Dialkyl Carbonates as Sacrifical Molecules: from Heterocycles to Macrocycles

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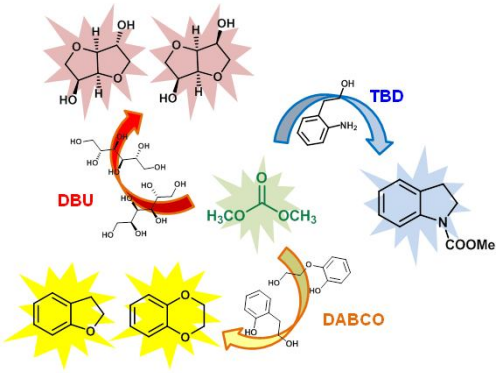
Abstract

Dialkyl carbonate (DACs) are well recognized green reagents and solvents for new synthetic pathways. In particular dimethyl carbonate (DMC), nowadays synthesized by CO_2 insertion into epoxides, has shown surprising high selectivity with different nucleophiles acting either as methoxycarbonylation ($B_{Ac}2$ mechanism) or methylaing ($B_{Al}2$ mechanism) agent.



In this lecture recent advances in DMC chemistry for chlorine-free synthesis of five- and six-membered heterocycles will be presented. Reaction of 1,4-diols with DMC in the presence of a base resulted in the chlorine-free synthesis of five-membered cyclic compounds. This synthetic procedure can be also used for the quantitative intramolecular heterocyclisation of bifunctional compounds, i.e., 4-amino-1-butanol to achieve pyrrolidine.[1]

Figure 1. Synthesis of heterocycles by DMC chemistry

Six-member cyclic carbamates have also been synthesized by chlorine-free approach employing DMC chemistry. In fact, reacting a primary amine or a hydrazine with a di(methylcarbonate) derivative of 1,3-diols oxazinan-2-ones can be synthesized in a one-pot chlorine-free reaction.[2]
Recently we also investigated the replacement of the chlorine by a carbonate moiety in half-nitrogen and -sulphur mustard compounds. Results collected demonstrated that the novel mustard carbonates are easily synthesized, don't show any toxicity and react with a wide range of nucleophiles in the absence of any base. These novel compounds can be employed for the synthesis of piperidines and thiopyrans. Furthermore, the polycondensation of a nitrogen mustard carbonate analogue with aromatic diols under dilution conditions resulted in a new synthetic approach to azacrowns previously not accessible.[3]

References

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