JOC*Note*

Catalysis by Ionic Liquid. A Green Protocol for the Stereoselective Debromination of *vicinal*-Dibromides by [pmIm]BF_4 under Microwave Irradiation

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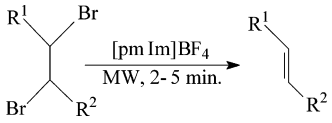
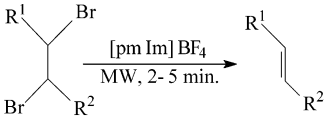


An easily accessible ionic liquid, 1-methyl-3-pentylimidazolium fluoroborate, [pmIm]BF_4, has been demonstrated to be an efficient catalyst as well as reaction medium for the stereoselective debromination of a variety of structurally diverse *vicinal*-dibromides to the corresponding (*E*)-alkenes in high yields under microwave irradiation. This reaction does not require any organic solvent and any metal or any conventional reducing agent, and the ionic liquid is recycled without any appreciable loss of its catalytic efficiency.

Since the introduction of ionic liquids in organic synthesis, these compounds have attracted increasing interest in the context of green chemistry because of their great potential as environmentally benign media.[1] Now they have crossed the barrier of solvent and entered very successfully into the area of catalysis.[2] Although one of the first successful uses of an ionic liquid, namely dialkylimidazolium chloroaluminate, as a catalyst in Friedel−Crafts acylation was reported in 1986,[2a] the moisture sensitivity and decomposition of this chloroaluminate salt under normal atmospheric conditions has led to the development of a second generation of more stable and user-friendly ionic liquids by replacement of chloroaluminate with anionic species such as tetrafluoroborate and hexafluorophosphate. As a part of our continuing program to explore novel uses of ionic liquids as catalysts as well as reaction media for useful transformations[3] avoiding hazardous organic solvents and toxic catalysts, we report here the application of an acidic, inexpensive, and easily accessible ionic liquid, [pmIm]BF_4, for stereoselective debromination of *vic*-dibromides to the corresponding (*E*)-alkenes (Scheme 1).

SCHEME 1. Debromination of *vic*-Dibromides



R^1, R^2 = alkyl, aryl, CN, CO_2Me, CO_2Et, COPh, NO_2

Usually the debromination reaction is carried out using a metal such as Sm,[4a] In,[4b] Mg,[4c] or Zn[4d] in a refluxing organic solvent such as THF and MeOH. Several other reducing agents (e.g., sodium borohydride,[5a] sodium sulfide with phase transfer agent,[5b,c] sodium naphthalenide,[5d] and dichloroindium hydride[5e]) have also been used for the reductive debromination. Thus, our approach using a nonreducing reagent such as an ionic liquid [pmIm]-BF_4 is novel.

The experimental procedure is very simple. A mixture of *vic*-dibromide and [pmIm]BF_4 was heated by microwave irradiation for 2−5 min (TLC) in a domestic microwave oven. The product was isolated by extraction with ether followed by purification through column chromatography.

A wide range of structurally varied *vic*-dibromides underwent debrominations by this procedure to provide the corresponding alkenes. The results are summarized in Table 1. Very significantly, only trans olefins are obtained from all the open chain substrates irrespective of whether the dibromides are meso/erythro or dl/threo. Thus, a (*Z*)-alkene such as diethyl maleate or *cis*-methyl cinnamate is easily converted to the corresponding (*E*)-isomer diethyl furmarate or *trans*-methyl cinnamate through their dibromides (entries 3 and 10). This procedure is equally effective for both aryl- or alkyl-substituted

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TABLE 1. Stereoselective Debromination of *vic*-Dibromides Catalyzed by [pmIm]BF_4

