5-Membered Cyclic Ethers Via Phenonium Ion-Mediated Cyclization Through Carbonate Chemistry

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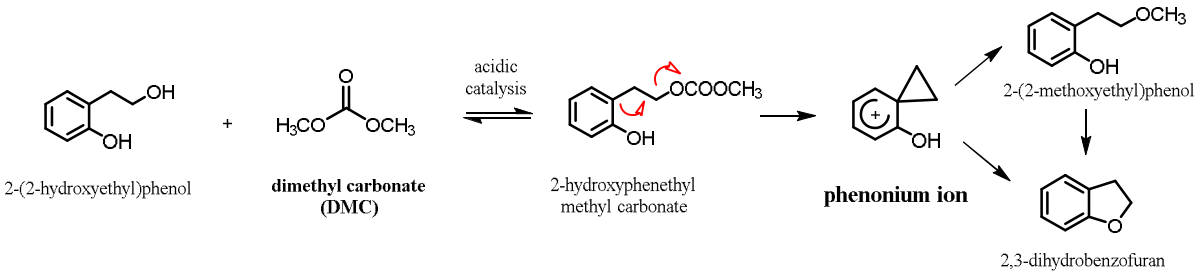
The production of dimethyl carbonate (DMC) on an industrial scale by green synthetic approaches, has boosted researchers' interest toward the use of organic carbonates (DACs) as green alternative of phosgene, dimethyl sulfate and methyl halides in alkylation and alkoxycarboniation reactions.[1] However, the intriguing chemistry of DACs and their versatility in organic reactions still need to be completely unveiled.[2] In this communication, it is reported the first study regarding the cyclization of 2-(2-hydroxyethyl)phenol by reaction with DMC chemistry in optimised acidic conditions. The reaction mechanism has been initially investigated via theoretical calculations carried out by using the GAUSSIAN09 system of programs. According to the *in silico* results, the most energetically favoured pathway encompasses the DMC-mediated formation of phenonium ion – stabilised by the hydroxyl group in *orto* position –[3] followed by the conversion into the 2-(2-methoxyethyl)phenol. The 2,3 dihydrobenzofuran is then achieved via intramolecular cyclization of this intermediate. The data collected by performing the reaction at 90 °C using DMC as solvent and testing a variety of acidic catalysts not only have confirmed the quantum mechanic hypothesis, but have also highlighted the roles played by DMC in this peculiar cyclisation: reaction medium, methoxycarbonylation agent and leaving group in the intramolecular cyclization leading to the phenonium ion.



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