

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 quantitatively 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 occurred 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/PR₃/maleic anhydride in the ratio of 1:2:2, which had shown high regioselectivity to give **2** in a solvent,⁵⁾ provided only

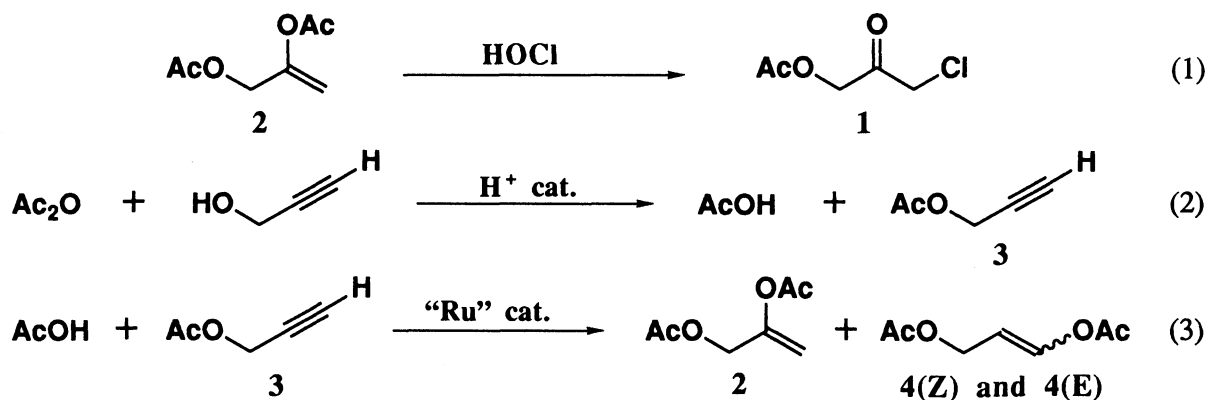


Table 1. $\text{AcOH} + 3 \xrightarrow{\text{catalyst}} 2 + 4(\text{Z}) \text{ and } 4(\text{E})$

Run	Catalyst ^{a)}	Conditions		Product distribution ^{c)/%}		
		Temp/°C	Time/h	2	4(Z)	4(E)
1	$\text{Ru}(\odot)_2/\text{PBu}_3/\text{MA}^{\text{b)}$ 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	$\text{Ru}_3/(\text{CO})_{12}/\text{PBu}_3/\text{MA}$ 1:6:6	98	4	90.2	4.2	5.6
5	$\text{RuCl}_3/\text{PBu}_3/\text{MA}$ 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 $\text{Ru}_3(\text{CO})_{12}$ 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**.

References

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