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Facile Synthesis of α-Hydroxybutenolides and α-Keto-β-allyl-γ-butyrolactones

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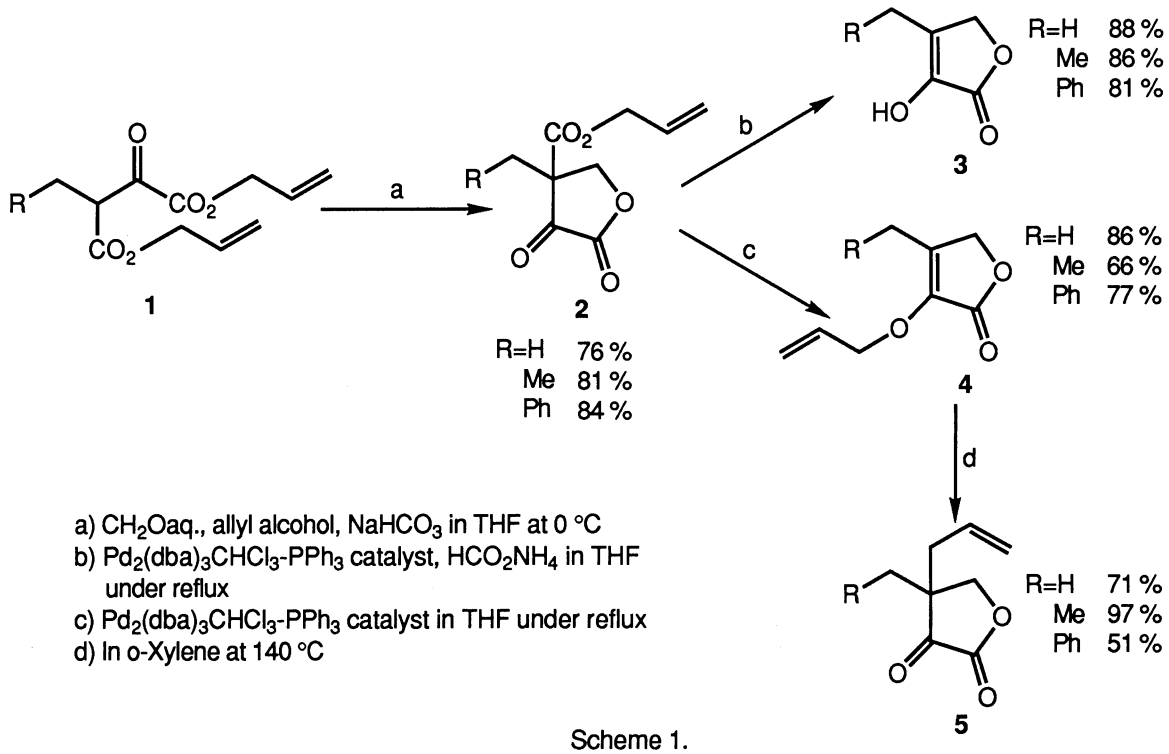
The reaction of α-keto-β-alkyl-β-allyloxycarbonyl-γ-butyrolactones with ammonium formate in the presence of palladium catalyst gave α-hydroxybutenolides in good yields. When the reaction was carried out without ammonium formate, decarboxylation-allylation took place to give allyl enol ethers of α-hydroxybutenolides, which were converted to α-keto-β-allyl-γ-butyrolactones by the thermal Claisen rearrangement.

Functionalized γ-butyrolactones and butenolides are well known as a component of a large number of biologically important natural products and as versatile intermediates for organic synthesis.[1] Enormous number of synthetic methods for γ-butyrolactones and butenolides have been reported,[2] but synthetic methods for α-hydroxybutenolides and α-keto-γ-butyrolactones are scarce.[3] In this paper we report a facile synthetic method for α-hydroxybutenolides and α-keto-β-allyl-γ-butyrolactones using the palladium-catalyzed decarboxylation and decarboxylation-allylation of allyl β-keto carboxylates.[4, 5]



Scheme 1.

The synthetic scheme is shown in Scheme 1. The starting diallyl α-oxalcarboxylates **1**[6] were converted to α-keto-β-alkly-β-allyloxycarbonyl-γ-butyrolactones **2** by the reaction with formalin (37%) using $NaHCO_3$ as a base. Removal of allylic ester groups of **2** was carried out in good yields by the reaction with ammonium formate in the presence of palladium catalyst to give the lactones **3** as enol forms. Decarboxylation-allylation of allyl β-keto carboxylates in the presence of palladium catalyst usually affords α-allyl ketones.[5] However, when the reaction of **2** was carried out without ammonium formate, no formation of *C*-allylated products was observed. Instead, allyl enol ethers **4** were obtained in good yields as *O*-allylated products. The *C*-allylated products **5** were obtained by the thermal Claisen rearrangement of **4**.

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