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Carbocatalysis: reduced graphene oxide-catalyzed Boc protection of hydroxyls and graphite oxide-catalyzed deprotection

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Abstract

A new metal-free method for *O*-Boc protection of alcohols and phenols was achieved with reduced graphene oxide (RGO) as an efficient and recyclable catalyst. Graphite oxide (GO) served as the catalyst for the deprotection of Boc group with methanol. The plausible mechanisms were proposed, in which RGO acted as a solid base catalyst and GO as a solid acid catalyst.

Keywords: Carbocatalyst; Reduced graphene oxide; Graphite oxide; Hydroxy compounds; Boc protection/deprotection.

The protection and deprotection of hydroxyl groups in alcohols and phenols are of great necessity in multistep synthesis. Traditionally, transforming alcohols and phenols to their carboxylic acid esters is a common protection approach.¹ In recent years, di-*tert*-butyldicarbonate (Boc₂O) has been widely used to introduce the *tert*-butoxycarbonyl (Boc) protecting group on hydroxyl groups.^{1,2} Comparing with ester protection, Boc protection has some advantages. The reaction products, *t*-butyl carbonates of alcohols and phenols, are generally more stable than the corresponding esters under basic conditions and/or in the presence of a wide range of nucleophiles. On the other hand, they are so labile under moderately acidic conditions that the strong bases are not necessary for the deprotection.³ Furthermore, Boc₂O is low-cost, lowly toxic and easily available, which makes it a good choice for protecting alcohols and phenols as unsymmetrical carbonates under mild conditions. Various metal catalysts, such as Zn(OAc)₂,^{4a} V(O)(OTf)₂,^{4b} Mg(NTf₂)₂,^{4c} BiCl₃,^{4d} NaLaTiO₄,^{4e} MgO-ZrO₂ nanoparticle,^{4f} and silica-supported Er(III) (Er^{III}-MCM-41)^{4g} have been involved in these transformations. Besides, 1-*tert*-butoxy-2-*tert*-butoxycarbonyl-1,2-dihydroisoquinoline (BBDI),^{5a}

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