Efficient regio- and stereo-selective cleavage of aziridines and epoxides using an ionic liquid as reagent and reaction medium

Brindaban C. Ranu, Laksmikanta Adak, and Subhash Banerjee

Abstract: Ionic liquids, containing a variety of functionalities such as halo, azido, and thiocyano, efficiently cleave aziridines and epoxides to the corresponding products in high yields. The cleavages are regio- and stereo-selective. The reactions are complete in 1 h at 60 °C and do not require any other catalyst or organic solvent. Thus, a convenient synthetic route to 1,2-haloamines, 1,2-azidoamines, 1,2-thiocyanoamines, 1,2-azidoalcohols, and 1,2-thiocyanoalcohols is developed.

Key words: aziridine, epoxide, ionic liquid, cleavage, regioselectivity, stereoselectivity

Résumé : Des liquides ioniques contenant diverses fonctions, telles halogéno, azido ou thiocyano, permettent de cliver efficacement les aziridines et les époxydes pour fournir les produits correspondants avec des rendements élevés. Les clivages sont régio- et stéréosélectifs. Les réactions sont complètes en moins d'une heure, à 60 °C, et elles ne nécessitent pas l'utilisation d'autres catalyseurs ou solvants organiques. On a donc développé une voie de synthèse commode pouvant conduire aux 1,2-halogénoamines, 1,2-azidoamines, 1,2-thiocyanoamines, 1,2-azidoalcools et 1,2-thiocyanoalcools.

Mots clés : aziridine, époxyde, liquide ionique, clivage, régiosélectivité et stéréosélectivité.

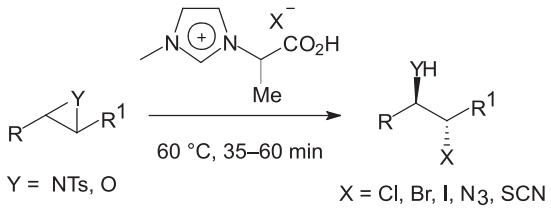
[Traduit par la Rédaction]

Introduction

Ionic liquids are attracting increasing attention in organic synthesis because of their unique advantages as reaction media (1), compared with organic solvents, and efficient promoters for a variety of reactions (2). However, the potential of ionic liquids as reagents has been less explored, and as a part of our activities in this area (3) we initiated an investigation to explore the utility of ionic liquids as efficient reagents (3*a*) for useful transformations.

Aziridines (4) and epoxides (5) are very useful synthetic intermediates. Because of their ring strain and high reactivity, their reactions with various nucleophiles lead to regio- and stereo-selective synthesis of various important synthons. Considerable progress towards the development of several procedures (6) has been achieved in the nucloephilic ring-opening reactions of aziridines and epoxides. The nucleophilic reagents involved in these procedures include tributylphosphine in H_2O (6*a*), $CeCl_3$ in CH_3CN (6*b*), NaN_3–$CeCl_3$ in CH_3CN (6*c*), Me_2SBr_2 in CH_3CN (6*d*), $LiClO_4$–NaX (where X = N_3, CN) in CH_3CN (6*e*), KSCN–sulfated zirconia in CH_3CN (6*f*), zinc halides in CH_2Cl_2 (6*g*), KSCN–$LiClO_4$ in CH_3CN (6*h*), KSCN–β-cyclodextrin in H_2O (6*i*), TBAX–β-cyclodextrin in H_2O (6*j*), $^nBu_4NF$–Me_3SiX in THF (6*k*), $TMSN_3$–$Sn(OTf)_2$ in benzene (6*l*), InX_3 in CH_3CN (6*m*), NaN_3 or KCN–SiO_2 in H_2O (6*n*), $TMSN_3$ in THF (6*o*), NaN_3 in ionic liquid H_2O (6*p*), activated DMF complexes (6*q*), NaX–$Ce(OTf)_4$ in micelle (6*r*), fluoride anion (6*s*), and aminosaccharides (6*t*) in the ionic liquid *N*-methylpyridinium tosylate, among others. However, most of these procedures involve a nucleophilic reagent (usually metal salts), an acid catalyst, and organic solvents like CH_3CN and CH_2Cl_2. We report here a new strategy for the cleavage of aziridines and epoxides with a variety of nucleophiles using a core ionic liquid, 1-(1-carboxy-ethyl)-3-methyl-3*H*-imidazolium derivative [PnMIm]X [where X = N_3, SCN, Cl, Br, I] without any additional reagent, catalyst, or organic solvent (Scheme 1).

