Tetrahedron Letters 50 (2009) 5532–5535

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Bromodimethylsulfonium bromide (BDMS): a useful reagent for conversion of aldoximes and primary amides to nitriles

Lal Dhar S. Yadav *, Vishnu P. Srivastava, Rajesh Patel

Green Synthesis Lab, Department of Chemistry, University of Allahabad, Allahabad 211 002, India

ARTICLE INFO

Article history:
Received 12 May 2009
Revised 14 July 2009
Accepted 17 July 2009
Available online 22 July 2009

Keywords:
Bromodimethylsulfonium bromide (BDMS)
Elimination
Aldoximes
Nitriles
Primary amides
Acetonitrile

ABSTRACT

An operationally simple and high yielding procedure has been developed for the preparation of nitriles from aldoximes and primary amides using bromodimethylsulfonium bromide (BDMS) as a novel and efficient reagent in the absence of any added base or catalyst. The optimal protocol is applicable to access a wide range of cyano compounds including aromatic, heterocyclic, and aliphatic species. The conversion of aldoximes to nitriles takes place at room temperature in acetonitrile, whereas acetonitrile at reflux temperature is required for rapid conversion in the case of primary amides.

Nitriles are particularly useful compounds endowed with rich chemistry that serve as precursors in several functional group transformations (e.g., RCN→RCOOH, $RCONH_2$, RCHO, RCH_2NH_2, and RCN_4 as well as Pinner and Ritter reactions).[1,2] The cyano group is a prominent functional motif found in several bioactive molecules[3a,b] and plays a significant role by hydrogen bonding to certain biological receptors.[3] Among numerous methods available for the synthesis of nitriles are the Sandmeyer reaction,[4] ammoxidation,[4] cyanation of alkyl halides,[4] metal-catalyzed cyanation of aryl halides and triflates,[5a–d] cyanation of secondary amines and phenols with trichloroacetonitrile and boron trichloride,[5e] addition of hydrogen cyanide, generated in situ from acetone cyanohydrin to alkenes,[5f] the oxidation of primary amines with Ru–Al_2O_3/O_2,[6] of hydrazones with *m*-chloroperbenzoic acid,[7a] HOF·MeCN,[7b] $MeReO_3$/H_2O_2,[7c] and oxone® on wet alumina under microwave irradiation.[7d] Many of these methods require hazardous and expensive reagents, and can be non-selective.

However, by far the most widely used method to synthesize nitriles is the transformation of aldoxime and primary amide functionalities. Thus, due to the increasing demand for generic procedures in solution-phase chemistry and the broad range of commercial importance of nitriles, it has become desirable to devise an improved protocol for the conversion of aldoximes and primary amides to nitriles.

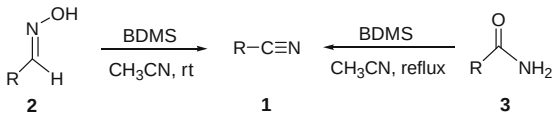
A plethora of reagents has been described for the transformation of aldoximes to nitriles. The most common reagents are acid anhydrides[1a,8] organic acids,[9a,b] strong mineral acids (H_2SO_4, $ClSO_3H$),[9c] the combination of acyl,[10] thionyl, silyl, or sulfonyl chloride and a base,[11] phosphorus based reagents, for example, diethyl chlorophosphite,[12] PPh_3/I_2,[13a] PPh_3/CCl_4,[13b] BOP/DBU,[13c] phosphoric acid diethyl ester, 2-phenylbenzimidazol-1-yl ester,[13d] PPh_3/NCS,[13e] (the driving force is the formation of a strong P=O bond), (*S*,*S*)-dimethyldithiocarbonates,[14a] DMAD,[14b] Burgess reagent,[14c] pyridine–$HCONH_2$,[14d] *N*-methylpyrrolidine,[14e] NBS/pyridine,[14f] polychloroheteroaromatic compounds such as tetrachloropyridine,[15a] or trichlorotriazine,[15b] quaternary ammonium,[16a] or imidazolium salts,[16b] certain main group/transition metals and their complexes,[17] Lewis acids,[18] ion exchangers,[19] modified or unmodified montmorillonite clays,[20] enzymatic systems,[21] or heating without[22] or with a catalyst.[23] Very recently, Pd-catalyzed synthesis of nitriles from aldoximes is also reported.[24] Similarly, a wealth of reagents is available to effect the conversion of primary amides to nitriles.[25,26] However, many of these methods are deficient in some respect or other. Some of these methods have only limited value due to low yields, expensive or not readily available reagents, use of strong acids or bases (toxic and hazardous chemicals), drastic reaction conditions, or tedious work-up and more importantly, the methods are not equally applicable to alkyl, aryl, and heterocyclic compounds. The use of clays generally requires long reaction times, reactive chemicals such as triflic anhydride involving inconveniently low temperatures (−78 °C); on the other hand, some reactions suffer from high temperatures. Therefore, the search for convenient, less toxic, and more affordable methods is ongoing.

