

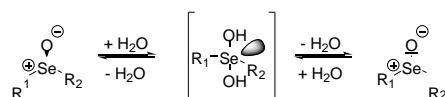


A KINETIC DYNAMIC EPIMERIZATION APPROACH TOWARDS OPTICALLY PURE SELENOXIDES

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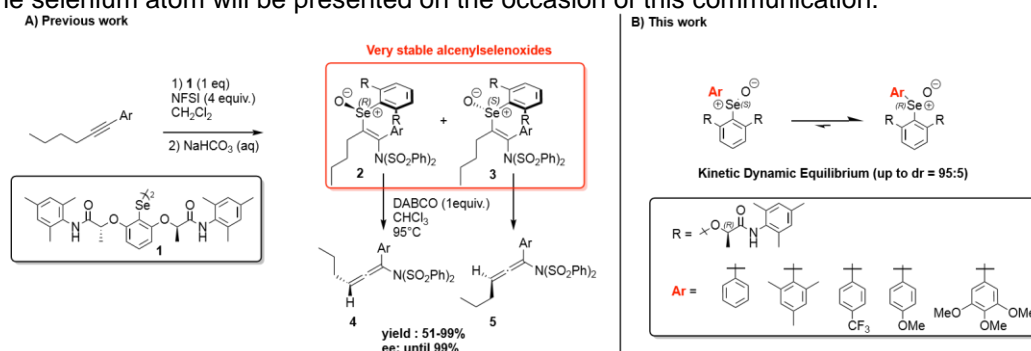
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One of the best-known property of enantioenriched selenoxides is undoubtedly their lower stereochemical stability compared to their sulfur analogues (sulfoxides).¹ This has been intensively studied, and the effect of water has been reported as a determining factor in this process. This is due to the formation of a possible transient hydrate species,² from which the elimination of a water molecule leads to two different enantiomers with respect to the selenoxide stereogenic center (See Scheme 1).



Scheme 1: Water-mediated racemization of enantioenriched selenoxides

Contrarily to what is commonly observed for enantioenriched selenoxides, our team recently reported a surprisingly stable set of optically pure alkenylselenoxides,³ which are interesting intermediates towards the formation enantioenriched allenes (See Scheme 2). Unfortunately, these intermediates couldn't be crystallized, and the precise reason for their high optical stability couldn't thus be fully understood. In order to better understand the possible stabilization effects occurring on these type of selenoxides bearing lactamide motifs, we decided to modify their structures and five different optically pure diarylselenoxides were synthesized. Their stereochemical stabilities were then monitored over time by NMR, and interestingly the selenium (IV) atom chirality was found to be unstable in this new series, systematically leading to one major diastereoisomer over time through Kinetic Dynamic Epimerization equilibriums. To date, reports describing dynamic chirality control of a polyvalent chalcogen atom are very scarce, and only one example reported by Back and co-workers has shown that this could occur thanks to intramolecular directing H-bonding interactions with a d.r of 2:1.⁴ Our results leading to much higher d.r. (up to 95:5) thanks to the presence of lactamide-type H-bond donors positioned in the ortho-position of the selenium atom will be presented on the occasion of this communication.



Scheme 2: a) Previous work on the β -elimination of selenoxides towards enantioenriched allenes b) Kinetic Dynamic Resolution of selenoxides bearing a lactamide units

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