Arabian Journal of Chemistry (2015) **8**, 865–867

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Triphenylphosphine dibromide: A useful reagent for conversion of aldoximes into nitriles

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Received 27 February 2012; accepted 19 September 2012
Available online 3 October 2012

KEYWORDS

Aldoxime;
Nitrile;
Dehydration;
Triphenylphosphine dibromide

Abstract A simple and convenient method for the synthesis of nitriles by dehydration of aldoximes has been developed using triphenylphosphine dibromide in acetonitrile at room temperature. A variety of aromatic and heteroaromatic aldoximes are converted into the corresponding nitriles in high yields.

1. Introduction

Nitriles represent an important class of organic compounds with a wide range of applications. This functional group has a key role in bioactive molecules (Romero et al., 2007; Yadav et al., 2009) and serves as a precursor for several group transformations e.g., carboxylic acids, aldehydes, amines, amide (Katritzky et al., 1995; Larock, 1999; Kukushkin and Pombeiro, 2002). Conversion of oxime into nitrile has been studied extensively in the literature (Magnus et al., 2001; Miller and Manson, 2001; Smith and March 2007). Dehydration of aldoximes to nitriles is one of the most common routes, avoiding toxic inorganic cyanide. Many methods have been developed for this conversion (Miller and Manson, 2001), the most recently reported procedures involve $Pd(OAc)_2/PPh_3$ in acetonitrile (Kim et al., 2009), Phthalic anhydride (Eng-Chi Wang et al., 2004), benzotriazole phosphonium hexafluorophosphate derivative/DBU in dichloromethane (Singh and Lakhshman, 2009), NCS/pyridine in DMF (Gucma and Golebiewski, 2008), diethylchlorophosphate in toluene (Sardarian et al., 2007), chlorosulfonic acid in toluene (Li et al., 2005), ionic liquid at 90 °C (Saha et al., 2009), and Zeolite under microwave irradiation (Heqedues et al., 2002). Each of these methods has one or more of the following drawbacks, for instance, the use of expensive and toxic catalyst, harsh reaction condition, tedious work up, and low yield. Thus, a mild and efficient method for the preparation of nitriles is in demand.

In the last decade, utilization of triphenylphosphine dibromide (TPPDB, PPh_3Br_2) has drawn considerable attention as a versatile reagent in organic synthesis. It has been used in various organic transformations, such as bromination of alcohols, phenols, enols, conversion of carboxylic acid derivatives into acyl bromides, (Paquette, 1995) and esters (Salome and Kahn, 2009). As the aforementioned, the TPPDB plays an important role as a versatile reagent in organic synthesis. Thus, it is of interest to examine the application of TPPDB in conversion of aldoximes into nitriles. Herein, we report a convenient and simple procedure for the conversion of various aromatic aldoximes into nitriles by inexpensive and easily accessible TPPDB (Scheme 1).

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Peer review under responsibility of King Saud University.

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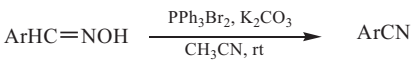
http://dx.doi.org/10.1016/j.arabjc.2012.09.008



Scheme 1

2. Results and discussion

To optimize the reaction conditions, the reaction between 3-bromobenzaldoxime, bromine, and triphenylphosphine was used as a model reaction. The effect of the molar ratio of the reactants as well as the reaction conditions on the efficiency of the dehydrating reaction was briefly examined. The best result was obtained when 1:1:1.5 of 3-bromobenzaldoxime/TPP/Br_2 in CH_3CN at room temperature were used in the dehydration reaction of 3-bromobenzaldoxime. The formation of the product was confirmed by a sharp band at 1740 cm^{-1} for C=O group stretching in the IR spectrum. To establish the generality and scope of the reaction, several aryl aldoximes were prepared (Furniss et al., 1986) and easily converted into the corresponding nitriles in high yields and short reaction times (Table 1).

3. Conclusion

This method offers several advantages such as mild reaction conditions, short reaction times, high yields, and simple experimental and isolation procedures making it an efficient route to the synthesis of aromatic nitriles from the corresponding aldoximes.

4. Experimental

4.1. Chemicals and apparatus

All the chemicals were purchased from the Merck company and used as received. Melting points were determined with Electrothermal 9100 Apparatus and were uncorrected. IR Spectra were obtained on an ABB FT-IR FTLA 2000 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were run on a Bruker DRX-300 (300 MHz and 75 MHz respectively) AVANCE instrument δ H, δ C in ppm, and J in Hz, using TMS as internal standard and $CDCl_3$ as solvent.

