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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

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To cite this article: Brindaban C. Ranu , Subhash Banerjee & Jhinuk Gupta (2007) Ionic Liquid-Promoted Stereoselective Synthesis of (Z)-Vinyl Bromides by [bmlm]OH under Organic Solvent-Free Conditions: A Green Approach, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 37:17, 2869-2876, DOI: <u>10.1080/00397910701471386</u>

To link to this article: http://dx.doi.org/10.1080/00397910701471386

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Synthetic Communications[®], 37: 2869–2876, 2007 Copyright © Taylor & Francis Group, LLC ISSN 0039-7911 print/1532-2432 online DOI: 10.1080/00397910701471386



Ionic Liquid–Promoted Stereoselective Synthesis of (Z)-Vinyl Bromides by [bmIm]OH under Organic Solvent–Free Conditions: A Green Approach

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Abstract: A simple and easily accessible ionic liquid, 1-butyl-3-methylimidazolium hydroxide ([bmIm]OH), has been demonstrated as an efficient promoter and reaction medium for the highly stereoselective synthesis of (*Z*)-vinyl bromides by the debrominative decraboxylation of dibrominated α , β -unsaturated carboxylic acids in high yields. The reaction does not require either a conventional base or an organic solvent.

Keywords: debrominative decarboxylation, green synthesis, ionic liquid, (*Z*)-vinyl bromides

INTRODUCTION

The vinyl bromides are very useful intermediates in organic synthesis, and thus development of procedures for their stereoselective synthesis is important. One of the classical methods involves Wittig olefination of an aldehyde with bromomethylene triphenylphosphorane,^[1] leading to primarily (*Z*)-vinyl bromides. However, this procedure is not very convenient as it entails a large amount of triphenyl phosphine oxides as waste, and in addition, preparation of the ylide is rather complicated. Thus, several methods have been developed for this transformation.^[2] The most common

Received in the USA January 19, 2007

Address correspondence to Brindaban C. Ranu, Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India. E-mail: ocbcr@iacs.res.in methods include metal-halogen exchange of metalloalkenes,^[2a] hydroboration of haloalkynes,^[2b] reduction of *gem*-dibromides,^[2c,2f] and debrominative decarboxylation of dibrominated α,β -unsaturated carboxylic acids using a variety of bases in different organic solvents.^[2g] However, several of these methods produce a mixture of (*E*)- and (*Z*)- bromoalkenes, and isolation of one pure isomer is often very tedious. Thus, development of a simpler highly stereoselective method in an environment-friendly reaction condition is appreciated.

During past few years we have been actively engaged in exploring ionic liquids^[3] as effective catalysts and regents for useful chemical transformations in organic solvent free conditions.^[4] As a part of this activity, we recently introduced a task-specific ionic liquid [bmIm]OH for Michael addition^[4h] and Knoevenagel condensation^[41] and report here another novel application of this ionic liquid for debrominative decarboxylation of dibrominated α , β -unsaturated carboxylic acid to (*Z*)-vinyl bromides (Scheme 1).

RESULTS AND DISCUSSION

The experimental procedure is very simple. A mixture of 2,3-dibromoalkanoic acid and [bmIm]OH was stirred at room temperature for a certain period of time (monitored by thin-layer chromatography, TLC). The product was then isolated by direct distillation from the reaction vessel under vacuum. The product obtained was of high purity, and no further purification was necessary.

A variety of 2,3-dibromoalkanoic acids underwent debrominative decarboxylations to produce the corresponding (Z)-alkenyl bromides in high yields. The results are summarized in Table 1. Both aromatic and aliphatic dibromoalkanoic acids were responsive to this reaction. The aromatic substrates bearing electron-withdrawing as well as electron-donating groups underwent reactions without any difficulty. As (Z) alkenyl bromides were produced in very high proportion from all substrates except p methoxy-substituted cinnamic acid dibromide where a (3:1) mixture of (Z)- and (E)- alkenyl bromides were obtained (entry 4), it is speculated that most of the reactions proceed via *trans-* β -elimination followed by simultaneous loss of CO₂ and Br ions to give (Z)-alkenyl bromide (Scheme 2). However, in the case of p-methoxy-substituted substrate, an unimolecular elimination process may



Scheme 1.

