THE REACTIVITY OF DIMETHYL CARBONATE

F. Arico[1], P. Tundo[2]

1 - Interuniversity Consortium Chemistry for the Environment, INCA

2 - Department of Environmental Science, Ca' Foscari University, Dorsoduro 2137, Venice (Italy)

fabio.arico@unive.it

DMC is a versatile compound which represents an attractive eco-friendly alternative to both methyl halides (or dimethylsulphate) and phosgene for methylation and carbonylation processes, respectively. DMC, produced nowadays by a clean process, possesses properties of no toxicity and biodegradability which makes it a true green reagent to be used in syntheses that prevent pollution at the source. The reactivity of DMC is tunable: at T ≤ 90 °C, methoxycarbonylations take place, while at higher reaction temperatures, methylation reactions are observed with a variety of nucleophiles. Besides, DMC-mediated methylations are catalytic reactions which use safe solids (alkaline carbonates) avoiding the formation of undesirable inorganic salts as by-products. The high selectivity in methylation reactions is due to the ambident electrophilic character of DMC which reacts on its hard centre (the carbonyl group) with harder nucleophiles and on its soft one (the methyl group) with softer nucleophiles, according to the Hard-Soft Acid and Base (HSAB) theory.
In the particular case of substrates susceptible to multiple alkylations (*e.g.* CH_2-active compounds and primary amines), DMC allows unprecedented selectivity towards mono-*C*- and mono-*N*-methylation reactions. Recently achieved selectivity with nucleophiles on N, O, S and C will be reported. Besides, lately some investigations have been conducted also on the reactivity of the ambident nucleophile phenylhydrazine and DMC. Phenylhydrazine contains two non-equivalent nitrogen nucleophilic centres. N-1 is relatively more acidic due to the electron withdrawing effect of the phenyl ring substituent while N-2 possesses reactivity similar to that of an aliphatic amine. Selective methylation and carboxymethylation of phenylhydrazine will be reported. Finally, in this lecture will be discussed as well: the reactivity of higher homologues of DMC (*i.e.* diethyl- and dibenzyl-carbonate) which are excellent mono-C- and mono-N-alkylating agents and the synthesis and reactivity of asymmetrical methyl alkyl carbonates ($ROCO_2Me$ with R ≥ C_3) undergo methylation processes with a chemo selectivity up to 99%.