* Corresponding author. Tel.: +91 5322500652; fax: +91 5322460533.
E-mail address: ldsyadav@hotmail.com (L. D. S. Yadav).

0040-4039/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2009.07.100

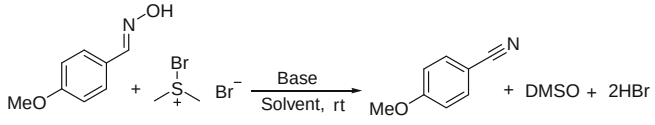
Bromodimethylsulfonium bromide (BDMS),[27] a light orange solid compound, has gained considerable interest in the field of organic chemistry after the discovery by Meerwein,[27b] due to its easy handling and low cost, as well as its easy access and varied applications both as a catalyst[28] and as an effective reagent.[29] However, its synthetic utility as a reagent in nitrile synthesis has not been explored until now. Nakajima and Ubukata[25d] have reported conversion of primary amides to nitriles under typical Swern oxidation condition via the generation chlorodimethylsulfonium chloride (CDMS), a well-known Swern intermediate and chloro analogue of BDMS. This report and our continued quest for the development of environmentally friendly new synthetic methodologies[30] have led us to investigate whether BDMS could be utilized as a reagent for the transformation of aldoximes and primary amides to nitriles, and we report herein the preliminary successful results (Scheme 1). The present method is associated with several advantages over the existing methods, such as application of an inexpensive reagent without using any added base or catalyst, operational simplicity, enhanced reaction rates, high yields, and wide applicability for heterocyclic, aromatic as well as aliphatic compounds.

Our initial work commenced with screening of solvent and base so as to obtain optimal reaction conditions for conversion of aldoximes to nitriles. Compiled in Table 1 are the results of the model study using *p*-methoxybenzaldehyde oxime as a substrate and BDMS as a hitherto unexplored reagent to afford *p*-methoxybenzonitrile. The efficiency of BDMS as a reagent was found to be the best in acetonitrile as a solvent using pyridine as a base (Table 1, entry 2). Interestingly, in the absence of a base BDMS led to fast conversion of aldoximes without any significant decrease in the yield (Table 1, entries 5 and 6). The underlying cause behind this fast conversion in the absence of a base is not fully understood. Probably, the added base competes with aldoxime in the reaction with BDMS, thereby making it sluggish (Scheme 2). Thus, BDMS in acetonitrile in the absence of a base (Table 1, entry 6) is considered the method of choice for transformation of aldoximes to nitriles.



Scheme 1. Conversion of aldoximes and primary amides to nitriles using BDMS.

Table 1
Conversion of *p*-methoxybenzaldehyde oxime to benzonitrile using BDMS[a]



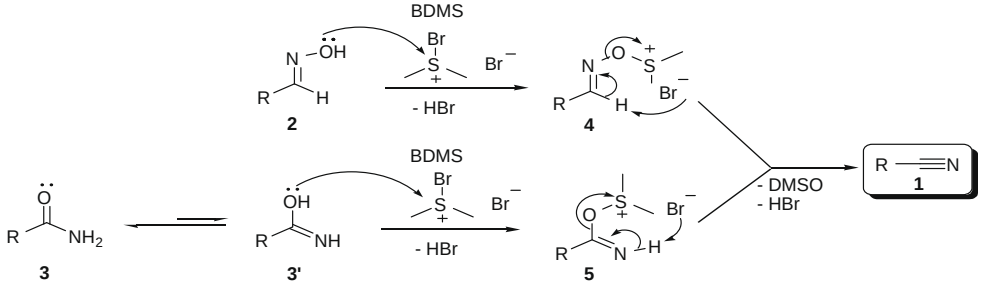
Entry	Solvent	Base[b]	Time (h)	Conv.[c] (%)	Yield[d] (%)
1	DCM	Pyridine	12	92	82
2	CH_3CN	Pyridine	10	96	85
3	DCM	Et_3N	14	91	80
4	CH_3CN	Et_3N	8	94	82
5	DCM	No base	6	93	84
6	CH_3CN	No base	4	98	91