Scheme 1.



Results and discussion

The general experimental procedure is very simple and convenient. A mixture of aziridine (or epoxide) and ionic liquid [PnMIm]X was heated at 60 °C for a certain period of time, as required to complete the reaction (TLC). The usual

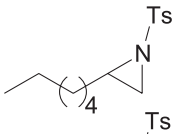
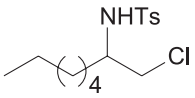
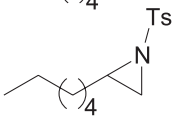
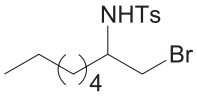
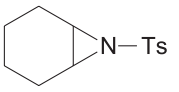
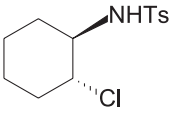
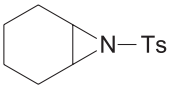
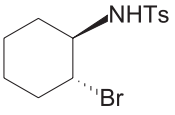
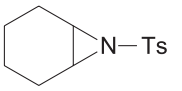
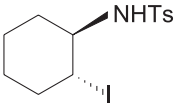
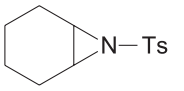
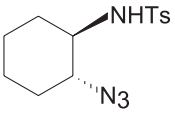
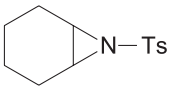
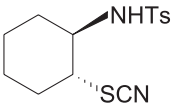
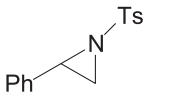
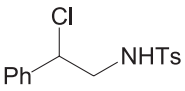
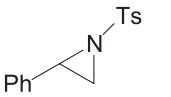
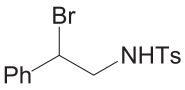
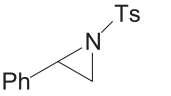
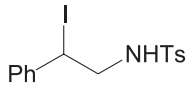
Received 5 March 2007. Accepted 23 April 2007. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 18 April 2007.

B.C. Ranu,[1] L. Adak, and S. Banerjee. Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India.

[1]Corresponding author (e-mail: ocbcr@iacs.res.in).

 doi:10.1139/V07-040

Table 1. Ring opening of aziridines by ionic liquids [PnMlm]X.

Entry	Aziridine	X	Product	Time (min)	Yield (%)[a]	Ref.
1		Cl		50	90	6q
2		Br		45	93	6q
3		Cl		40	92	6q
4		Br		35	95	6q
5		I		35	95	6b
6		N_3		35	91	6c
7		SCN		45	90	6f
8		Cl		45	92	6q
9		Br		45	94	6q
10		I		40	95	6b

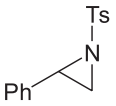
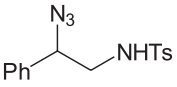
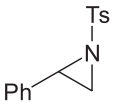
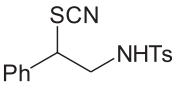
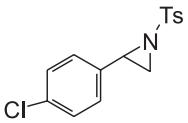
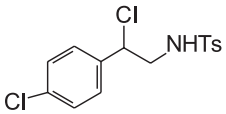
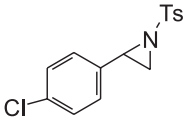
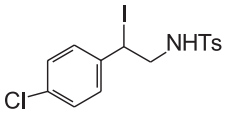
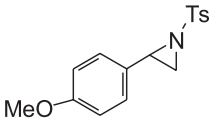
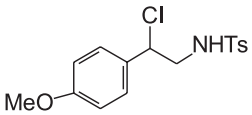
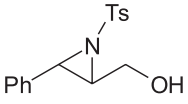
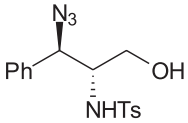
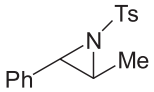
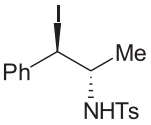
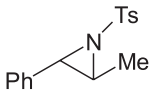
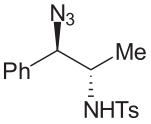
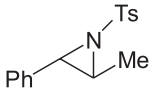
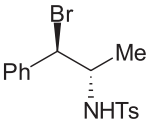
work-up and purification by column chromatography provided the product.

