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DEOXYGENATION OF TRIPHENYLARSINE OXIDE TO TRIPHENYLARSINE BY LOW VALENT TITANIUM

Yi De Xing, Xue Long Hou and Nai Zheng Huang*[1]
Shanghai Institute of Organic Chemistry
Academia Sinica
345 Linglin Lu, Shanghai, China.

Summary. *Low valent titanium was used to deoxygenate triphenylarsine oxide to triphenylarsine*

The applications of triphenylarsenic ylides in olefin synthesis as well as other synthetic reactions[2] have been reported. These reactions have several advantages over the conventional Wittig reaction. In the practical sense, the arsenic ylides are more reactive and the triphenylarsine oxide formed can be removed easily by washing with dilute aqueous hydrochloric acid.

For economic reasons, it is desired that the obtained triphenylarsine oxide could be reduced to the starting triphenylarsine. Several methods[3] have been recorded for the reduction of triphenylphosphine oxide to triphenylphosphine. However, there is only one report[4,5,6] in the literature for the reduction of triphenylarsine oxide (1) to triphenylarsine (2).

$$\underset{(1)}{Ph_3AsO} \longrightarrow \underset{(2)}{Ph_3As}$$

At elevated temperature, triphenylarsine (2) was obtained in good yield from triphenylarsine oxide (1) by deoxygenation with triphenylphosphine[4]. This method is greatly hampered by the fact that heating of a sealed tube in a Carius furnace and separation of the reaction mixture by column chromatography are necessary. Here we would like to report several successful deoxygenation experiments on triphenylarsine oxide (1) by applying low valent titanium[7], in which triphenylarsine (2) could be isolated in fair to good yields[8] (see table).

Reagent	Molar Ratio Oxide:$TiCl_4$:Reducing agent	Yield
$TiCl_4$-$LiAlH_4$	1 : 2 : 1[a,b]	79%
$TiCl_4$-$NaBH_4$	1 : 8 : 6[a,c,d]	61%
$TiCl_4$-Zn	1 : 2 : 4[a,d]	75%
$TiCl_4$-Mg	1 : 2 : 6[a,d]	79%

a. THF as solvent.
b. stirred at room temperature for 24 hours.
c. one molar equivalent of triethylamine was added.
d. stirred at reflux for 24 hours.

In a typical experiment, zinc (1.23 g, 18.8 mmol) was added to a stirred and cooled mixture of triphenylarsine oxide (1) (1.52 g, 4.72 mmol) and titanium tetrachloride (1.80 g, 9.4 mmol) in THF (70 ml) under N_2. The mixture was then refluxed under N_2 for 24 hours. It was then allowed to cool to room temperature and poured into 20% aqueous K_2CO_3 solution (200 ml). The resulting suspension was filtered. The filter cake was washed thoroughly with ether. The filtrate was extracted several times with ether. The combined ether solution was dried ($MgSO_4$) and evaporated. The residue was recrystallized from abs.EtOH to furnish triphenylarsine (2) (1.13 g, 75%) as colorless needles, m.p. 58-60°, ^{1}H-NMR ($CDCl_3$): τ 2.8.

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References and Notes.

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8. The physical and spectroscopic properties of the obtained triphenylarsine are identical with those of an authentic sample.

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