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Kolbe Electrolysis as a Novel Way of Generating Non-Proteinogenic Amino Acids

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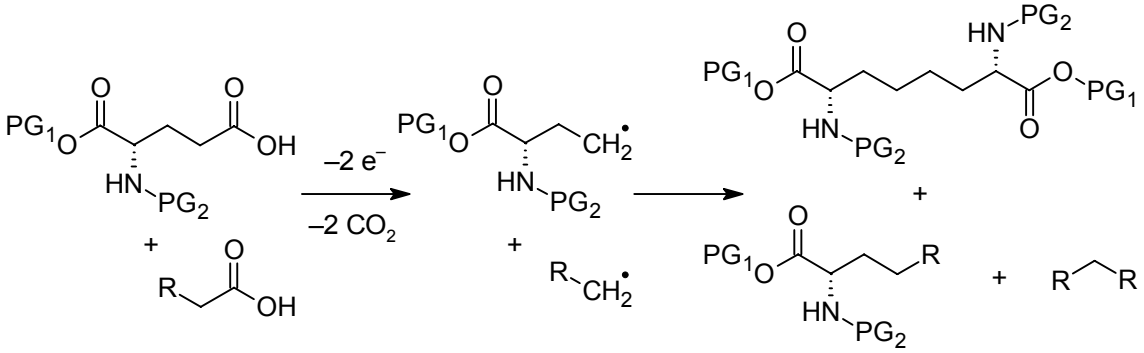
By using Kolbe electrolysis [1], an anodic oxidation, carboxylic acids are able to form dimers through precent decarboxylation and generation of radicals. The scope of the Kolbe reaction can be considerably enhanced by cross-reaction of two different carboxylic acids. L-glutamic acid (Glu), which is blocked at the α-carboxyl and the amino group by protective groups, opens a new way for the synthesis of non-proteinogenic amino acids with defined stereochemistry. As examples *Z*-L-norleucine and amino acids containing a second amino group at its side chain were synthesized.



Reaction scheme of Kolbe electrolysis using Glu and an aliphatic carboxylic acid

For this work, the radical Kolbe electrolysis was optimized by varying reaction parameters (current density, solvent, degree of neutralisation, temperature, reaction time and distance between the electrodes) in order to maximize yields and minimize byproducts.

The steric retention during the Kolbe electrolysis was proofed by enantiomer separation via capillary electrophoresis (CE) [2].

[1] Kolbe H. Untersuchungen über die Elektrolyse organischer Verbindungen. Ann Chem Pharm. 1849; 69: 257–294. doi:10.1002/jlac.18490690302

[2] Gübitz G, Schmid MG. Chiral separation principles in capillary electrophoresis. J Chromatogr A. 1997; 792: 179–225. doi:10.1016/S0021-9673(97)00871-6