Lewis acid in highly diastereoselective addition of nucleophiles to Cr(CO)₃-complexed aryl aldehydes was recently demonstrated by us.¹⁹a The results indicated that MgBr₂·OEt₂ can form an effective seven-membered chelate.

(I) MgBr₂·OEt₂ could afford 3-hydroxyazetidines by a highly regio- and stereoselective cyclization of 2,3-epoxy amines.²⁰

References


