PALLADIUM-CATALYZED CONVERSION OF ALDEHYDES TO ALKENES IN THE PRESENCE OF TRI-N-BUTYLPHOSPHINE

Yanchang Shen^{*} and Yuefen Zhou Shanghai Institute of Organic Chemistry, Academia Sinica 345 Lingling Lu, Shanghai 200032, China

Summary. Palladium-catalyzed conversion of aldehydes to alkenes in the presence of tri-n-butylphosphine is described.

Since the widespread upsurge of interest in palladium chemistry, organopalladium compounds have found increasing uses as versatile reagents or catalysts in organic synthesis, particularly in various carbon-carbon bond forming reactions.¹ Many useful synthetic transformations, which seemed to be impossible by conventional methods, have been discovered^{1b} and applied to the synthesis of natural products.² Alkenation of carbonyl compounds is one of the most important methods in organic synthesis.³ Moreno-Manas and Trius reported a palladium-catalyzed reaction of allylic alcohols with aldehydes in the presence of triphenylphosphine resulting in the formation of alkenes as a mixture of E- and Z-stereoisomers in 12-68% yields.⁴ However, the synthetic application of organopalladium compounds to the alkenation of carbonyl compounds seems to remain limited. We now wish of bromoacetic ester with to report a palladium-catalyzed reaction aldehydes in the presence of tri-n-butylphosphine leading to the conversion of aldehydes to alkenes with high stereoselectivity in 52-85% yields.

The reaction is shown as follows:

RCHO + BrCH₂CO₂C₂H₅ + n-Bu₃P
$$\xrightarrow{25\% \text{ mol Pd}(PPh_3)_4}$$
 RCH=CHCO₂C₂H₅
1 2

On treatment of ethyl bromoacetate with aldehydes in the presence of tri-n-butylphosphine and a catalytic amount (25 mol%) of $Pd(PPh_3)_4$, the aldehydes were completely consumed after certain time and the alkenes were obtained in good yields.

In general procedure, tri-n-butylphosphine (1.0 mmol) was injected into a mixture of aldehydes 1 (0.8 mmol), ethyl bromoacetate (1.0 mmol) and $Pd(PPh_3)_4$ (0.2 mmol) under nitrogen. The mixture was stirred and heated for several hours (see Table 1). After the reaction, chromatography on silica gel eluting with petroleum ether (bp. 60-90°C)/ethyl acetate (9:1) gave the products 2. The results are shown in Table 1.

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Compound	R	Condition		Yielda	
		Temp(°C)	Time(h)	(%)	E:Z ^b
2a	^с 6 ^н 5	110	24	85	100:0
2b	4-C1C6H4	110	24	71	100:0
2c	$4-FC_6H_4$	110	24	85	100:0
2đ	4-CH30C6H4	110	24	67	93:7
2e	4-CH3C6H4	110	24	87	91:9
2 £	4-NO2 ^{C6^H4}	110	1.5	62	90:10
2g	$2-BrC_{6}H_{4}$	110	24	69	86:14
2h	с _б н ₅ сн=сн	110	24	62	100:0
2 i	^{c-C} 6 ^H 11	110	24	58	100:0
2j	3-pyridy1 ^c	80	24	52	88:12
2k	SI.	110	24	77	93:7

Table 1. Palladium-catalyzed Conversion of Aldehydes to Alkenes

a Isolated yields. All products were characterized spectroscopically. b The ratios of E- and Z-isomers are estimated on the basis of NMR spectra or isolated products. c Benzene (2 ml) was used as a solvent.

The reaction offers a wide scope. The aldehydes may be aromatic, alicyclic or heterocyclic. They may contain a double bond. A double bond conjugated with a carbonyl group does not interfere the reaction, the attack being at the carbonyl carbon.

It is noteworthy that the present one-pot reaction is the simplified version of normal Wittig reaction which involves three steps: preparation of phosphonium salts, its base treatment to ylides, and reaction of the ylides with carbonyl compounds. Not only that, the present method has advantages over Wittig reaction, because it does not need base and the products are stereoselective.

Further study on the application of this type reaction to organic synthesis and the mechanism of this reaction is being pursued.

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