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Glycolaldehyde as bio-based C1 building block for the selective N-formylation of secondary amines

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PURPOSE OF THE ABSTRACT
Glycolaldehyde, also known as hydroxyacetaldehyde is the building block sugars are made off. It is possible to let glucose undergo a retro-aldol reaction to erythrose and glycolaldehyde and the erythrose can undergo a further retro-aldol reaction to form two more equivalents of glycolaldehyde. Thus far the best result was obtained by Taarning and co-workers who subjected an aqueous solution of glucose to thermal cracking over a bed of glass beads at 515 °C which resulted in a 74% yield of glycolaldehyde. It is also the most abundant product in pyrolysis oil obtained from biomass. It is usually isolated in the form of its dimer, 2,5-dihydroxy-1,4-dioxane. We were investigating the use of glycolaldehyde in the synthesis of cleavable conjugated polymers and serendipitously found out that reaction of glycolaldehyde with secondary amines in the presence of air or oxygen leads to formation of the N-formylated amines in excellent yields. The reaction works best in refluxing acetonitrile and does not need any catalysts. We were able to convert a range of secondary amines into the formamides with yields between 61-92% (Scheme 1). Primary amines do not undergo this reaction.
We were able to isolate a number of intermediates that gave us a deeper insight into the mechanistic pathway of this reaction and we propose the following mechanism (Scheme 2).

FIGURES

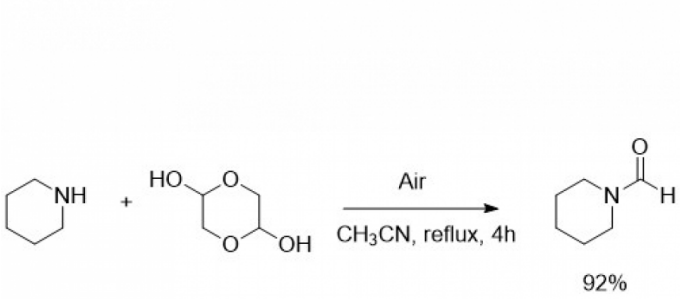

FIGURE 1
Scheme 1
Oxidative formylation of secondary amines with glycolaldehyde

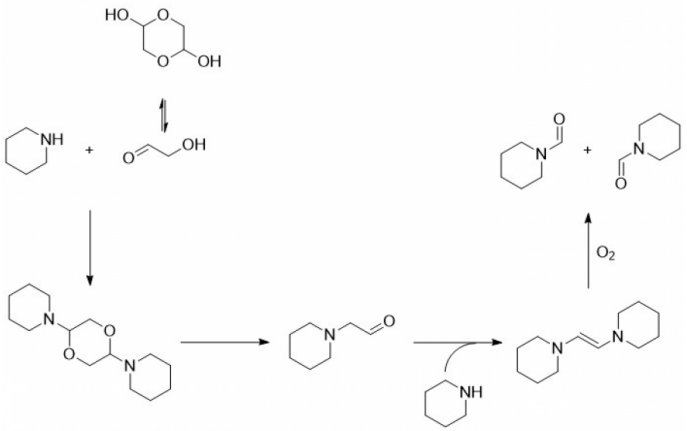

FIGURE 2
Scheme 2
Mechanism of oxidative formylation of secondary amines with glycolaldehyde

KEYWORDS
renewable | oxidative | formylation | glycolaldehyde

BIBLIOGRAPHY

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