Several structurally diverse aziridines underwent cleavages by this procedure using a core ionic liquid [PnMIm]X (where X = Cl, Br, I, N_3, SCN) to provide the corresponding 2-chloro-, bromo-, iodo-, azido-, and thiocyano-amines. The results were summarized in Table 1. Both alkyl- and aryl-substituted aziridines participated in this reaction. The alkyl-substituted aziridines underwent nucleophilic attack at the less hindered (substituted) carbon atom (Table 1, entries 1 and 2), whereas in aryl-substituted aziridines nucleophiles attacked at the benzylic positions (Table 1, entries 8–23) because of their electronic factor. The cyclohexene azide provided trans isomers by this cleavage, as indicated by the ^{1}H NMR spectra of the corresponding amines (Table 1, entries 3–7). The disubstituted aziridines also furnished trans-functionalized amines (Table 1, entries 16–23).

The epoxides also underwent cleavages by this ionic liquid, producing 2-azido-, nitro-, and thiocyano-alcohols under this procedure. The cleavages by halo-bearing ionic liquids were reported earlier (3*a*). The reactions of alkyl- and aryl-substituted as well as cyclohexene epoxides proceeded smoothly. The results are reported in Table 2. The epoxide of an α,β-unsaturated ketone underwent nucleophilic attack at the α-carbon atom followed by subsequent dehydration to furnish the corresponding α-azido α,β-unsaturated ketone (Table 2, entry 9) under the reaction conditions.

In general, the reactions were very clean, fast, and high-

Table 1 (*concluded*).

Entry	Aziridine	X	Product	Time (min)	Yield (%)[a]	Ref.
11		N_3		40	93	6c
12		SCN		45	89	6f
13		Cl		60	86	6b
14		I		55	90	6b
15		Cl		45	84	-
16		N_3		60	80	9
17		I		45	91	-
18		N_3		40	94	10
19		Br		45	87	11

[a]Yields of pure isolated products characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data.

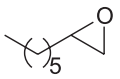
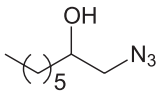
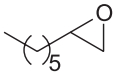
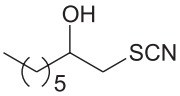
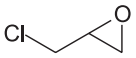
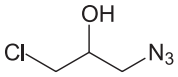
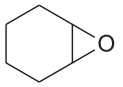
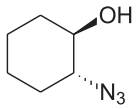
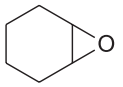
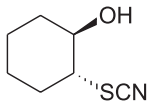
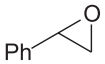
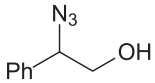
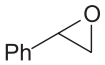
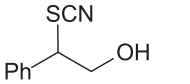
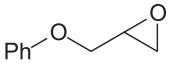
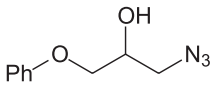
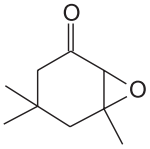
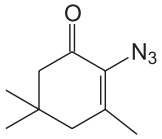
yielding. The cleavages of both aziridines and epoxides by this reagent were highly regioselective, affording a single product. The stereochemistry of products was determined as trans by the coupling constant (*J* value) of the hydrogens at the cleaved carbon atoms. It has been observed that nucleophilic attack occurred at the less-substituted carbon atoms of the alkyl-substituted terminal aziridines and epoxides, whereas aryl-substituted substrates underwent attack at the benzylic position, being dictated by the electronic factor. It may be anticipated that these cleavage reactions proceed through the usual S_N2 path as outlined in our earlier paper on epoxide cleavage (3*a*). Several functional groups, such as Cl, OMe, and OPh, remained unaffected during this reaction. The ionic liquids were easily prepared by substitution reaction of the core imidazolium bromide with the sodio-salt of the corresponding anion.

