Synthesis of α-Oxoaldehyde Hydrates by the Oxidation of Diazo Compounds Using Dimethyldioxirane

Biography

Akinobu Matsuzawa was born and raised in Kanagawa, Japan. After receiving his Ph.D. from the University of Tokyo in 2015 under the supervision of Prof. Masakatsu Shibasaki, he joined Prof. Sugita's group at Hoshi University as an assistant professor. His research interests include the development of new and practical methodologies in organic synthesis.

Institution

Hoshi University, Tokyo, Japan

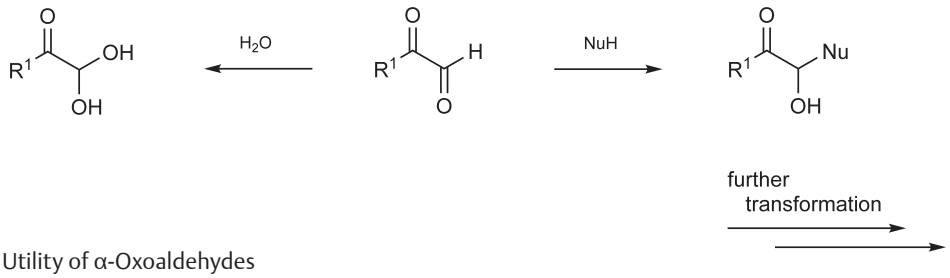
Abstract

Thieme's *Science of Synthesis* Online was used to find possible synthetic routes to α-oxoaldehyde hydrates (Scheme 1). The structure-based search was very useful to reach the article we wanted, and the content of the article was informative and concise. Thus, *Science of Synthesis* Online was found to be an excellent tool to find possible synthetic routes to the compounds of interest.

Scheme 1 Oxidation of Diazo Compounds by Dimethyldioxirane

Discussion

α-Oxoaldehydes are useful buiding blocks that readily react with various carbon nucleophiles to form a new C—C bond (Scheme 2). The resultant products have a ketone moiety, which can be further transformed into various functional groups. In spite of the potential utility of α-oxoaldehydes, they are rarely used in organic synthesis because they are unstable and must be prepared just before use. One of the solutions to this problem is to convert α-oxoaldehydes into α-oxoaldehyde hydrates, which are bench-stable. In this context, we decided to synthesize α-oxoaldehyde hydrates and investigate their transformation under asymmetric catalysis.



Scheme 2 Synthetic Utility of α-Oxoaldehydes

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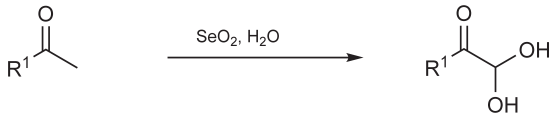
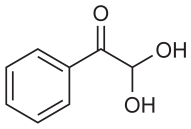
Initially, we synthesized α-oxoaldehyde hydrates by oxidation of methyl ketones using selenium dioxide (Scheme 3). However, we found that it was difficult to prepare α-oxoaldehyde hydrates by this method when R^1 is a hetaryl, alkyl, or alkenyl group.



Scheme 3 Initial Synthetic Method to α-Oxoaldehydes

In order to synthesize these α-oxoaldehyde hydrates, we decided to use Science of Synthesis Online because it is easily accessible online, and the content is searchable by text/structure. The structure of phenylglyoxal hydrate (Scheme 4) was searched to obtain potential synthetic routes to α-oxoaldehyde hydrates. Although the search gave us 66 hits, some were not directly useful to us and we used the search filter option to help us reach the article we wanted. Thus, after filtering the search result by "Exact Match" and "Reaction Product", the number of hits was reduced from 66 to 1. This article described the synthesis of α-oxoaldehyde hydrates by the oxidation of diazo compounds using dimethyldioxirane (DMDO). What was most important in the article was that alkyl and hetaryl derivatives were successfully synthesized in excellent yields. The article was informative and concise, and the general experimental procedure given there was very useful to try the same reaction in the laboratory. In addition, the potential dangers of dimethyldioxirane were also described, and this should help less-experienced students. Furthermore, a direct link to the original paper was helpful to obtain further information on the reaction.



Scheme 4 Structure of Phenylglyoxal Hydrate

Conclusion

Science of Synthesis Online was a very useful tool to obtain a promising procedure to synthesize α-oxoaldehyde hydrates. *Science of Synthesis* Online is easily accessible, and the structure-based search as well as search filter function allowed us to quickly find the article we wanted. The article was well-written, and the general experimental procedure was useful to try the reaction in the laboratory. *Science of Synthesis* Online can be recommended to less-experienced students because potential hazards of reagents (e. g., DMDO) are also described.