Iodine-catalyzed tandem synthesis of terminal acetals and glycol mono esters from olefins and biomass-derived glycols

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Abstract

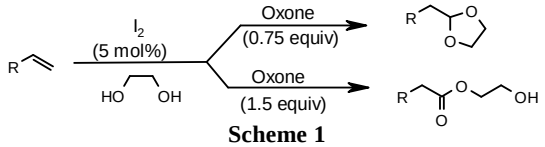
A new metal-free protocol is described for the synthesis of terminal acetals by tandem oxidative rearrangement of olefins using oxone as an oxidant in the presence of iodine in *ethylene glycol (a versatile chemical derived from biomass or fossil fuels) medium. Moreover, a one-pot procedure for the preparation of glycol mono esters from olefins is also presented for the first time using the same reagent system.*

Keywords: *acetals, esters, diols, biomass, rearrangement*

1. Introduction

In the last decade, the research of renewable reactants has become a key issue for a sustainable chemistry [1]. Approximately 75% of the biomass produced by nature through the process of photosynthesis corresponds to carbohydrates, but only between 3% and 4% of these compounds are used for food and non-food purposes [2]. Therefore, the use of carbohydrates as raw materials for the production of basic chemicals is an area of increasing interests [3]. In this sense, a variety of glycols (1,2-ethanediol, 1,2-propanediol, 1,2-butanediol, or 2,3-butanediol) can be obtained from carbohydrates [1] as well as from glycerol [4] via bio- or chemocatalytic reactions. Those glycols could be used as starting reactants to obtain products with higher added value.

The aim of the present work is to obtain terminal acetals and glycolmono esters starting from olefins and glycols derived from biomass, through a tandem oxidative rearrangement process (Scheme 1). Protection of a carbonyl function as its acetal is a widely used synthetic route for the manipulation of various multifunctional organic molecules [5]. Acetals can also be used for C–C bond formations [6], the synthesis of ethers [7] and esters [8]. Classical methods for the synthesis of acetals involve the treatment of aldehydes or ketones with an alcohol using either a protic or Lewis acid catalyst [5]. Unfortunately, these procedures have some disadvantages such as the use of corrosive and costly reagents or additives and high catalyst loading. The palladium(II)-catalyzed oxidation (Wacker process) of terminal olefins in water furnishes the methyl ketones [9] and a similar reaction in alcohol gives their corresponding internal acetals [10]. Acetalization at the terminal carbon atom of a cheaper terminal olefin instead of a costlier aldehyde as substrate is a challenging task. Consequently some Pd catalyzed protocols have been developed for this important functional group transformation [11].



Scheme 1

2. Materials and Methods

All chemicals used were reagent grade and used as received without further purification. ^{1}H NMR spectra were recorded at 300, 400 and 500 MHz and ^{13}C NMR spectra 75 MHz in $CDCl_3$ or DMSO-D_6. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR spectra. Column chromatography was carried out using silica gel (100-200 mesh).

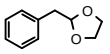
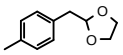
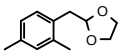
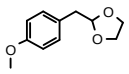
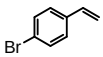
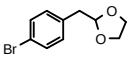
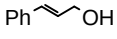
General procedure for the synthesis of acetals/ glycol mono esters

Oxone (1.5 mmol for acetal/ 3 mmol for glycol mono ester) was slowly added to a well stirred solution of olefine (2 mmol) and I_2 (0.1 mmol) in ethylene glycol (2 ml), then the reaction mixture was stirred at room temperature. After completion of the reaction (as indicated by TLC), the reaction mixture was quenched with aqueous sodium thiosulfate and extracted with DCM (3×20 ml). Finally, the combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude reaction mixture was further purified by column chromatography using silica gel (100-200 mesh) afforded the pure products.

3. Results and Discussion

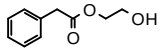
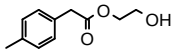
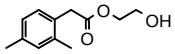
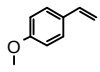
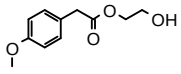
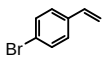
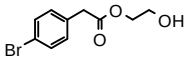
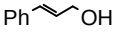
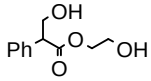
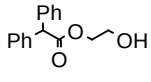
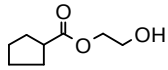
A variety of reaction conditions were employed to achieve the optimal conditions. The results revealed that a 2 : 1.5 : 0.1 mole ratio of styrene, oxone and I_2 at room temperature was shown to be the optimum reaction conditions for terminal acetalization and 3 mmol of oxone is required for complete conversion of olefin to ester.

Table 1. Synthesis of acetals form various olefins[a]

Entry	Olefin	Time (h)	Product	Yield[b] (%)
1		1.3		95
2		3.3		90
3		3		76
4		3.3		89
5		5		95
6		2.3		95
7		7		80
8		1.3		64

[a]Olefine (2 mmol), I_2 (0.1 mmol), Oxone (1.5 mmol), Ethylene glycol (2 ml), r.t. [b]Products were characterized by NMR, mass spectra and quantified by GC.

Table 2. Synthesis of esters from various olefins[a]

Entry	Olefin	Product	Yield[b] (%)
1			94
2			90
3			51
4			60
5			88
6			65
7			-
8			60

[a]Olefine (2 mmol), I_2 (0.1 mmol), Oxone (3 mmol), Ethylene glycol (2 ml), 24 h, r.t. [b]Products were characterized by NMR, mass spectra and quantified by GC.

After optimizing the reaction conditions, we explored the scope of this novel transformation with a variety of olefins and yielded the corresponding acetals/esters in good to excellent yields. Styrene produced the respective terminal cyclic acetal/ester with excellent yield. Whereas, relatively longer reaction times were required where activating or deactivating groups were present on the aromatic ring of styrene to provide excellent yields of the corresponding acetals/esters. However, 2,4-dimethyl styrene gave a relatively low yield, probably due to steric hindrance. Asymmetric and symmetric olefins also underwent oxidative rearrangement and afforded good yields of the corresponding acetals/esters. It is worth mentioning that in the case of cyclic olefin, the ring-contraction product was observed.

Initial support for the proposed mechanism was obtained by acetalization of styrene-β,β-d_2, which gives a benzylic deuterated product. In situ ESI-MS and ^{13}C NMR experimental data also support the proposed mechanism. Further, computational studies at the B3LYP/6-31G* level, clearly demonstrate the propensity for O^- attack on α-C rather than on β-C in the phenonium ion intermediate.

4. Conclusions

In conclusion, we have developed a remarkably mild, efficient and selective metal-free method for the synthesis of terminal acetals from olefins in biomass-derived glycols. A one pot protocol for the preparation of glycol mono esters from olefins has also been introduced using the same reagent system.

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