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In situ generated glutaconaldehyde performs the transformation of aminoacids and esterified derivatives into their corresponding pyridiniums

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Pvridiniums are six-membered cationic nitrogen-containing heterocycles found in both natural and synthetic compounds. The multiple properties associated with these structures make them usable in materials science or for the synthesis of biologically active natural products. Additionally, pyridiniums serve as important building blocks for the preparation of nitrogenated structures, such as piperidines, which are easily obtained by reduction of the heterocycle (Figure 1a).

Along with sugars, terpenes, alkaloids and fatty acids, amino acids make up one of the five major classes of natural products. Playing an essential role in biology, they and their derivatives are one of the main sources of chiral compounds, valuable for organic synthesis. In this context, we are interested in the conversion of amino acids into their corresponding pyridinium. In 2007, Marazano et al. proposed the use of Zincke salt to achieve this transformation. After a two-step reaction, expected compounds were obtained in poor yields (30%) after five days (Figure 1b). Low yields were primarily due to the need for reduced temperatures (below 45 °C) to avoid unwanted side reactions, such as decarboxylation or racemization. In 2021, Zhao et al. attempted to improve the method (Figure 1b). However, reaction times remained long (around 24 hours) and yields proved substrate-dependent (20-98%).

In this context, we propose an alternative approach using *in- situ* generated glutaconaldehyde and based on a protocol initially developed for the transformation of anilines and heteroaromatic derivatives (Figure 1c). With our method, amino acids and their esterified derivatives are efficiently converted into their corresponding pyridiniums. The poster will detail the experimental conditions we developed to optimize this reaction and will highlight the advantages of using a potassium salt of glutaconaldehyde as a reagent to perform this transformation. Antibacterial activities of the pyridiniums thus prepared will also be presented.

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a) Valorization of pyridiniums and derivatives







piperidino-alaninol (ligand for asymmetric catalysis)

b) Transformation of primary amines using Zincke salts



c) Transformation of primary amines using Glutaconaldehyde salt



Figure 1 a) Valorization of pyridiniums and derivatives. b) Preparation of pyridiniums from amino acids using Zincke salt. c) Preparation of pyridiniums from primary amines by action of *in situ* generated glutaconaldehyde.

Biography

Rammiya Ramanathan graduated from the East Paris University of Creteil (UPEC, France) with a Master's degree in Bioactive Molecules Chemistry in 2022. She is a third-year PhD student in organic chemistry, under the supervision of Dr Michael Rivard, Associate Professor at UPEC. Her thesis focuses on the synthesis and valorization of nitrogen heterocycle derivatives. She is currently working at the East Paris Institute of Chemistry and Materials (ICMPE, France), known for its research in chemistry and materials science, as well as for its works developed at the interface with physics, engineering and biology.

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