[a] All reactions were performed using oxime **2** (1 equiv), BDMS (1.1 equiv), and base (2.2 equiv).
[b] Base was added to reaction mixture at 0 °C.
[c] Conversion (%) of **2b** as determined by GC analysis with diphenyl or naphthalene as an internal standard.
[d] Yield of isolated and purified products.

The generality of the method is apparently demonstrated by conversion of various kinds of structurally diverse aldoximes to nitriles as summarized in Table 2.

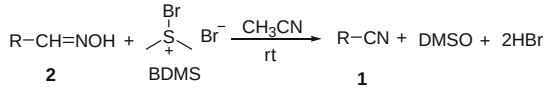
Benzaldoximes were smoothly converted to the corresponding benzonitriles in excellent yields (Table 2, entries 2a–f). Not only aromatic aldehyde-derived oximes but also aliphatic ones could be transformed to the corresponding nitriles (Table 2, entries 2h–j). The heteroaromatic aldoximes such as 2-thiophenealdoxime and 2-furaldoxime (Table 2, entries 2k and 2l) were found to be compatible with the employed reaction conditions and reaction proceeded smoothly within 3–6 h to afford 84–87% yield without forming any side products. In addition, olefinic aldoximes like *trans*-cinnamaldoxime was conveniently converted to the corresponding nitriles with stereochemical retention of the double bond (Table 2, entry 2g).

The synthetic efficacy of the present method was further demonstrated by transforming primary amide functionality to the cyano group, which has extensive utility in organic synthesis and the results are shown in Table 3. Initially, we tried the conversion of benzamide, as a model substrate, to benzonitrile under the above optimized reaction conditions for obtaining nitriles from aldoximes. Thus, the solution of benzamide (1 equiv) in acetonitrile was treated with BDMS (1.1 equiv) in the absence of a base, but starting material was not consumed at all after the prolonged (20 h) stirring of the reaction mixture at rt. However, upon raising the temperature up to reflux, starting material disappeared within 2 h to afford the corresponding benzonitrile in 91% yield (Table 3, entry 3a). In a similar manner various aromatic and aliphatic primary amides were converted to corresponding nitriles with BDMS in the absence of a base in refluxing acetonitrile within 2–4 h in excellent yields (Table 3). As in the case of aldoximes, the addition of a base (pyridine or Et_3N) does not show any notable enhancement of the reaction rate or yields of the product. The use of acetonitrile as a solvent appeared to be critical for the conversion of primary amides to nitriles, because when the reaction was performed in DCM, THF or 1,4-dioxane as a solvent either at rt or at reflux temperature, no appreciable formation of the desired nitrile was observed even after 6–7 h.



Scheme 2. Plausible pathway for the formation of nitriles **1** from aldoximes **2** and primary amides **3** using BDMS.

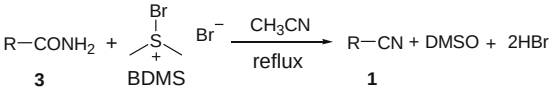
Table 2
Conversion of aldoximes to nitriles with BDMS[a]



Entry	R	Nitrile[b]	Time (h)	Conv.[c] (%)	Yield[d,e] (%)
2a	Ph	**1a**	5.5	>99	94
2b	4-$MeOC_6H_4$	**1b**	4	98	91
2c	3,4,5-$(MeO)_3C_6H_2$	**1c**	3	>99	96
2d	4-ClC_6H_4	**1d**	5	96	89
2e	4-$NO_2C_6H_4$	**1e**	6	98	92
2f	4-MeC_6H_4	**1f**	4	97	88
2g	C_6H_5CH=CH	**1g**	3	97	90
2h	$CH_3(CH_2)_2$	**1h**	4	90	76
2i	$CH_3(CH_2)_3$	**1i**	4.5	93	81
2j	$C_6H_5(CH_2)_2$	**1j**	4	89	78
2k	2-Furyl	**1k**	6	92	84
2l	2-Thienyl	**1l**	3	>99	87

