The Current Status and Future Trends in Oxidation Chemistry

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A state of the art reaction should proceed with inexpensive, probably renewable reagents, in standard equipment to give the desired product in quantitative yield and 100% atom economy. Obviously, only very few known chemical transformations fulfill these criteria. Thus, the development of more environmentally benign and clean synthetic methodologies is one of the most important goals of current research in organic chemistry. From its beginning *Advanced Synthesis & Catalysis* has been devoted to a large extent to publishing articles which go in this direction. In this respect the following issue tries to give an overview of the current status and future trends in oxidation chemistry. One could ask, why especially oxidation chemistry? A simple answer is provided by the fact that although oxidation reactions constitute industrial core technologies for converting bulk chemicals to useful products of a higher oxidation state, they are among the most problematic transformations. Until today most of the known textbook oxidation reactions are unacceptable with regard to selectivity and waste generation. Hence, it is not surprising that several papers in this issue stress the general need for the development of more clean and safe oxidation procedures.

By comparing the different oxidation methods it is apparent that, especially, those reactions which allow for the conversion of olefins and hydrocarbons – the basic raw materials for the chemical industry – into more valuable products such as epoxides, diols, alcohols, and carbonyl compounds are of general importance. Thus, most of the following manuscripts are related to inventions or gradual improvements in these areas. In addition, it is nicely demonstrated by several papers that the development of selective oxidations of alcohols constitutes an area of active research.

An important trend for all kinds of oxidation reactions is the use of environmentally more benign oxidants and catalysts. The choice of the respective oxidant determines to a large extent the practicability and efficiency of the respective reaction. Clearly, the use of stoichiometric "toxic" metal oxides should be avoided. Nevertheless, even today a number of examples of such reactions appear in the literature. Among the different oxidants air is the ideal reagent for oxidation reactions. However, the use of air or pure O_2 is sometimes difficult to control and may result in combustion. Unfortunately, in general only one from both oxygen atoms in O_2 is used productively for oxidation ($=50\%$ atom efficiency). Thus, oxidations with molecular oxygen typically require an (over)stoichiometric amount of extra reducing agents to capture the second oxygen atom during the reaction. There is a need to develop more examples in which both oxygen atoms of O_2 are used productively. In addition to molecular oxygen, hydrogen peroxide, H_2O_2, is a "green", waste-avoiding oxidant. It can oxidize organic compounds with an atom efficiency of 47% and generates theoretically only water as co-product. Due to its properties H_2O_2 is particularly useful for liquid-phase oxidations for the synthesis of fine chemicals, pharmaceuticals or agrochemicals, and electronic materials. However, there exists a recent trend to use this oxidant also for bulk processes, e.g., the production of racemic propylene oxide. At this point it is interesting to note that most academic laboratories put a main focus on the methodological development of catalytic asymmetric oxidation reactions such as epoxidation and dihydroxylation. Here, often the "value" of an oxidation catalyst is judged solely by the observed selectivity (chemo-, regio- and stereoselectivity). However, selectivity is only one important issue among others, which determines the usefulness of catalysts. I am convinced that organic chemists should pay more attention to catalyst productivity, activity and recycling. These are key factors for a general application, too. As an example a precious metal catalyst which gives 99% ee with a turnover frequency of $1\ h^{-1}$ is very difficult to apply on a larger scale. From an industrial point of view ***both*** the development of more active and productive catalysts for stereoselective and racemic oxidation reactions using H_2O_2 or O_2 are important and challenging goals in oxidation chemistry.

When we first discussed the potential content of this oxidation issue with Joe Richmond and Roger Sheldon it was immediately clear that this issue should also try to bridge the gap between homogeneous, heterogeneous

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and biocatalysis areas. After having received a number of excellent contributions from each of these areas we can state that this goal has been achieved quite nicely. It is my opinion that we have to cross these traditional boundaries more regularly and that members of each subdiscipline can learn from one other. For example, for me coming from transition metal catalysis it is always fascinating to read about the success of biocatalysts under rather mild reaction conditions. Here, chemists can learn especially from nature to improve the efficiency of their oxidation reactions and to run oxidation processes under milder conditions.

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