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Dimethyl Carbonate and its derivative for Green Chemistry

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Abstract:

Dialkyl carbonates (DACs) and in particular dimethyl carbonate (DMC) occupy a privileged position on Green on Chemistry due to their low toxicity, high biodegradability and peculiar reactivity and also because their utilization of CO₂ and CO₂-based compounds.

Their behavior in organic synthesis as feedstocks is very remarkable and just exploded by three decades.

DACs are ambident electrophiles, which under appropriate conditions can undergo BAc₂- or BAl₂-nucleophilic substitutions to give, respectively, alkoxycarbonylation and alkylation reactions. The reactivity of DMC is tunable: at 90 °C, methoxycarbonylations take place, whereas at higher reaction temperatures methylation reactions are observed with a variety of nucleophiles. In the particular case of substrates susceptible to multiple alkylations (e.g., CH₂-active compounds and primary amines), DMC allows unprecedented selectivity toward mono-C- and mono-N-methylation reactions with a chemoselectivity up to 99%. Moreover, DMC-mediated methylations are truly catalytic reactions that use safe solids (alkaline carbonates or zeolites), thereby avoiding the formation of undesirable inorganic salts as byproducts.

This groundbreaking achievement has definitely drawn attention toward the conception of procedures to activate the rather stable DACs with the aim of employing these compounds as green alternatives to their reactive chlorinated analogues.

The lecture will report on DACs as alkoxycarbonylating agents and their applications in industry and fine synthesis, as well as alkylating agents including allylic alkylation using palladium catalysts and anchimerically driven alkylations via mustard carbonates analogues. The reactivity of organic carbonates toward several substrates and under different reaction conditions will be described along with some distinctive DAC-mediated cyclization and transposition reactions which can be carried out under continuous-flow conditions.

The many efforts devoted to improving the industrial suitability of organic carbonates have unveiled an intriguing and innovative chemistry as demonstrated by the numerous publications and patents published on these compounds over the last thirty years.

Your photos
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