The products of this cleavage reaction, 2-azidoalcohols, 2-thiocyanoalcohol, 2-azido amines, 2-haloamines, and 2-thiocyanoamines are very useful intermediates and have wide applications in organic synthesis (7, 8).

Conclusion

In conclusion, the present procedure provides a novel and

Table 2. Ring opening of epoxides by ionic liquids [PnMlm]X.

Entry	Epoxide	X	Product	Time (min)	Yield (%)[a]	Ref.
1		N_3		45	95	6p
2		SCN		50	89	12
3		N_3		40	90	13
4		N_3		35	94	6c
5		SCN		50	88	12
6		N_3		40	95	6p
7		SCN		45	90	12
8		N_3		45	91	6p
9		N_3		40	87	14

[a]Yields of pure isolated products characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data.

general route to the cleavage of epoxides and aziridines by a variety of nucleophiles carried out by an inexpensive and easily accessible ionic liquid [PnMIm]X, which itself works as reagent, catalyst, and reaction medium. The other significant advantages offered by this method are operational simplicity, considerably fast reaction time (30–60 min), high isolated yields of products, general applicability to a wide variety of substrates, excellent regio- and stereo-selectivity, thus providing a better and practical alternative to the existing procedures (6). Moreover, this demonstrates the potential of ionic liquids as efficient reagents and shows promise for further useful applications.

Experimental

General

IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids using a Shimadzu 8300 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and d_6-DMSO solution at 300 and 75 MHz, respectively (Bruker 300 DPX instrument).

General experimental procedure for the preparation of ionic liquid [PnMIm]x

2-Bromopropionic acid (3.06 g, 20 mmol) was added dropwise to a cooled (0–5 °C) solution of *N*-methylimidazole (1.64 g, 20 mmol) in dry acetonitrile (10 mL). The reaction mixture was then stirred for 12 h at room temperature (RT). The crude product, obtained by evaporation of solvent, was washed with Et_2O (2 × 5 mL) and dried under vacuum to provide the bromo ionic liquid, [PnMIm]Br, ready to be used for cleavage reactions.

The iodo and chloro analogues were prepared from the corresponding 2-iodopropionic acid and 2-chloropropionic acid following the same procedure.

*1-(1-Carboxy-ethyl)-3-methyl-3*H*-imidazol-1-ium bromide [PnMIm]Br*

Viscous liquid. IR (neat, cm^{-1}) ν: 3389, 3001, 2945, 1745, 1579, 1454, 1176, 1091. ^{1}H NMR (DMSO-d_6 + $CDCl_3$) δ:

1.73 (d, J = 7.4 Hz, 3H), 3.92 (s, 3H), 5.48 (quartet, J = 7.35 Hz, 1H), 7.49 (s, 1H), 7.65 (s, 1H), 9.25 (s, 1H), 9.60 (broad, 1H). ^{13}C NMR (DMSO-d_6 + $CDCl_3$) δ: 15.8, 34.0, 55.4, 117.9, 121.4, 133.8, 168.5. HRMS calcd. for $[M + H]^+$ – Br: 156.0899; found: 155.0284. HRMS calcd. for $[M + Na]^+$ – Br: 178.0719; found: 177.0060. Anal. calcd. for $C_7H_{11}BrN_2O_2$: C 35.76, H 4.72, N 11.92; found: C 35.65, H 4.62, N 11.83.