4.2. General procedure for dehydration of aldoxime

Bromine (1.5 mmol) was added slowly to a mixture of aldoxime (1 mmol), triphenyl phosphine (1.0 mmol), and anhydrous potassium carbonate (3.3 mmol) in dry acetonitrile (10 ml) at room temperature. After completion of the reaction, which was confirmed by TLC (*n*-hexane/EtOAc, 7:3), the reaction mixture was filtered, and the solvent was removed to obtain the crude product. Purification by column chromatography afforded the pure corresponding nitrile. All products were identified by comparison of their physical and spectral data with the authentic samples.

4.3. Selected spectral data

4.3.1. Benzonitrile

IR (neat): 2223, 1596, 1493 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.50 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 132.8, 132.0, 129.1, 118.8, 112.2.

4.3.2. 3-Methyl benzonitrile

IR (ν_{max}, neat): 2228 (C≡N), 1586 (C=C arom.), 1480, 1300, 800 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.55 (s, 1H, Ph), 7.40 (m, 3H, Ph), 2.40 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 139.2, 133.6, 132.5, 129.0, 128.9, 119.0, 112.2, 21.1.

4.3.3. 2,4-Dichlorobenzonitrile

Mp 58–60 °C (mp 59–62, Hendrickson et al., 1976). IR (ν_{max}, KBr): 2228 (C≡N), 1581 (C=C arom.) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.65 (d, 1H, J = 8.2 Hz), 7.50 (s, 1H. Ph), 7.35, (d, 1H, J = 8.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 140.1, 137.7, 134.6, 130.2, 127.9, 115.2, 111.8.

4.3.4. 3-Bromobenzonitrile

Mp 40–41 °C (mp 37–40, Attanasi et al., 1983). IR (ν_{max} neat): 2233 (C≡N), 1581(C=C arom.), 1471 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.81 (s, 1H), 7.76 (d, 1H, J = 8.7 Hz), 7.62 (d, 1H, J = 8.4 Hz), 7.38 (t, 1H,

Table 1 TPPDB catalyzed conversion of aromatic aldoximes into nitriles.

Entry	Ar	Reaction time (min)	Yield (%)	Found	Mp (°C) reported	Ref.
1	C_6H_5	15	81	–	–	
2	3-BrC_6H_4	18	93	40–41	37–40	Attanasi et al. (1983)
3	3-MeC_6H_4	7	85	–	–	
4	4-MeC_6H_4	12	74	Oil	26–28	Khezri et al. (2007)
5	4-$MeOC_6H_4$	30	80	59–60	57–59	Kukhar and Pasternak (1974)
6	3-$O_2NC_6H_4$	20	81	114–116	115–117	Hendrickson et al. (1976)
7	2-H_2N C_6H_4	13	84	47	46–49	Haynes (1991)
8	2-HOC_6H_4	8	93	93–95	92–95	Niknam et al. (2005)
9	2-Thienyl	10	91	190–192	192	Saha et al. (2009)
10	1-Naphthyl	15	96	35–37	36–38	Olah et al. (1980)
11	10-Anthracenyl	11	96	165–167	167–168	Haynes (1991)
12	2,4-$Cl_2C_6H_3$	7	94	58–60	59–62	Haynes (1991)
13	4-NCC_6H_4	13	90	229	224–227	Kazemi and Kiasat (2003)
14	4-(HC=NOH)C_6H_4	35	69	223–225	224–227	Kazemi and Kiasat (2003)

J = 8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 135.1, 133.7, 129.7, 129.4, 121.9, 116.3., 113.2.

4.3.5. 4-Methoxybenzonitrile

Mp 59–60 °C (mp 57–59, Kukhar and Pasternak, 1974). IR (ν_{max}, KBr): 2227 (C≡N), 1602 (C=C arom.), 1494 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.60 (d, 2H, J = 8.8 Hz), 6.97 (d, 2H, J = 8.8 Hz), 3.87 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 160.7, 131.8, 117.1, 112.7, 101.7, 53.5.

4.3.6. 1-Cyanonaphtanlene

Oil (Olah et al., 1980). IR (ν_{max}, $CHCl_3$): 2223 (C≡N), 1589 (C=C arom.), 1509 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.60 (d, 2H, J = 8.8 Hz), 7.5 (s, 1H, Ph), 6.97 (d, 2H, J = 8.8 Hz), 3.87 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 160.7, 131.8, 117.1, 112.7, 101.7, 53.5.

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