New Trends in Solid Acid-Base Catalysed Transformations

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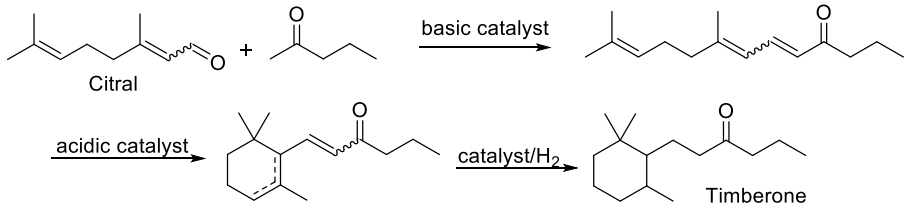
Catalysis plays the major role in the research and development of new products and processes, especially in the fine chemical industry [1]. In the field of acid-base catalysis usually Brønsted acid or bases are used. The majority of the processes are acid catalysed. Only a few base catalysed industrial processes were known around twenty years ago [2]. For more than a decade a main trend in large scale industrial processes is replacement of sulfuric acid by solid acids [3]. The new procedures and processes have various advantages compared to liquid acids and bases: less waste formation, easy product and/or catalyst separation, and solvent recovery. Thus, solid catalysts offer often environmentally benign and more economical pathways for the production of fine chemicals.

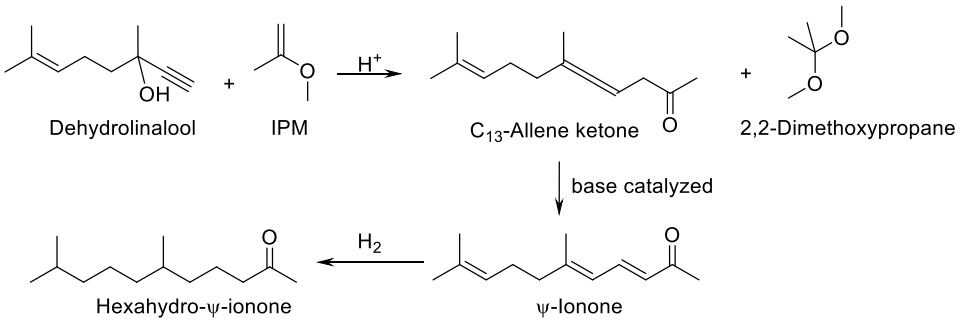
The synthesis of the fragrance timberone was investigated. The current process used stoichiometric amounts of reagents and/or protecting group chemistry. It was found that a base catalysed cross-Aldol condensation of citral and 2-pentanone (Scheme 1) can be performed in excellent yield and selectivity, especially under continuous operation, by applying a base ion exchange resin such as Amberlyst A26-OH. Furthermore, the subsequent acid catalysed cyclization reaction of the corresponding condensation product was carried out in presence of a solid acid. Here an ion exchange resin replaced sulfuric acid [4].



Scheme 1. Synthesis of timberone.

An industrially important reaction is the ethynylation of carbonyl compounds into α-alkynols, which are key starting materials for flavour compounds or isoprenoic building blocks. Usually ethyne addition to carbonyl compounds is performed by the Grignard reaction or base catalysed reaction in ammonia. Performing the ethynylation in presence of a solid base in fixed-bed set-up results in excellent yield. The catalyst can be selected from the group of ion exchange resin [5].

The C3 elongation reaction of α-alkynols into allene-ketones is acid catalysed and the following base catalysed rearrangement reaction results in the formation of α,β-unsaturated ketones. For this type of rearrangement reaction solid base catalysts were evaluated and a high performance system was established in the presence of an ion exchange resin (Scheme 2) [6].



Scheme 2. Allene ketone transformation.

A modern trend in industrial process research and development is the combination of unit operations and the research for multifunctional catalysts, which can be applied in different reaction types. A promising approach of this concept is shown in the manufacturing of a fragrance intermediate. The monoketone reduction of 5,5-dimethylcyclohexane-1,3-dione was carried out in presence of a solid acid coated with a noble metal. The new process has the advantage of higher yields, less waste formation and by-passing of corrosion problems [7].

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