1-(1-Carboxy-ethyl)-3-methyl-3*H*-imidazol-1-ium iodide [PnMIm]I

Viscous liquid. IR (neat, cm^{-1}) ν: 3417, 3107, 2984, 1715, 1620, 1454, 1393, 1281, 1177. ^{1}H NMR (DMSO-d_6 + $CDCl_3$) δ: 1.84 (d, J = 7.1 Hz, 3H), 3.95 (s, 3H), 5.20 (q, J = 7.42 Hz, 1H), 7.31 (s, 1H), 7.45 (s, 1H), 7.68 (s, 1H), 9.57 (broad, 1H). ^{13}C NMR (DMSO-d_6 + $CDCl_3$) δ: 16.8, 34.1, 57.7, 119.7, 120.3, 134.5, 169.8. HRMS calcd. for $[M + H]^+$ – I: 156.0899; found: 155.0193. HRMS calcd. for $[M + Na]^+$ – I: 178.0719; found: 177.0168. Anal. calcd. for $C_7H_{11}IN_2O_2$: C 29.81, H 3.93, N 9.93; found: C 29.70, H 3.81, N 9.79.

1-(1-Carboxy-ethyl)-3-methyl-3*H*-imidazol-1-ium chloride [PnMIm]Cl

Viscous liquid. IR (neat, cm^{-1}) ν: 3391, 3105, 2951, 2897, 2750, 1740, 1580, 1427, 1176. ^{1}H NMR δ: 1.78 (d, J = 7.2 Hz, 3H), 4.04 (s, 3H), 5.25 (q, J = 7.41 Hz, 1H), 7.35 (s, 1H), 7.48 (s, 1H), 8.79 (s, 1H), 10.04 (broad, 1H). ^{13}C NMR δ: 16.1, 33.5, 55.9, 121.1, 122.2, 135.9, 167.2. HRMS calcd. for $[M + H]^+$ – Cl: 156.0899; found: 155.0481. HRMS calcd. for $[M + Na]^+$ – Cl: 178.0719; found: 177.0191. Anal. calcd. for $C_7H_{11}ClN_2O_2$: C 44.10, H 5.82, N 14.70; found: C 43.93, H 5.71, N 14.56.

The bromo ionic liquid was then used for the preparation of other derivatives (X = N_3, SCN) by treatment with NaN_3 (or NaSCN) (30 mmol) in acetonitrile (5 mL) under stirring for 24 h at RT. The precipitated NaBr was filtered and the filtrate was evaporated under vacuum to give the crude product, which was washed with Et_2O (2 × 5 mL) and thoroughly dried under vacuum to furnish the pure ionic liquid characterized by spectroscopic data provided in the following sections.

1-(1-Carboxy-ethyl)-3-methyl-3*H*-imidazol-1-ium thiocyanate

Yellow viscous liquid. IR (neat, cm^{-1}) ν: 3420, 3147, 2058, 1693, 1614, 1394, 1172. ^{1}H NMR (DMSO-d_6 + $CDCl_3$) δ: 2.20 (d, J = 7.2 Hz, 3H), 4.36 (s, 3H), 5.56 (quartet, J = 7.29 Hz, 1H), 7.82 (s, 1H), 7.91 (s, 1H), 9.01 (broad, 1H), 9.12 (s, 1H). ^{13}C NMR (DMSO-d_6 + $CDCl_3$) δ: 16.8, 33.6, 57.6, 120.6, 120.9, 134.4, 170.1. HRMS calcd. for $[M + H]^+$ – SCN: 156.0899; found: 154.9482. HRMS calcd. for $[M + Na]^+$ – SCN: 178.0719; found: 176.9132. Anal. calcd. for $C_8H_{11}N_3O_2S$: C 45.06, H 5.20, N 19.70; found: C 44.95, H 5.30, N 19.58.

