

A FACILE SYNTHESIS OF  $\gamma,\delta$ -UNSATURATED ESTERS  
BY THE Pd(II) CATALYZED CLAISEN REARRANGEMENT

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A mixed ortho ester is prepared under mild conditions from an allyl alcohol and a ketene acetal in the presence of  $\text{PdCl}_2(\text{COD})$ . The ortho ester thus formed is successively treated with a catalytic amount of  $\text{PdCl}_2(\text{PPh}_3)_2$  in refluxing p-xylene to afford a  $\gamma,\delta$ -unsaturated ester in a high yield under neutral conditions.

The Claisen rearrangement provides a useful route to  $\gamma,\delta$ -unsaturated carbonyl compounds from allyl alcohols, and is frequently employed as an important step in the synthesis of natural products. The synthesis of a  $\gamma,\delta$ -unsaturated ester is often achieved by the ortho ester Claisen rearrangement.<sup>1)</sup> However, the synthetic procedure requires the addition of an acid catalyst such as propionic acid to the mixture of an allyl alcohol and an ortho ester. So it is desired to develop the new type of the ortho ester Claisen rearrangement, which proceeds under mild conditions, especially for the application to acid sensitive substrates. In this communication, we wish to describe a facile synthesis of  $\gamma,\delta$ -unsaturated esters from allyl alcohols and ketene acetals under neutral conditions by the palladium promoted ortho ester Claisen rearrangement.

In the previous paper,<sup>2)</sup> we reported on the novel protective reagents for hydroxyl groups, and it was shown that  $\text{PdCl}_2(\text{COD})$  effectively catalyzed the addition of alcohols to vinyl ethers. So it could be expected that a mixed ortho ester (3), the intermediate of the ortho ester Claisen rearrangement, was formed under mild conditions from an allyl alcohol (1) and a ketene acetal (2) using  $\text{PdCl}_2(\text{COD})$  as a catalyst. Thus, alcohols were treated with ketene acetals in the presence of  $\text{PdCl}_2(\text{COD})$ , and several mixed ortho esters were obtained in 80-90% yields.

Next, we screened the reaction conditions for the preparation of a  $\gamma,\delta$ -unsaturated ester (5) from the mixed ortho ester (3), and it was found that the desired ester was obtained in a good yield under neutral conditions, when the ortho ester (3) was refluxed in the presence of a catalytic amount of  $\text{PdCl}_2(\text{PPh}_3)_2$  in p-xylene. It was assumed that  $\text{PdCl}_2(\text{PPh}_3)_2$  effectively promoted both the elimination of ethanol (or methanol) from the ortho ester (3) and the rearrangement of the ketene acetal (4) to the  $\gamma,\delta$ -unsaturated ester (5).<sup>3)</sup> Several  $\gamma,\delta$ -unsaturated esters were prepared in good yields as summarized in Table 1. As shown in entry 4, the allyl alcohol having an acid-labile functional group gave the product in a high yield according to the present procedure.

