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2-(Sulfooxy)propane-1,2,3-tricarboxylic acid as novel and versatile catalyst for the formylation of alcohols and amines using ethyl formate under neat conditions

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Abstract

2-(Sulfooxy)propane-1,2,3-tricarboxylic acid (supported on silica gel) has been introduced as novel and green catalyst for the formylation of alcohols and amines with ethyl formate, as mild formylation agent, under neat conditions at room temperature.

Keywords: Alcohol; Amine; 2-(Sulfooxy)propane-1,2,3-tricarboxylic acid; Formylation; Ethyl formate

Finding molecules which are able to catalyze the reaction between others is an important contribution of molecular chemists to increase the efficiency of chemical reactions whereby our daily life based on consumption of chemicals is shifted closer to an ecologically and economically tolerable equilibrium with our environment [1]. The development of heterogeneous catalysts for fine chemicals synthesis has become a major area of research mainly because the reactions are carried out under mild conditions and the organic products are easily isolated from the reaction media.

Formylation of alcohols and amines is an important transformation in organic synthesis and provides an efficient method for protection of hydroxyl and amino groups [2]. *O*-Formylation might be the method of choice for protecting a hydroxyl group in a complex synthetic sequence because deformylation can be occurred selectively in the presence of acetate or other ester groups. Also, formamides are Lewis bases, valuable intermediates in the synthesis of pharmaceutically compounds [3,4], catalysts for organic transformations and reagents in Vilsmeier formylation.

Even though, various formylating systems have been presented in the literatures in the last years [5–10], there are still serious limitations for the preparation of alkyl formats and formamides due to the drastic reaction conditions. Therefore, in this project a new catalytic procedure has been designed for the formylation of alcohols and amines.

In continuation of our ongoing effort to find new catalysts or catalytic systems [11–16], we decided to prepare 2-(sulfooxy)propane-1,2,3-tricarboxylic acid (Fig. 1) as new catalyst for the preparation of formamides and alkyl formates.

2-(Sulfooxy)propane-1,2,3-tricarboxylic acid was prepared *via* reaction of citric acid with chlorosulfonic acid ($ClSO_3H$) (Scheme 1). Because of gummy properties of this compound, it was supported on silica gel and applies as catalyst for the formylation of alcohols and amines.

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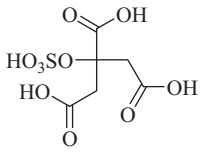
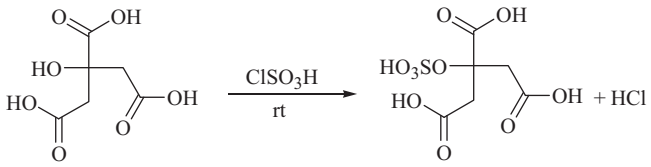


Fig. 1. 2-(Sulfooxy)propane-1,2,3-tricarboxylic acid.



Scheme 1. Preparation of 2-(sulfooxy)propane-1,2,3-tricarboxylic acid.

Table 1
Formylation of 2-phenylethanol by ethyl formate under different conditions.

Entry	Catalyst[a]	Solvent	Time (h)	Yield (%)[b]
1	2-(Sulfooxy)propane-1,2,3-tricarboxylic acid	Chloroform	24	25
2	2-(Sulfooxy)propane-1,2,3-tricarboxylic acid	Acetonitrile	24	45
3	2-(Sulfooxy)propane-1,2,3-tricarboxylic acid	*n*-Hexane	24	20
4	No catalyst	Solvent-free	24	5
5	Citric acid	Solvent-free	24	25
6	2-(Sulfooxy)propane-1,2,3-tricarboxylic acid	Solvent-free	2.25	94

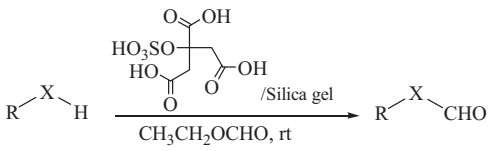
[a] Substrate/catalyst/ethyl formate for entries 1–3: 1 mmol/0.13 g/2 mmol; for entry 4: 1 mmol/–/2 mL; for entry 5: 1 mmol/0.2 mmol/2 mL; for entry 6: 1 mmol/0.13 g/2 mL.
[b] Isolated yield.

Initially, in order to find optimal conditions, 2-phenylethanol was formylated in different conditions. The results have been presented in Table 1.

As is evident from Table 1, the reaction of 2-phenylethanol as a model compound with ethyl formate was examined under various conditions. The reaction in the absence of catalyst and solvent produced only a trace amount of product. The yields were somewhat increased in the presence of catalyst. The solvent screening has also been studied. The best yields were obtained with 0.13 g of supported 2-(sulfooxy)propane-1,2,3-tricarboxylic acid on silica gel and 2 mL of ethyl formate under solvent-free conditions at room temperature. This optimal condition has been applied for all of the formylation reactions.

Consequently, herein we disclosed a new catalytic protocol for the formylation of primary, secondary and tertiary alcohols; also primary amines to produce the corresponding formylated products, using ethyl formate and a catalytic amount of supported 2-(sulfooxy)propane-1,2,3-tricarboxylic acid on silica gel under neat conditions, at room temperature (Scheme 2 and Table 2).

O- and *N*-formylation of alcohols and amines was carried out heterogeneously under mild and solvent-free conditions. Alkyl formate or formamide easily obtained by mixing 1 mmol of alcohol or amine, 0.13 g of supported 2-(sulfooxy)propane-1,2,3-tricarboxylic acid on silica gel and 2 mL of ethyl formate; then stirring of the resulting



R= Alkyl or aryl; X= O or N

Scheme 2. Formylation of alcohols and amines.