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Studies on the Baeyer-Villiger oxidation of cyclic ketones to lactones with hydrogen peroxide

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Lactones are important specialty chemicals, characterised by a wide range of application possibilities. They are used as flavour and fragrance additives, solvents, monomers, and intermediates for the production of herbicides and pharmaceuticals. Due to their useful properties the demand for lactones is still increasing. In the industrial scale lactones can be obtained *via* the Baeyer-Villiger (BV) oxidation of cyclic ketones. In a standard protocol, peracids are used as oxidising agents; however, they are instable, shock sensitive, and they cause waste generation. The main challenge in the BV oxidation procedures currently developing is to apply hydrogen peroxide, which is believed to be a safer and environmentally-benign alternative to peracids. Unfortunately, hydrogen peroxide is kinetically inert and it requires a catalyst to act as an effective oxidant in this reaction.

The objective of the study was to develop new methods of Baeyer-Villiger oxidation of cyclic ketones to lactones with hydrogen peroxide. The key challenge to achieve this goal was to design new catalytic systems active in the reaction conditions, in particular in a water-containing system.

In order to meet contemporary requirements for clean BV oxidation five new methods of lactones synthesis were developed during doctoral studies. The methods in the presence of following acidic catalysts were designed: chlorogallate(III) ionic liquids, gallium(III) triflate immobilised onto silica and gallium incorporated into silica, as well as tin(II) triflate immobilised onto multi-walled carbon nanotubes. In addition, an enzymatic catalyst for a chemo-enzymatic version of the BV oxidation comprised of *Candida antarctica* lipase B immobilised onto multi-walled carbon nanotubes was also developed (CALB-MWCNTs).

The next objective of the studies was to evaluate the application potential of the above methods for the production of selected lactone and find an industrial partner interested in further development of the method.

Taking into account the advantages, such as very high selectivity, mild reaction conditions, and commercial availability of the support, the method using CALB-MWCNTs seemed to have the biggest industrial potential, which was also recognised by Grupa Azoty Zakłady Azotowe Puławy S.A. (GAZAP). Cooperation with GAZAP resulted in the financial support from the National Research and Development Centre within the INNOCHEM programme. The project was focused on the development of a process for the production of ε-caprolactone from cyclohexanone and hydrogen peroxide. ε-Caprolactone is a valuable specialty chemical, used mainly to obtain a modern, biodegradable polymer – poly(ε-caprolactone). As a result, a new method of the chemo-enzymatic BV oxidation in the presence of a commercially available aqueous solution of lipase forming an emulsion with other reagents was developed. This specific form of the reaction mixture facilitates mass transfer, which results in a higher yield of ε-caprolactone in a shorter reaction time in comparison to the typical biphasic systems. Currently, works related to the construction of a pilot plant equipped with a 100 L oxidation reactor are in progress. The start of the production in the pilot plant, located in GAZAP, is planned for the end of 2018.