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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-I₂ (Scheme 1).

In a typical procedure, treatment of 3,4,5-trimethoxybenzaldoxime (entry **a**) with TPP-I₂ 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

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$$R H \frac{TPP-I_2}{DCM, RT} R-CN$$

$$1 2$$

$$Scheme 1.$$

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 ¹H 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

Entry	Substrate	Product ^a	Reaction time (h)	Yield $(\%)^b$
a	CH=N-OH MeO OMe		3.0	95
b	CH=N-OH		4.0	92
c	CCCH=N-OH	C CN	5.0	89
d	Ко №он	<pre></pre>	3.5	91
e	CI CH=N-OH	CI CN	4.5	93
f	CH=N-OH	€ CN	4.0	84
g	N-OH H	C CN	5.0	86
h		MeO	4.0	91

Table 1. TPP-I₂-catalyzed synthesis of nitriles from aldoximes

Table 1.	Continued
<i>I able 1</i> .	Continued

i	CH=N-OH	CN	4.5	93
j	MeO OMe CH=N-OH		5.0	89
y k	N-OH	~~~~~ CN	6.0	85
1	N-OH H	~~~ CN	6.0	87
m	CH=N-OH	CN CN	3.5	90
n	C CH=N-OH		4.0	88
0	CH=N-OH	CN CN	5.0	86

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

^bYields 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 Na₂SO₄, and the residue was purified on silica gel by eluting with ethylacetate-n-hexane (1:9).

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