Novel Conversion of Aldehydes to Alkenes Mediated by Tri-n-butylarsine and Zinc

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Tri-n-butylarsine and zinc have been found to mediate the conversion of aldehydes to alkenes in good yields.

Alkenation of carbonyl compounds is a useful and fundamental reaction in the synthesis of a variety of natural products.[1] However, the normal Wittig route involves three steps: preparation of the phosphonium salt, treatment of the salt with a base to convert it into the ylide, and reaction of the ylide with a carbonyl compound to give the alkene products.

Recently we reported a novel bisacylation *via* halophilic reaction of tri-n-butylarsine and its application to the synthesis of tetrasubstituted methanes with four electron-withdrawing groups.[2] We now report a novel conversion of aldehydes to alkenes mediated by tri-n-butylarsine and zinc [reaction (1)].

$$\underset{(1)}{\text{RCHO}} + \text{BrCH}_2\text{CO}_2\text{Me} \xrightarrow{\text{Bu}^{n}{}_3\text{As/Zn}} \underset{(2)}{\text{RCH=CHCO}_2\text{Me}} \qquad (1)$$

The reaction is of wide scope (Table 1). The aldehyde may be aromatic, aliphatic, or heterocyclic, and may contain a double bond. Double bonds conjugated with the carbonyl group do not interfere, the attack being at the carbonyl carbon.

It is noteworthy that in the absence of zinc powder, the tri-n-butylarsine would react with methyl bromoacetate to give the arsonium salt, while in the absence of tri-n-butylarsine, the Reformatsky reaction would occur to give a β-hydroxy ester. A catalytic amount of zinc powder can also be used to perform the reaction.

This one-pot synthesis of alkenes is convenient, simplifies the procedure as compared with the Wittig reaction, as base is not needed, and the reaction gives the *E*-isomer exclusively as judged by n.m.r. spectroscopy.

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Table 1. Alkene formation using $\text{Bu}^n{}_3\text{As}$ and zinc.[a]

Compound	R	Conditions		Yield[b]
		Temp./°C	Time/h	(%)
(2a)	Ph	80	12	81
(2a)[c]	Ph	80	11	80
(2a)[d]	Ph	80	11	68
(2b)	4-$\text{NO}_2\text{C}_6\text{H}_4$	80	5	97(89)[e]
(2c)	4-BrC_6H_4	80	6	83
(2d)	4-ClC_6H_4	80	6	77
(2e)	4-MeC_6H_4	80	14	81
(2f)	4-FC_6H_4	80	11	75
(2g)	4-MeOC_6H_4	110	23	81
(2h)	2-Pyridyl	80	4	68
(2i)	PhCH=CH	80	6	64
(2j)	$\text{Me(CH}_2\text{)}_5$	100	14	93

[a] The general procedure is as follows: tri-n-butylarsine (2.0 mmol) was injected into a suspension of the aldehyde (2.0 mmol), methyl bromoacetate (2.0 mmol), and zinc powder (2.0, 1.0, or 0.5 mmol) under nitrogen. The mixture was stirred and heated for several hours. After the disappearance of the aldehyde, chromatography on silica gel with light petroleum (b.p. 60—90 °C)–ethyl acetate (85 : 15) as eluant gave the product. [b] Isolated yields. All products were characterised spectroscopically; the double bonds formed were exclusively in the *E* configuration. [c] Zn (cat. amount, 1.0 mmol). [d] Zn (cat. amount, 0.5 mmol). [e] 0.1 mol scale. Isolated by recrystallisation.

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