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Simple One-Pot Preparation of 1,2-Diacetoxy-2-propene. A Convenient Precursor of 1-Acetoxy-3-chloro-2-propanone

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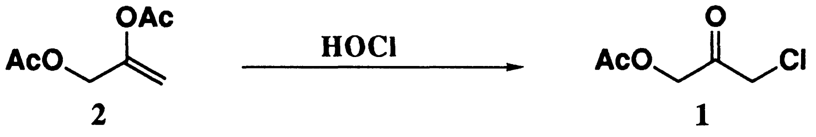
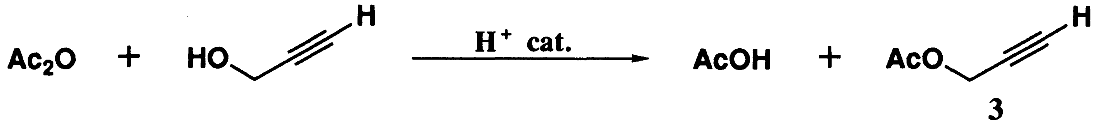
From a neat mixture of acetic anhydride and propargyl alcohol, 1,2-diacetoxy-2-propene was prepared by successive treatment with an acid catalyst and a Ru catalyst in one-pot procedure. The product was a convenient precursor of 1-acetoxy-3-chloro-2-propanone.

1-Acetoxy-3-chloro-2-propanone (**1**)1) has been known as an important synthetic reagent for various heterocycles,2) and cephalosporins.3) We found out that the acetone derivative **1** could be obtained quantatively by the action of hypochlorous acid on 1,2-diacetoxy-2-propene (**2**) (equation 1).4) The process seems to provide an useful preparative method of **1**, if **2** was available conveniently. Here, we wish to describe on the effort to prepare **2** by a simple practical procedure.

When an equimolar mixture of propargyl alcohol and acetic anhydride without solvent was treated with a trace amount of acid such as sulfuric acid, a vigorous reaction occured to give an equimolar mixture of 1-acetoxy-2-propyne (**3**) and acetic acid (equation 2). The next step of regioselective addition of acetic acid to the triple bond on **3** was achieved in the reaction mixture using a Ru catalyst system (equation 3) as shown in Table 1. A recently reported catalyst system, composed of Ru(η^5-cyclooctadienyl)$_2$/ PR$_3$ /maleic anhydride in the ratio of 1:2:2, which had shown high regioselectivity to give **2** in a solvent,5) provided only



(1)



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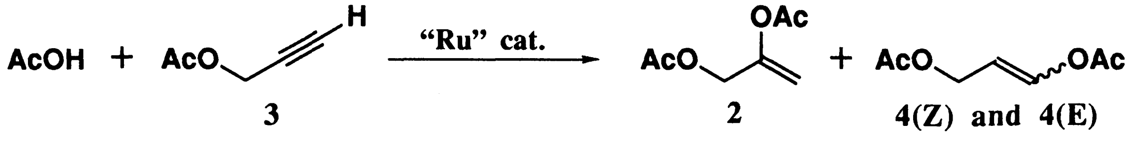

(3)

Table 1. $AcOH + \mathbf{3} \xrightarrow{catalyst} \mathbf{2} + \mathbf{4}(Z)$ and $\mathbf{4}(E)$

Run	Catalyst[a]	Conditions Temp/°C	 Time/h	Product distribution[c]/% **2**	 **4**(Z)	 **4**(E)
1	Ru()$_2$/PBu_3/MA[b] 1:2:2[4]	98	3	58.5	14.9	26.6
2	1:4:4	98	4	85.4	5.7	8.9
3	1:6:6	98	4	90.0	4.9	5.1
4	Ru_3/$(CO)_{12}$/PBu_3/MA 1:6:6	98	4	90.2	4.2	5.6
5	$RuCl_3$/PBu_3/MA 1:6:6	98	4	86.2	6.6	7.2

a) 0.5 M% for Ru nucleus was applied. The catalyst was prepared in acetic acid by heating the mixture (1.5 M solution for Ru) until it become a clear solution. The catalyst solution was added with syringe into the reaction mixture. b) MA=maleic anhydride. c) The ratio was determined by GLC.

a poor selectivity (run 1). But, increased ratio of ligands to Ru nucleus improved the regioselectivity sharply (runs 2 and 3). Moreover, the catalyst systems prepared from other Ru compounds such as $Ru_3(CO)_{12}$ and anhydrous $RuCl_3$ (runs 4 and 5) provided nearly the same regioselectivity when compared with the result of run 3. The results suggested that the catalyst systems prepared from these Ru compounds should have a common structure. In practice, **2** was isolated purely in 82% conversion yield by direct distillation from the reaction mixture in a large scale trial.

In conclusion, we developed a convenient and practical method for the preparation of 1,2-diacetoxy-2-propene (**2**), starting from a neat mixture of propargyl alcohol and acetic anhydride in one-pot procedure, by successive treatment with an acid catalyst and a Ru catalyst, utilizing both of acetyl and acetoxy groups in acetic anhydride molecule for the formation of two acetoxy groups on **2**.

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