[a] See Ref. 31a for general procedure.
[b] All are known compounds.[32]
[c] Conversion (%) of **2** as determined by GC analysis with diphenyl or naphthalene as an internal standard.
[d] Products were characterized by comparison of their mp or bp, TLC, IR, and ^1H NMR data with those of authentic samples.
[e] Yields of the isolated pure compounds.

Table 3
Conversion of primary amides into nitriles with BDMS[a]



Entry	R	Nitrile[b]	Time (h)	Conv.[c] (%)	Yield[d,e] (%)
3a	Ph	**1a**	2	>99	91
3b	4-$MeOC_6H_4$	**1b**	2	96	86
3c	4-ClC_6H_4	**1d**	3	96	89
3d	4-$NO_2C_6H_4$	**1e**	4	95	90
3e	3,4-$(MeO)_2C_6H_3$	**1m**	2	>99	94
3f	$C_6H_5CH_2$	**1n**	3.5	92	78
3g	Cyclohexyl	**1o**	3	94	80
3h	$CH_3(CH_2)_6$	**1p**	4	94	87

[a] See Ref. 31b for general procedure.
[b] All are known compounds.[32]
[c] Conversion (%) of **3** as determined by GC analysis with diphenyl or naphthalene as an internal standard.
[d] Products were characterized by comparison of their mp or bp, TLC, IR, and ^1H NMR data with those of authentic samples.
[e] Yields of the isolated pure compounds.

A mechanistic rationale for the preparation of nitriles **1** from aldoximes **2** and primary amides **3** is depicted in Scheme 2. It is easily conceivable that the aldoxime **2** and primary amide **3** are initially coupled with BDMS to form an active O-derivative intermediate **4** or **5**, respectively, which in turn undergo bromide anion-induced elimination to deliver the corresponding nitriles **1** along with DMSO and HBr. The aldoximes **2** were converted to nitriles **1** at rt but primary amides **3** required reflux temperature probably due to demand of high energy for the breakage of more strong C–O bond involved during elimination process in primary amide-derived O-intermediate **5** than that of N–O bond breakage operated in aldoxime-derived O-intermediate **4**. Moreover, among the solvents tested (CH_3CN, DCM, THF, and 1,4-dioxane), the transformation of primary amide to nitriles took place only in CH_3CN. This suggests that in CH_3CN the equilibrium concentration of tautomer **3′** is enough to attack BDMS to afford the corresponding nitrile **1** (Scheme 2), whereas in THF or 1,4-dioxane it is too low to bring about the reaction. Thus, the conversion of primary amides **3** to nitriles **1** with BDMS is favorable in acetonitrile, which is in conformity with the solvent effect earlier observed with PPh_3/CCl_4 system.[13b]

In conclusion, bromodimethylsulfonium bromide (BDMS) has been employed here for the first time as a mild and efficient reagent for the conversion of the wide range of aldoximes and primary amides to the corresponding nitriles. The method offers a useful alternative to the existing methodologies, as it is simple, high yielding and requires no added base or catalyst. The present work has opened up a new aspect of the synthetic utility of BDMS.

Acknowledgment

We sincerely thank SAIF, Punjab University, Chandigarh, for providing microanalyses and spectra.

