MgBr₂·OEt₂ – A Versatile Reagent in Organic Synthesis

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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 acetones, TBS and TIPS ethers and O-silylated cyanohydrins. 15 A variety of functionalities including alcohols, esters, benzyl groups, dithianes, and methoxy acetals are tolerated.
(F) The MgBr₂·OEt₂ system was used for a mild and chemoselective deprotection of p-methoxybenzyl (PMB) ethers in the presence of 1,3-diene, tert-butyldimethylsilyl (TBDMs) 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.

(G) A stereodivergent opening of the oxirane ring with MgBr₂·OEt₂ was recently described. While MgBr₂·OEt₂ alone resulted in the anti-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. The results indicated that MgBr₂·OEt₂ can form an effective seven-membered chelate.

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

References


