

*Environment and Green Chemistry**Green Chemistry - IV*

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**SYNTHESIS OF CYCLIC CARBONATES FROM WASTE CARBON DIOXIDE****M. NORTH<sup>1</sup>**<sup>1</sup> *Newcastle University, Chemistry, Newcastle Upon Tyne, United Kingdom*

World-wide production of oil and gas is expected to peak before 2020. Therefore, since over 90% of all commercially available organic chemicals are sourced from crude oil, a major challenge for chemistry over the next 10 years is to find alternative, sustainable feedstocks for the chemicals industry. One particularly attractive reaction in this respect is the 100% atom economical reaction between CO<sub>2</sub> and epoxides leading to cyclic carbonates. Cyclic carbonates are already manufactured commercially and have a number of applications including as electrolytes for lithium ion batteries and as polar aprotic solvents.

In this presentation, the development of bimetallic aluminium(salen) based catalysts which, in the presence of a tetraalkylammonium cocatalyst, allow this reaction to be achieved at atmospheric pressure and room temperature will be discussed. Mechanistic studies on cyclic carbonate synthesis using these catalysts will be presented, which subsequently led to the synthesis of one-component versions of the catalysts. The immobilisation of the one-component catalysts on inorganic supports and their use in gas-phase flow reactors at temperatures and pressures suitable for direct utilization of power station flue-gas will be described. The tolerance of the catalysts to the NO<sub>x</sub> and SO<sub>x</sub> impurities present in simulated flue-gas will be reported as will the results of studies in which the catalysts were exposed to real flue gas from a combustion test-rig burning natural gas or coal.

In view of the scale of the possible use of the catalysts (up to 50 tonnes of catalyst per reactor), it is essential that the cost of catalyst production is as low as possible. Therefore, a cost analysis of the catalysts will be presented along with a modified synthesis which avoids all of the expensive reagents and solvents.

**Keywords:** *carbon dioxide fixation; aluminium; sustainable chemistry;*

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**DIMETHYL CARBONATE AS GREEN REAGENT FOR CHLORINE-FREE SYNTHESIS****F. ARICO<sup>1</sup>, P. TUNDO<sup>1</sup>**<sup>1</sup> *Universita Ca' Foscari, Dept of Environmental science informatics and statistics, Venezia, Italy*

Dialkyl carbonate (DACs) in general, and dimethyl carbonate (DMC) in particular, are well recognized green reagents and solvents for new synthetic pathways. DMC, nowadays synthesized by CO<sub>2</sub> insertion into epoxides, has shown surprising high selectivity with different monodentate and bidentate nucleophiles. DMC can act as methoxycarbonylation agent via a B<sub>Ac</sub>2 mechanism at reflux temperature and as methylating agent via a B<sub>Al</sub>2 mechanism at higher temperature. Both reactions give as only by-product methanol and eventually CO<sub>2</sub>.

In this work, we report recent advances in DMC chemistry for chlorine-free synthesis of 5- and 6-membered heterocycles and for the synthesis of nitrogen and sulphur half-mustards carbonate analogues.

In particular, the reaction of 1,4-diols with DMC in the presence of a base resulted in the chlorine-free synthesis of 5-membered cyclic compounds. This reaction pathway to cyclic ethers is of general application as it can be employed for the preparation of small heterocycles as well as of industrially relevant compounds *i.e.* (-)-norlabdane oxide and isosorbide. This synthetic procedure can be also used for the quantitative *intramolecular* heterocyclisation of bifunctional compounds *i.e.* 4-amino-1-butanol to achieve pyrrolidine.

Six-member cyclic carbamates have also been synthesised by chlorine-free approach employing DMC chemistry. In fact, reacting a primary amine or a hydrazine with a di(methyl carbonate) derivative of 1,3-diols oxazinan-2-ones can be synthesised in a one-pot chlorine-free reaction.

Recently we also investigated the replacement of the chlorine by a carbonate moiety in half-nitrogen and -sulphur mustard compounds. This resulted in new, unexplored and safe compounds that showed good reactivity. Results collected demonstrated that the novel mustard carbonates are easily synthesised, don't show any toxicity and react with a wide range of nucleophiles in the absence of any base.

**Keywords:** *Dimethyl Carbonate; Cyclisation; Heterocycles; Mustard Compounds; Green Chemistry;*