Chinese Chemical Letters Vol. 14, No. 3, pp 243 – 244, 2003
http://www.imm.ac.cn/journal/ccl.html

Novel Stereoselective Synthesis of (E)-α, β-Unsaturated Esters by the Tandem Reaction of Deprotonation-Oxidation-Wittig Reaction from Phosphonium and Arsonium Salt

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Abstract: Phosphonium or arsonium salt **1** can undergo the tandem reaction of deprotonation -oxidation-Wittig reaction with alcohol **2** in the presence of sodium hydroxide and manganese dioxide, which affords a general simplified method for the stereoselective synthesis of (E)- α, β-unsaturated esters **3**.

Keywords: Phosphonium salt, arsonium salt, alcohol, ylide, α, β-unsaturated esters, Wittig reaction, tadem reaction, synthesis.

Wittig reaction is one of the most important method for the formation of carbon-carbon double bond and has been widely used in the synthesis of natural products[1,2]. Recently it was found that alcohols can undergo *in situ* oxidation-Wittig reaction with phosponium ylides to give corresponding olefination products, which has great potential utilities in organic synthesis[3]. To simplify the procedure of the reaction further, we considered to combine the deprotonation of ylide, oxidation of alcohol and Wittig reaction into one tandem reaction.

We utilized phosphonium or arsonium salt **1** (1.4 mmol) as starting material to react with alcohol **2** (1.2 mmol) in the presence of sodium hydroxide (2.0 mmol) and manganese dioxide (10mmol) and found that the tandem reaction of deprotonation -oxidation-Wittig reaction took place readily to form the desired product **3** (See **Scheme 1**). The tandem reaction has moderate to excellent yield and very high stereoselectivity to give (E)- α, β-unsaturated esters predominantly **3** (See **Table 1**). It is the first example of *in situ* oxidation-Wittig reaction *via* arsonium ylide. Moreover, the alcohols can be aromatic, allylic, propargylic and unactive aliphatic. This protocol can be used as a general simplified method for the stereoselective synthesis of. (E)- α, β-unsaturated esters. Further research on the application of this tandem reaction in organic synthesis is in progress at our laboratory.

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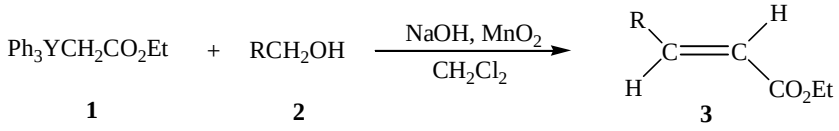
Scheme 1



1 **2** **3**

Y = P, As.

Table 1 Tandem Reaction of Deprotonation-Oxidation-Wittig reaction

Product	Y	R	Temp(°C)	Reaction Time(hr)	Isolated Yields(%)[a]	Z / E[b]
3a	P	C_6H_5	r.t.	1	95	100/0
3b	P	4-$CH_3OC_6H_4$	r.t.	3	73	99/1
3c	P	C_6H_5CH=CH	r.t.	2	80	100/0
3d	P	CH_2=CH	Reflux	18	58	95/5
3e	P	CH≡C	Reflux	37	61	100/0
3f	P	$CH_3(CH_2)_{14}$	Reflux	48	52	100/0
3a	As	C_6H_5	Reflux	2	85	99/1
3b	As	4-$CH_3OC_6H_4$	Reflux	4	68	98/2
3c	As	C_6H_5CH=CH	Reflux	3	73	100/0

a. The structure of the products are confirmed by ^{1}H NMR, IR, and MS.

b. The ratioes of Z-isomer to E-isomer are determined by ^{1}H NMR or GC.

Acknowledgments

We thank the National Natural Science Foundation of China for financial support of the project 29972036 and the Foundation of Educational Ministry for the Scholars Returning from Abroad.
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Received 15 April, 2002