1-(1-Carboxy-ethyl)-3-methyl-3*H*-imidazol-1-ium azide

Colourless viscous liquid. IR (neat, cm^{-1}) ν: 3419, 3099, 2104, 1738, 1614, 1583, 1394, 1176. ^{1}H NMR δ: 2.19 (d, J = 7.0 Hz, 3H), 4.36 (s, 3H), 5.57 (quartet, J = 7.21 Hz, 1H), 7.74 (s, 1H), 7.84 (s, 1H), 7.98 (broad, 1H), 9.0 (s, 1H). ^{13}C NMR δ: 17.5, 34.9, 58.3, 120.8, 121.4, 135.2, 170.8. HRMS calcd. for $[M + H]^+ - N_3$: 156.0899; found: 155.0016. HRMS calcd. for $[M + Na]^+ - N_3$: 178.0719; found: 176.9774. Anal. calcd. for $C_7H_{11}N_5O_2$: C 42.64, H 5.62, N 35.51; found: C 42.54, H 5.51, N 35.40.

General experimental procedure for the ring opening of aziridines. Representative procedure for the ring opening of 2-hexyl-1-(toluene-4-sulfonyl)-aziridine with [PnMIm]Cl (Table 1, entry 1)

A mixture of 2-hexyl-1-(toluene-4-sulfonyl)-aziridine (281 mg, 1 mmol) and [PnMIm]Cl (225 mg, 1.3 mmol) was heated at 60 °C with stirring for 50 min (TLC). The reaction mixture was quenched with saturated brine and extracted with ether (3 × 10 mL). Evaporation of ether left the crude product, which was purified by column chromatography over silica gel (hexanes–Et_2O 50:50) to provide the pure *N*-(1-chloromethyl-heptyl)-4-methyl-benzenesulfonamide as a colourless liquid (285 mg, 90%), whose spectroscopic data (IR, ^{1}H, and ^{13}C NMR) are in good agreement with those reported (6*q*).

This procedure was followed for the nucleophilic cleavage of all aziridines listed in Table 1. The known compounds (referenced in Table 1) were identified by the comparison of their spectroscopic data with those reported. The unknown compounds (Table 1, entries 15 and 17) were properly characterized by its spectroscopic data and elemental analysis.

N-*[2-Chloro-2-(4-methoxy-phenyl)-ethyl]-4-methyl-benzenesulf onamide (Table 1, entry 15)*

Colourless viscous liquid. IR (neat, cm^{-1}) ν: 3493, 3282, 2922, 1612, 1514, 1454, 1326, 1250, 1159. ^{1}H NMR δ: 2.38 (s, 3H), 2.97–3.24 (m, 2H), 3.76 (s, 3H), 4.74 (dd, J_1 = 3.72 Hz, J_2 = 8.64 Hz, 1H), 5.10 (t, J = 4.75 Hz, 1H), 6.85 (d, J = 8.64 Hz, 2H), 7.19 (d, J = 8.64 Hz, 2H), 7.29 (d, J = 7.98 Hz, 2H), 7.72 (d, J = 8.34 Hz, 2H). ^{13}C NMR δ: 21.9, 50.6, 55.7, 72.8, 114.4 (2C), 127.5 (2C), 127.5 (2C), 130.1 (2C), 133.3, 137.1, 143.9, 159.9. Anal. calcd. for $C_{16}H_{18}ClNO_3S$: C 56.55, H 5.34, N 4.12; found: C 56.48, H 5.25, N 4.01.

N-*(2-Iodo-1-methyl-2-phenyl-ethyl)-4-methyl-benzene sulfonamide (Table 1, entry 17)*

Colourless viscous liquid. IR (neat, cm^{-1}) ν: 3500, 3273, 1596, 1450, 1326, 1161, 1091. ^{1}H NMR δ: 1.13 (d, J = 6.54 Hz, 3H), 2.42 (s, 3H), 3.57–3.64 (m, 1H), 4.93 (d, J = 8.37 Hz, 1H), 5.05 (d, J = 5.73 Hz, 1H), 7.15–7.33 (m, 7H), 7.73 (d, J = 8.16 Hz, 2H). ^{13}C NMR δ: 19.9, 21.5, 38.5, 56.1, 127.0 (2C), 128.5 (2C), 129.0, 129.3 (2C), 129.7 (2C), 139.0, 139.3, 143.6. Anal. calcd. for $C_{16}H_{18}INO_2S$: C 46.27, H 4.37, N 3.37; found: C 46.16, H 4.29, N 3.28.