Entry	R	Product(s)	Time (h)	Yield $(\%)^a$	(Z/E) ratio ^b	Ref.
1		Br	1.0	90	100/0	2g
2	CI	CI	1.5	88	99/1	2g
3		Br	1.5	90	100/0	
4	Br	Br MeO Br	2.0	85	75/25	2g
5		Br	1.5	82	99/1	_

Table 1. Synthesis of (*Z*)-vinyl btomides by [bmlm]OH

₿r



Stereoselective Synthesis of (Z)-Vinyl Bromides

Table 1.	Continued
	001101000

Entry	R	Product(s)	Time (h)	Yield $(\%)^a$	(Z/E) ratio ^b	Ref.
6		Br	1.5	86	98/2	2g
7	Me	Br	1.5	88	97/3	2g
8		Br	2.0	85	98/2	2g
9	$O_2 N^{-1}$	D ₂ N Br	1.5	80	99/1	2g
10	C ₇ H ₁₅	C ₇ H ₁₅ Br	1.0	85	100/0	2g

^{*a*}Yields refer to those of pure isolated products characterized by spectroscopic (IR, ¹H NMR, and ¹³C NMR) data. ^{*b*}The ratio was determined by ¹H NMR.



be involved to give relatively stable carbocations, followed by elimination of CO_2 to give a mixture of (*Z*)- and (*E*)-isomers (Scheme 3).

In general, the reactions are very clean and reasonably fast. The reaction conditions are mild to tolerate a variety of functional groups such as Cl, Br, OMe, NO₂, and OCH₂O- present in the substrates. The (*Z*)-isomers were easily identified from the coupling constant (J = 7.9-8.4 Hz) in ¹H NMR spectra of these compounds. The ionic liquid works here as promoter as well as reaction medium, and thus no additives or organic solvents are required.

CONCLUSION

In conclusion, the present procedure using an easily accessible basic ionic liquid, [bmIm]OH,^[4h] as an effective promoter, and reaction medium provides an efficient methodology for the synthesis of (*Z*)-vinyl bromides. The significant advantages offered by this method are a) operational simplicity, b) remarkable stereoselectivity, and c) environmentally friendly procedure that avoids toxic catalyst and hazardous organic solvent. We are not aware of any such use of ionic liquid for the debrominative decarboxylation reaction. Moreover, this procedure demonstrates the potential of ionic liquids and provides great promise for further useful applications in organic synthesis.

EXPERIMENTAL

General

¹H NMR spectra were recorded at 300 MHz in $CDCl_3$ solutions with trimethylsilane as internal standard. ¹³C NMR spectra were run at 75 MHz in $CDCl_3$ solutions. IR spectra were taken as neat for liquids and as KBr pellets for solids on a Shimadzu FT-8300 spectrometer. Elemental analyses were done by a Perkin-Elmer autoanalyzer. Column chromatography was performed on silica gel (60–120 mesh, SRL, India).

General Procedure for the Debrominative Decarboxylation of Dibrominated α , β -Unsaturated Carboxylic acids: Preparation of (Z)- β -Bromostyrene (Entry 1, Table 1)

A mixture of *anti*-3-phenyl-2,3-dibromopropionic acid (915 mg, 3 mmol) and [bmIm]OH (312 mg, 2 mmol) was stirred for 1 h at room temperature until completion of the reaction (TLC). The product was then directly distilled from the reaction vessel under vacuum to provide a colorless liquid (516 mg, 90%), which was identified as (*Z*) β -bromostyrene because its spectroscopic data (IR, ¹H NMR, and ¹³C NMR) are in good agreement with those reported.^[2g] This procedure is followed for all reactions listed in Table 1. Most of the products are known compounds except two (entries 3 and 5). The known compounds were easily identified by comparison of their spectroscopic data with the reported values.^[2g] The unknown compounds were characterized by their spectroscopic data and elemental analysis.

Data

1-Bromo-3-(2-bromovinyl)benzene (Entry 3, Table 1)

Colorless oil; IR (neat): 1640, 1450, 960 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.48 (d, J = 8.1 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 7.17–7.23 (m, 1H), 7.43–7.46 (m, 1H), 7.58–7.62 (m, 1H), 7.81 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 107.8, 122.1, 127.4, 129.6, 130.9, 131.1, 136.7. Anal. calcd. for C₈H₆Br₂: C, 36.68; H, 2.31. Found: C, 36.45; H, 2.10.

1-(2-Bromovinyl)-3-methoxybenzene (Entry 5, Table 1)

Colorless liquid; IR (neat): 1645, 1451, 940 cm⁻¹; ¹H NMR δ 3.82 (s, 3H), 6.57 (d, J = 8.4 Hz, 1H), 6.75–6.79 (m, 2H), 7.18 (d, J = 8.4 Hz, 1H), 7.37–7.38 (m, 1H), 7.46–7.49 (m, 1H); ¹³C NMR δ 55.1, 106.4, 114.2,

Stereoselective Synthesis of (Z)-Vinyl Bromides

121.5, 129.1, 132.1, 136.0, 159.2. Anal. calcd. for C₉H₉BrO: C, 50.73, H, 4.26. Found: C, 50.54; H, 4.05.

If the reaction was carried out in a smaller scale (<1 mmol) or a solid product was formed, the product can be isolated by extraction with ethyl acetate followed by purification over column chromatography.

ACKNOWLEDGMENTS

This investigation has enjoyed financial support from Council of Scientific and Industrial Research (CSIR), New Delhi [Grant No. 01(1936)/04]. S. B. also thanks CSIR for this fellowship.

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