

Regioselective reaction of a cyclic Baylis-Hillman adduct with alcohols and thiols

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Cyclic Baylis-Hillman adduct **1** reacts with alcohols and thiols in the presence of *p*-TsOH to give regioselectively the corresponding allylic ethers **4** and thioethers **6** in satisfactory to good yields.

Keyword: cyclic Baylis-Hillman adduct

In the course of our study on the synthesis and the potentiality of cyclic Baylis-Hillman derivative **1**^{1–6}, we have found that the reaction of this compound **1** with ethylene glycol, in the presence of *p*-toluene sulfonic acid (*p*-TsOH), did not lead to the expected ketal alcohol **2** but afforded a mixture of products **3**, **4a** and **5a** in moderate yield ~50% (Scheme 1).

The obtained allylic ether **4a** could be a structurally interesting material since some of compound **1** derivatives exhibit biological properties.^{7,8} In this paper, we wish to report our results concerning the behaviour of compound **1** towards monofunctional alkyl alcohols and thiols in the presence of *p*-TsOH.

The treatment of 2-(hydroxymethyl)-2-cyclohexenone **1** with a large excess of various alcohols at reflux in the presence of *p*-TsOH (1 equiv), gave regioselectively the allylic ethers **4b–d**^{9–10} in satisfactory to good yields (Scheme 2).

Similarly, keto alcohol **1** reacted with thiols (2 equiv) in the presence of *p*-TsOH (0.3 equiv) in refluxing THF, affording allylic sulfur compounds **6**¹¹ in satisfactory to good yields (Scheme 1 inset Fig. 1).

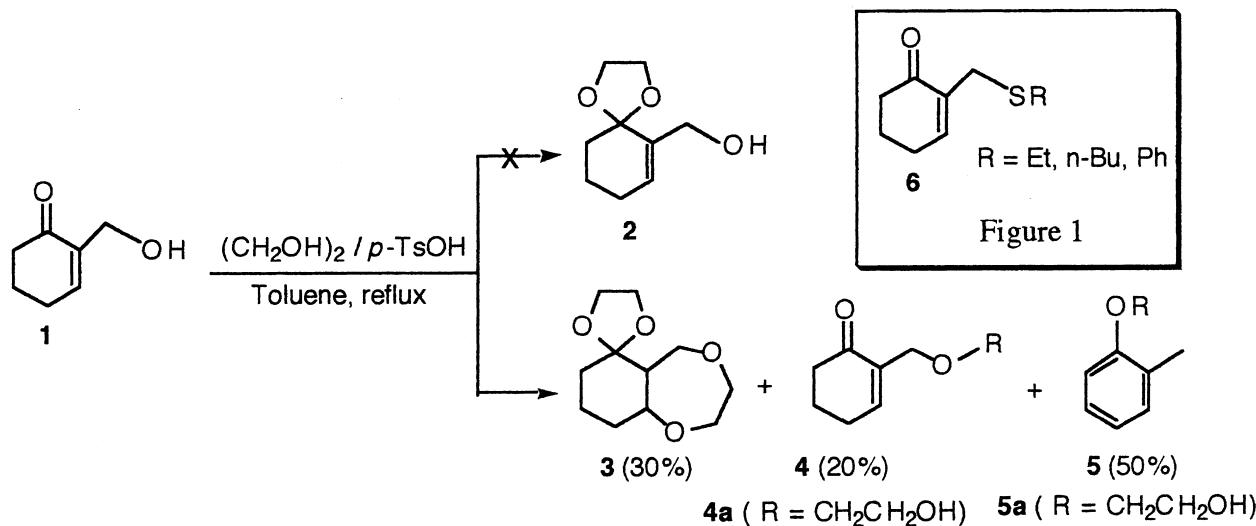
Techniques used: IR, ¹H NMR, ¹³C NMR, MS

References: 11 ; Schemes: 2

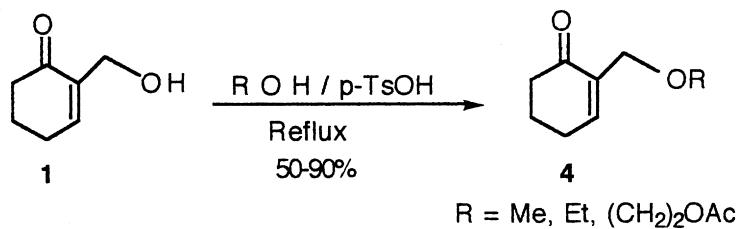
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Scheme 1 Reaction of **1** with ethylene glycol.



Scheme 2 Reaction of **1** with alcohols.

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