General experimental procedure for the ring opening of epoxides. Representative procedure for the ring opening of 2-hexyl-oxirane by [PnMIm]N_3 (Table 2, entry 1)

A mixture of 2-hexyl-oxirane (128 mg, 1 mmol) and [PnMIm]N_3 (256 mg, 1.3 mmol) was heated at 60 °C with stirring for 45 min (TLC). The reaction mixture was quenched with saturated brine and extracted with ether (3 × 10 mL). Evaporation of ether left the crude product, which was purified by column chromatography over silica gel (hexane–Et_2O 80:20) to provide the pure 1-azido-octan-2-ol

as a colourless liquid (162 mg, 95%). The product was identified by comparison of its IR, ^{1}H, and ^{13}C NMR spectroscopic data with those previously reported (6p).

This procedure was followed for the nucleophilic cleavage of all oxiranes listed in Table 2. The products were all known compounds (referenced in Table 2) and were identified by comparison of their spectroscopic data with those reported.

Acknowledgements

This investigation has enjoyed financial support from the Council of Scientific and Industrial Research, New Delhi (CSIR) [Grant No. 01(1936)/04]. LA and SB thank CSIR for their fellowships.

References

1. (*a*) T. Welton. Chem. Rev. **99**, 2071 (1999); (*b*) P. Wasserscheid and W. Keim. Angew. Chem. Int. Ed. **39**, 3773 (2000); (*c*) J.S. Wilkes. Green. Chem. **4**, 73 (2002); (*d*) H.M. Zerth, N.M. Leonard, and R.S. Mohan. Org. Lett. **5**, 55 (2003); (*e*) A. Kumar and S.S. Pawar. J. Org. Chem. **69**, 1419 (2004); (*f*) D.-G. Gu, S.-J. Ji, Z.-Q. Jiang, M.-F. Zhou, and T.-P. Loh. Synlett, 959 (2005).
2. (*a*) J.A. Boon, J.A. Levinsky, J.I. Pflug, and J.S. Wilkes. J. Org. Chem. **51**, 480 (1986); (*b*) J.R. Harjani, S.J. Nara, and M.M. Salunkhe. Tetrahedron Lett. **43**, 1127 (2002); (*c*) V.V. Namboodiri and R.S. Varma. Chem. Commun. (Cambridge), 342 (2002); (*d*) W. Sun, C.-G. Xia, and H.-W. Wang. Tetrahedron Lett. **44**, 2409 (2003); (*e*) K. Qiao and C. Yakoyama. Chem. Lett. **33**, 472 (2004); (*f*) T. Akaiyama, A. Suzuki, and K. Fuchibe. Synlett, 1024 (2005).
3. (*a*) B.C. Ranu and S. Banerjee. J. Org. Chem. **70**, 4517 (2005); (*b*) B.C. Ranu, S. Banerjee, and R. Jana. Tetrahedron, **63**, 776 (2007) and refs. cited therein.
4. (*a*) J.E.G. Kemp. *In* Comprehensive organic synthesis. *Vol. 7. Edited by* B.M Trost and I. Fleming. Pergamon, Oxford, UK. 1991. pp. 469–513; (*b*) H.M.I. Osborn and J. Sweeney. Tetrahedron: Asymmetry, **8**, 1693 (1997); (*c*) R.S. Coleman. Synlett, 1031 (1998).
5. (*a*) R.E. Parker and N.S. Isaacs. Chem. Rev. **59**, 737 (1959); (*b*) C. Bonini and G. Righi. Synthesis, 225 (1994); (*c*) M. Shimizu, A. Yoshida, and T. Fujisawa. Synlett, 204 (1992); (*d*) J.U.G. Smith. Synthesis, 629 (1984).
