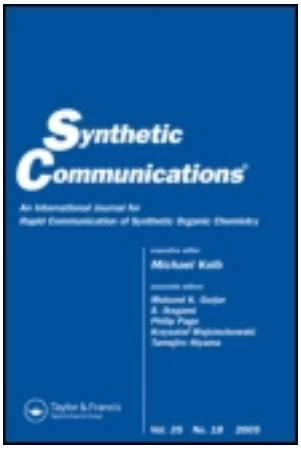

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Triphenylphosphine-Iodine: An Efficient Reagent System for the Synthesis of Nitriles From Aldoximes

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Published online: 15 Aug 2006.

To cite this article: A. Venkat Narsaiah , D. Sreenu & K. Nagaiah (2006) Triphenylphosphine-Iodine: An Efficient Reagent System for the Synthesis of Nitriles From Aldoximes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 36:2, 137-140, DOI: 10.1080/00397910500333225

To link to this article: http://dx.doi.org/10.1080/00397910500333225

Synthetic Communications®, 36: 137–140, 2006

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910500333225

Triphenylphosphine–Iodine: An Efficient Reagent System for the Synthesis of Nitriles From Aldoximes

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Abstract: A wide range of aldoximes were smoothly converted to the corresponding nitriles with triphenylphosphine–iodine.

Keywords: Aldoximes, dehydration, iodine, nitriles, triphenlyphosphine

INTRODUCTION

Among the various methods available for the dehydration of aldoximes to synthesize nitrites was found to be a convenient, mild, and efficient transformation[1] and many protocols were developed.[2] As part of our ongoing program directed at the development of efficient synthetic methodologies,[3] under mild reaction conditions, we report the conversion of aldoxime into nitrile with TPP-I_2 (Scheme 1).

In a typical procedure, treatment of 3,4,5-trimethoxybenzaldoxime (entry **a**) with TPP-I_2 in dichloromethane afforded 3,4,5-trimethoxybenzonitrile in 95% yield. The reaction was completed in 3 h at room temperature. The versatility of this methodology was examined with structurally diverse aldoximes derived from aliphatic (entries **c**, **l**, **k**, **o**), aromatic (entries **b**, **e**, **h**, **i**, **j**, **m**, **n**), and heterocyclic (entries **d**, **f**) precursors. In all cases, the reactions

Received in India July 14, 2005
IICT Communication No. 050106.
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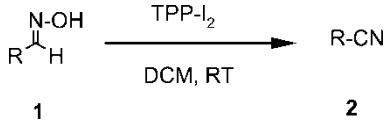
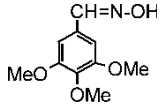
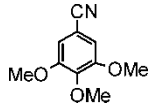
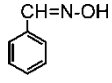
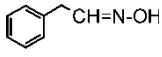
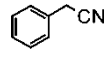
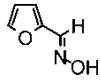
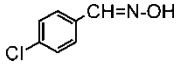
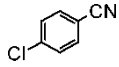
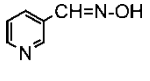
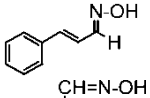
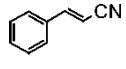
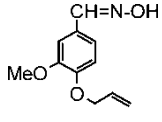
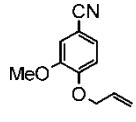


Scheme 1.

proceeded efficiently. The dehydration of cinnamaldoxime (entry **g**) provided α,β-unsaturated nitrile. The method was compatible with a wide range of functional groups such as methoxy, methylenedioxy, phenoxy ethers, and halogens present in the substrate. It appears that electron-withdrawing or electron-donating groups had little effect on the rate of reaction. All the products were characterized by ^{1}H NMR, IR, and mass spectroscopy and compared with literature reports.[2]

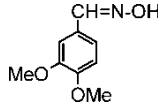
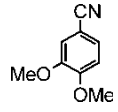
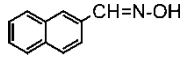
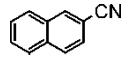
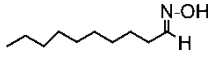
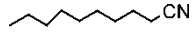
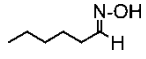
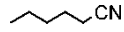
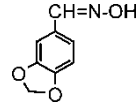
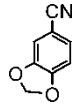
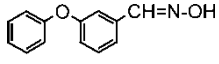
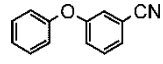
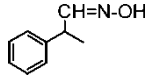
The IR spectra were recorded on a Perkin-Elmer Infracord model 337. NMR spectra were recorded on a Varian FT-200 MHz (Gemini) and

Table 1. TPP-I_2–catalyzed synthesis of nitriles from aldoximes

Entry	Substrate	Product[a]	Reaction time (h)	Yield (%)[b]
a			3.0	95
b			4.0	92
c			5.0	89
d			3.5	91
e			4.5	93
f			4.0	84
g			5.0	86
h			4.0	91

(*continued*)

Table 1. Continued

i			4.5	93
j			5.0	89
k			6.0	85
l			6.0	87
m			3.5	90
n			4.0	88
o			5.0	86

[a]All the products were confirmed by their IR, ^{1}H NMR, and mass spectroscopy[8] and compared literature reports.

[b]Yields were isolated and not optimized.

Brucker 300 MHz (Avance). Mass spectra were recorded on a Finnigan Mat 1210 or Micro Mass 7070 spectrometer at 70 eV using a direct inlet system.

GENERAL PROCEDURE

Triphenylphosphine (2 mmol) was added to a stirred mixture of aldoxime (2 mmol), in methylenedichloride (10 mL), followed by iodine (2 mmol). The resulting mixture was stirred at room temperature for a specified period (Table 1). It was diluted with methylenedichloride (20 mL) and washed with dilute sodium thiosulphate solution, followed by water and brine. The organic layer was dried over Na_2SO_4, and the residue was purified on silica gel by eluting with ethylacetate–n-hexane (1 : 9).

ACKNOWLEDGMENT

D. S. thanks Council of Scientific and Industrial Research (CSIR), New Delhi, India, for the award of fellowship.

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