References and notes

1. (a) Smith, M.; March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 6th ed.; Wiley Interscience: Chichester, 2007; (b) Larock, R. C. *Comprehensive Organic Transformations*, 2nd ed.; Wiley: New York, 1999; (c) Trost, B. M.; Fleming, I. *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, 1991; (d) Katritzky, A. R.; Meth-Cohn, O.; Rees, C. W. *Comprehensive Organic Functional Group Transformations*; Pergamon Press: Oxford, 1995.
2. (a) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771; (b) Gaspar, B.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4519; (c) Yadav, V. K.; Babu, K. G. *Eur. J. Org. Chem.* **2005**, 452; (d) Jayachitra, G.; Yasmeen, N.; Rao, K. S.; Ralte, S. L.; Srinivasan, R.; Singh, A. K. *Synth. Commun.* **2003**, *33*, 3461; (e) Sharifi, A.; Mohsenzadeh, F.; Mojtahedi, M. M.; Saidi, M. R.; Balalaie, S. *Synth. Commun.* **2001**, *31*, 431.
3. (a) Romero, M.; Renard, P.; Caignard, D. H.; Atassi, G.; Solans, X.; Constans, P.; Bailly, C.; Pujol, M. D. *J. Med. Chem.* **2007**, *50*, 294; (b) Pei, Z.; Li, X.; Longenecker, K.; von Geldern, T. W.; Wiedemann, P. E.; Lubben, T. H.; Zinker, B. A.; Stewart, K.; Ballaron, S. J.; Stashko, M. A.; Mika, A. K.; Beno, D. W. A.; Long, M.; Wells, H.; Kempf-Grote, A. J.; Madar, D. J.; McDermott, T. S.; Bhagavatula, L.; Fickes, M. G.; Pireh, D.; Solomon, L. R.; Lake, M. R.; Edalji, R.; Fry, E. H.; Sham, H. L.; Trevillyan, J. M. *J. Med. Chem.* **2006**, *49*, 3520; (c) Sakya, S. M.; Hou, X. J.; Minich, M. L.; Rast, B.; Shavnya, A.; DeMello, K. M. L.; Cheng, H.; Li, J.; Jaynes, B. H.; Mann, D. W.; Petras, C. F.; Seibel, S. B.; Haven, M. L. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 1076; (d) Iyengar, B. S.; Dorr, R. T.; Remers, W. A. *J. Med. Chem.* **2004**, *47*, 218; (e) Kamath, S.; Buolamwini, J. K. *J. Med. Chem.* **2003**, *46*, 4657.
4. (a) Fatiadi, A. J. In *Preparation and Synthetic Applications of Cyano Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1983; (b) Miller, J. S.; Manson, J. L. *Acc. Chem. Res.* **2001**, *34*, 563.
5. (a) Jin, F.; Confalone, P. N. *Tetrahedron Lett.* **2000**, *41*, 3271; (b) Connor, J. A.; Gibson, D.; Price, R. *J. Chem. Soc., Perkin Trans. 1* **1987**, 619; (c) Tagaki, K.; Sakakibara, Y. *Chem. Lett.* **1989**, 1957; (d) Kubota, H.; Rice, K. C. *Tetrahedron Lett.* **1998**, *39*, 2907; (e) Adachi, M.; Sugasawa, T. *Synth. Commun.* **1990**, *20*, 71; (f) Jackson, W. R.; Perlmuter, P. *Chem. Ber.* **1986**, 338.
6. Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1480.
7. (a) Mlochowski, J.; Kloc, K.; Kubicz, E. *J. Prakt. Chem.* **1994**, *336*, 467; (b) Carmeli, M.; Shefer, N.; Rozen, S. *Tetrahedron Lett.* **2006**, *47*, 8969; (c) Stanković, S.; Espenson, J. H. *Chem. Commun.* **1998**, 1579; (d) Ramalingam, T.; Reddy, B. V. S.; Srinivas, R.; Yadav, J. S. *Synth. Commun.* **2000**, *30*, 4507.
8. (a) Wang, E.-C.; Lin, G.-J. *Tetrahedron Lett.* **1998**, *39*, 4047; (b) Hendricson, J. B.; Hussoin, M. S. *J. Org. Chem.* **1987**, *52*, 4137.
9. (a) Yale, H. L.; Spitzmiller, E. R. *J. Heterocycl. Chem.* **1978**, *15*, 1373; (b) Chandrasekhar, S.; Gopalaiah, K. *Tetrahedron Lett.* **2003**, *44*, 7437; (c) Li, D.; Shi, F.; Guo, S.; Deng, Y. *Tetrahedron Lett.* **2005**, *46*, 671.
10. (a) Sarvari, M. H. *Synthesis* **2005**, 787; (b) Saednya, A. *Synthesis* **1983**, 748.
11. (a) Sharghi, H.; Sarvari, M. H. *Synthesis* **2003**, 243; (b) Ortiz-Marciales, M.; Pinero, L.; Algarin, W.; Morales, J. *Synth. Commun.* **1998**, *28*, 2807; (c) Chaudhari, S. S.; Akamanchi, K. G. *Synth. Commun.* **1999**, *29*, 1741.
12. (a) Jie, Z.; Rammoorty, V.; Fischer, B. *J. Org. Chem.* **2002**, *67*, 711; (b) Sardarian, A. R.; Shahsavari-Fard, Z.; Shahsavari, H. R.; Ebrahimi, Z. *Tetrahedron Lett.* **2007**, *48*, 2639.
13. (a) Narsaiah, A. V.; Sreenu, D.; Nagaiah, K. *Synth. Commun.* **2006**, *36*, 137; (b) Kim, J. N.; Chung, K. H.; Ryu, E. K. *Synth. Commun.* **1990**, *20*, 2785; (c) Singh, M. K.; Lakshman, M. K. *J. Org. Chem.* **2009**, *74*, 3079; (d) Kokare, N. D.; Shinde, D. B. *Monatsh. Chem.* **2009**, *140*, 185; (e) Iranpoor, N.; Firouzabadi, H.; Aghapour, G. *Synth. Commun.* **2002**, *32*, 2535.
14. (a) Khan, T. A.; Peruncheralathan, S.; Junjappa, I. H. *Synlett* **2004**, 2019; (b) Coskun, N. *Synth. Commun.* **2004**, *34*, 1625; (c) Miller, C. P.; Kaufman, D. H. *Synlett* **2000**, 1169; (d) Paraskar, A. S.; Jagtap, H. S.; Sudalai, A. *J. Chem. Res., Synop.* **2000**, 30; (e) Kumar, H. M. S.; Reddy, B. V. S.; Reddy, P. T.; Yadav, J. S. *Synthesis* **1999**, 586; (f) Gucma, M.; Golebiewski, W. M. *Synthesis* **2008**, 1997.
15. (a) Lingaiah, N.; Narender, R. *Synth. Commun.* **2002**, *32*, 2391; (b) De Luca, L.; Giacomelli, G.; Porcheddu, A. *J Org. Chem.* **2002**, *67*, 627.
16. (a) Sahu, S.; Patel, S.; Mishra, B. K. *Synth. Commun.* **2005**, *35*, 3123; (b) Isobe, T. *J. Org. Chem.* **1999**, *64*, 6984.