6. (*a*) R.-H. Fan and X.-L. Hou. J. Org. Chem. **68**, 726 (2003); (*b*) G. Sabitha, R.S. Babu, M. Rajkumar, Ch. S. Reddy, and J.S. Yadav. Tetrahedron Lett. **42**, 3955 (2001); (*c*) G. Sabitha, R.S. Babu, M. Rajkumar, and J.S. Yadav. Org. Lett. **4**, 343 (2002); (*d*) B. Das, M. Krishnaiah, and K. Venkateswarlu. Tetrahedron Lett. **47**, 4457 (2006); (*e*) J.S. Yadav, B.V.S. Reddy, G. Parimala, and P.V. Reddy. Synthesis, 2383 (2002); (*f*) B. Das, R. Ramu, B. Ravikanth, and K.R. Reddy. Tetrahedron Lett. **47**, 779 (2006); (*g*) M.K. Ghorai, K. Das, A. Kumar, and K. Ghosh. Tetrahedron Lett. **46**, 4103 (2005); (*h*) J.S. Yadav, B.V.S. Reddy, B. Jyothirmai, and M.S.R. Murty. Tetrahedron Lett. **46**, 6385 (2005); (*i*) M.S. Reddy, M. Narender, Y.V.D. Nageswar, and K.R. Rao. Tetrahedron Lett. **46**, 6437 2005); (*j*) M. Narender, K. Surendra, N.S. Krishnaveni, M.S. Reddy, and K.R. Rao. Tetrahedron Lett. **45**, 7995 (2004); (*k*) J. Wu, X.-L. Hou, and L.-X. Dai. J. Org. Chem. **65**, 1344 (2000); (*l*) M. Chandrasekhar, G. Sekar, and V.K. Singh. Tetrahedron Lett. **41**, 10079 (2000); (*m*) J.S. Yadav, B.V.S. Reddy, and G.M. Kumar. Synlett, 1417 (2001); (*n*) S. Minakata, D. Kano, Y. Oderaotoshi, and M. Komatsu. Angew. Chem. Int. Ed. **43**, 79 (2004); (*o*) H. Konno, E. Toshiro, and N. Hinoda. Synthesis, 2161 (2003); (*p*) J.S. Yadav, B.V.S. Reddy, B. Jyothirmai, and M.S.R. Murty. Tetrahedron Lett. **46**, 6559 (2005); (*q*) M.K. Pandey, A. Bisai, and V.K. Singh. Tetrahedron Lett. **45**, 9661 (2004); (*r*) N. Iranpoor, H. Firouzabadi, and M. Shekarize. Org. Biomol. Chem. **1**, 724 (2003); (*s*) J. Kroutil and K. Jenistova. Collect. Czech. Chem. Commun. **70**, 2075 (2005); (*t*) J. Kroutil and M. Budesinsky. Carbohydr. Res. **342**, 147 (2007).
7. (*a*) J. Schubert, R. Schwesinger, and H. Prinzbach. Angew. Chem. Int. Ed. Engl. **23**, 167 (1984); (*b*) G.A. Jacobs, J.A. Tino, and R. Zahler. Tetrahedron Lett. **30**, 6955 (1989); (*c*) E.F.V. Scriven and K. Turnbull. Chem. Rev. **88**, 297 (1988).
8. (*a*) M.T. Reets, R. Jaeger, R. Drewlies, and M. Hubel. Angew. Chem. Int. Ed. Engl. **30**, 103 (1991); (*b*) D. Lucet, T. Le Gall, and C. Mioskowski. Angew. Chem. Int. Ed. **37**, 2850 (1998).
9. G.D.K. Kumar and S. Baskaran. Synlett, 1719 (2004).
10. J. Wu, X. Sun, and H.-G. Xia. Eur. J. Org. Chem. 4769 (2005).
11. V.V. Thakur, S.K. Talluri, and A. Sudalai. Org. Lett. **5**, 861 (2003).
12. H. Sharghi, M.A. Nasseri, and K. Niknam. J. Org. Chem. **66**, 7287 (2001).
13. G.D.K. Kumar and S. Baskaran. J. Org. Chem. **70**, 4520 (2005).
14. M. Mizuno and T. Shioiri. Tetrahedron Lett. **40**, 7105 (1999).