17. (a) Ishihara, K.; Furuya, Y.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2983; (b) Yang, S. H.; Chang, S. *Org. Lett.* **2001**, *3*, 4209; (c) Zuidema, D. R.; Dennison, A. L.; Park, E. Y.; Mebane, R. C. *Synth. Commun.* **2008**, *38*, 3810; (d) Hanada, S.; Motoyama, Y.; Nagashima, H. *Eur. J. Org. Chem.* **2008**, 4097; (e) Yamaguchi, K.; Fujiwara, H.; Ogasawara, Y.; Kotani, M.; Mizuno, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 3922; (f) Tamilselvan, P.; Basavaraju, Y. B.; Sampathkumar, E.; Murugesan, R. *Catal. Commun.* **2009**, *10*, 716.
18. (a) Boruah, M.; Konwar, D. *J. Org. Chem.* **2002**, *67*, 7138; (b) Saini, A.; Kumnar, S.; Sandhu, J. S. *Indian J. Chem., Sect. B* **2005**, *44*, 1427; (c) Yan, P.; Batamack, P.; Prakash, K. S.; Olah, G. A. *Catal. Lett.* **2005**, *101*, 141; (d) Barman, D. C.; Thakur, A. J.; Prajapati, D.; Sandhu, J. S. *Chem. Lett.* **2000**, 1196; (e) Iranpoor, N.; Zeynizadeh, B. *Synth. Commun.* **1999**, *29*, 2747.
19. (a) Tamami, B.; Kiasat, A. R. *Synth. Commun.* **2000**, *30*, 235; (b) Wang, X. C.; Li, L.; Quan, Z. J.; Gong, H. P.; Ye, H. L.; Cao, X. F. *Chin. Chem. Lett.* **2009**, *20*, 651.
20. (a) Meshram, H. M. *Synthesis* **1992**, 943; (b) Bandgar, B. P.; Sadavarte, V. S.; Sabu, K. R. *Synth. Commun.* **1999**, *29*, 3409.
21. (a) Hart-Davis, J.; Battioni, P.; Boucher, J.-L.; Mansuy, D. *J. Am. Chem. Soc.* **1998**, *120*, 12524; (b) Kato, Y.; Ooi, R.; Asano, Y. *Mol. Catal. B: Enzym.* **1999**, *6*, 249.
22. (a) Wagner, G.; Briel, D. *Pharmazie* **1982**, *37*, 251; (b) Supsana, P.; Liaskopoulos, T.; Tsoungas, P. G.; Varvonis, G. *Synlett* **2007**, 2671.
23. (a) Campbell, J. A.; MacDougald, G.; MacNab, H.; Rees, L. V. C.; Tyas, R. G. *Synthesis* **2007**, 293; (b) De Montigny, F.; Argouarch, G.; Lapinte, C. *Synthesis* **2006**, 293.
24. Kim, H. S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2009**, *50*, 1717.
25. (a) Bose, D. S.; Narsaiah, A. V. *Synthesis* **2001**, 373; (b) Narsaiah, A. V.; Nagaiah, K. *Adv. Synth. Catal.* **2004**, *346*, 1271; (c) Wang, E. C.; Huang, K. S.; Chen, H. M.; Wu, C. C.; Lin, G. J. *J. Chin. Chem. Soc.* **2004**, *51*, 619; (d) Nakajima, N.; Ubukata, M. *Tetrahedron Lett.* **1997**, *38*, 2099.
26. (a) Kuo, C.-W.; Zhu, J.-L.; Wu, J.-D.; Chu, C.-M.; Yao, C.-F.; Shia, K.-S. *Chem. Commun.* **2007**, 301. and references cited therein; (b) Bose, D. S.; Goud, P. R. *Tetrahedron Lett.* **1999**, *40*, 747; (c) Bose, D. S.; Jayalakshmi, B. *J. Org. Chem.* **1999**, *64*, 1713; (d) Ley, S. V.; Leach, A. G.; Storer, R. I. *J. Chem. Soc., Perkin Trans. 1* **2001**, 358.
27. (a) Olah, G. A.; Vankar, Y. D.; Arvanaghi, M.; Surya Prakash, G. K. *Synthesis* **1979**, 720; (b) Meerwein, H.; Zenner, K. F.; Gipp, R. *Justus Liebigs Ann. Chem.* **1965**, *67*, 688; (c) Choudhury, L. H. *Synlett* **2006**, 1619. and references cited therein; (d) Furukawa, N.; Inoue, T.; Aida, T.; Oae, S. *J. Chem. Soc., Chem. Commun.* **1973**, 212a.
28. (a) Khan, A. T.; Parvin, T.; Gazi, S.; Choudhury, L. H. *Tetrahedron Lett.* **2007**, *48*, 3805; (b) Khan, A. T.; Parvin, T.; Choudhury, L. H. *Eur. J. Org. Chem.* **2008**, 834; (c) Khan, A. T.; Parvin, T.; Choudhury, L. H. *J. Org. Chem.* **2008**, *73*, 8398; (d) Khan, A. T.; Mondal, E.; Borah, B. M.; Ghosh, S. *Eur. J. Org. Chem.* **2003**, 4113; (e) Khan, A. T.; Islam, S.; Majee, A.; Chattopadhyay, T.; Ghosh, S. *J. Mol. Catal. A: Chem.* **2005**, *239*, 158; (f) Khan, A. T.; Sahu, P. R.; Majee, A. *J. Mol. Catal. A: Chem.* **2005**, *226*, 207; (g) Khan, A. T.; Mondal, E.; Ghosh, S.; Islam, S. *Eur. J. Org. Chem.* **2004**, 2002; (h) Das, B.; Holla, H.; Srinivas, Y. *Tetrahedron Lett.* **2007**, *48*, 61; (i) Bhalerao, D. S.; Akamanchi, K. G. *Synlett* **2007**, 2952; (j) Das, B.; Ramu, R.; Ravikanth, B.; Reddy, K. R. *Synthesis* **2006**, 1419; (k) Kudrimoti, S.; Bommena, V. R. *Tetrahedron Lett.* **2005**, *46*, 1209; (l) Das, B.; Ravikanth, B.; Thirupathi, P.; Rao, B. V. *Tetrahedron Lett.* **2006**, *47*, 5041.
29. (a) Khan, A. T.; Ali, A.; Goswami, P.; Choudhury, L. H. *J. Org. Chem.* **2006**, *71*, 8961; (b) Das, B.; Krishnaiah, M.; Venkateswarlu, K. *Tetrahedron Lett.* **2006**, *47*, 4457; (c) Jiang, B.; Dou, Y.; Xu, X.; Xu, M. *Org. Lett.* **2008**, *10*, 593; (d) Das, B.; Srinivas, Y.; Holla, H.; Laxminarayana, K.; Narender, R. *Tetrahedron Lett.* **2007**, *48*, 6681; (e) Das, B.; Srinivas, Y.; Sudhakar, C.; Ravikanth, B. *J. Chem. Res.* **2008**, 188; (f) Das, B.; Venkateswarlu, K.; Krishnaiah, M.; Holla, H.; Majhi, A. *Helv. Chim. Acta* **2006**, *89*, 1417; (g) Rani, S.; Babu, J. L.; Vankar, Y. D. *Synth. Commun.* **2003**, *33*, 4043.
30. (a) Yadav, L. D. S.; Yadav, S.; Rai, V. K. *Green Chem.* **2006**, *8*, 455; (b) Yadav, L. D. S.; Yadav, B. S.; Rai, V. K. *Synthesis* **2006**, 1868; (c) Yadav, L. D. S.; Patel, R.; Rai, V. K.; Srivastava, V. P. *Tetrahedron Lett.* **2007**, *48*, 7793; (d) Yadav, L. D. S.; Rai, V. K. *Synlett* **2007**, 1227; (e) Yadav, L. D. S.; Patel, R.; Srivastava, V. P. *Synlett* **2008**, 1789; (f) Yadav, L. D. S.; Srivastava, V. P.; Patel, R. *Tetrahedron Lett.* **2008**, *49*, 5652; (g) Yadav, L. D. S.; Patel, R.; Srivastava, V. P. *Tetrahedron Lett.* **2009**, *50*, 1335.
31. (a) *General procedure for conversion of aldoximes* **2** *to nitriles* **1**: To a solution of aldoxime **2** (1 mmol) in acetonitrile (5 mL), bromodimethylsulfonium bromide (BDMS) (1.1 mmol) was added at rt and reaction mixture was stirred at the same temperature for 3–6 h (Table 2). After completion of reaction (monitored by TLC), the solvent was evaporated under reduced pressure and H_2O (10 mL) was added. The mixture was extracted with EtOAc (3×10 mL) and combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography (EtOAc–hexane, 1:9) to give the corresponding nitrile **1**. The structure of the products was confirmed by comparison of their mp or bp, TLC, IR, or ^{1}H NMR data with authentic sample obtained commercially or prepared by literature methods.
(b) *General procedure for conversion of primary amides* **3** *to nitriles* **1**: To a solution of primary amide **3** (1 mmol) in acetonitrile (5 mL), bromodimethylsulfonium bromide (BDMS) (1.1 mmol) was added at rt and the reaction mixture was heated at reflux for 2–4 h (Table 3). After completion of reaction as indicated by TLC, the reaction mixture was cooled to rt. The isolation, purification, and characterization of the products **1** was done by following the same procedure as described above for the conversion of aldoximes **2** to nitriles **1** (Ref. 31a).
32. *Registry numbers of the nitrile products*: **1a**: 100-47-0, **1b**: 874-90-8, **1c**: 1885-35-4, **1d**: 623-03-0, **1e**: 619-72-7, **1f**: 104-85-8, **1g**: 1885-38-7, **1h**: 109-74-0, **1i**: 110-59-8, **1j**: 645-59-0, **1k**: 617-90-3, **1l**: 1003-31-2, **1m**: 2024-83-1, **1n**: 140-29-4, **1o**: 766-05-2, **1p**: 124-12-9.