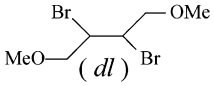
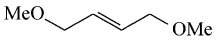
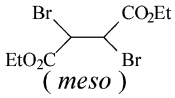
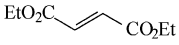
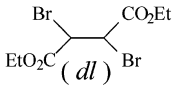
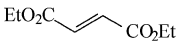
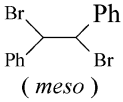
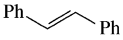
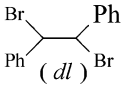
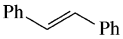
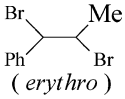
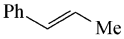
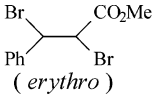
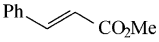
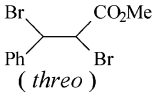
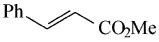
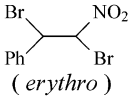
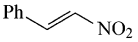
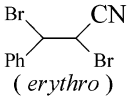
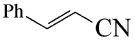
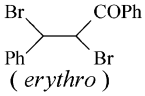
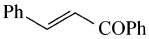
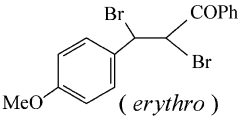
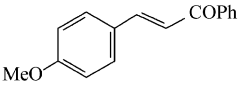
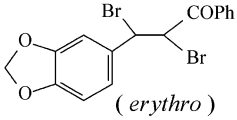
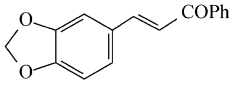
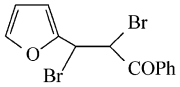
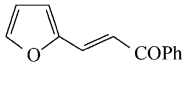
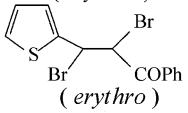
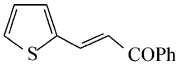
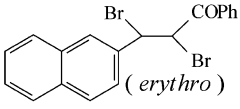
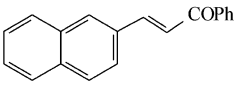
entry	substrate	time(min)	product	yield(%)[a]	ref.
1	 (*dl*)	5		72	5e
2	 (*meso*)	3		92	5e
3	 (*dl*)	5		82	5e
4	1,2-dibromocyclooctane (*trans*)	5	cyclooctene	65	6
5	1,2-dibromocycloheptane (*trans*)	5	cycloheptene	62	6
6	 (*meso*)	2		89	4b
7	 (*dl*)	5		75	4b
8	 (*erythro*)	3		85	4b
9	 (*erythro*)	2		95	4b
10	 (*threo*)	4		85	4b
11	 (*erythro*)	3		89	6
12	 (*erythro*)	3		91	5e
13	 (*erythro*)	2		92	4b
14	 (*erythro*)	2·5		94	3d
15	 (*erythro*)	2·5		90	7
16	 (*erythro*)	2		82	8
17	 (*erythro*)	2		85	9
18	 (*erythro*)	2		92	4b

Table 1. (Continued)

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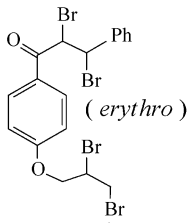
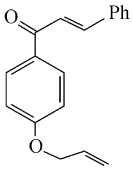
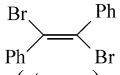
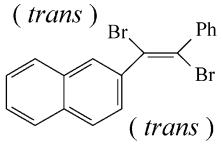
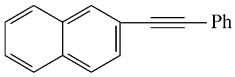
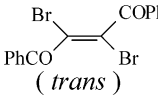
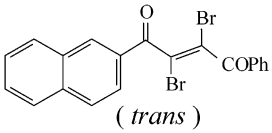
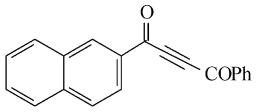
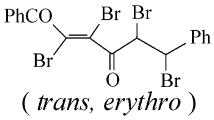
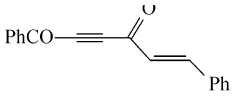
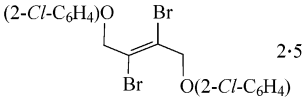
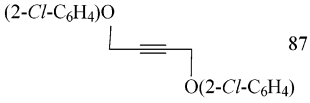
19	 (*erythro*)	3		72	10
20	 (*trans*)	3·5		92	4b
21	 (*trans*)	3		90	4b
22	 (*trans*)	2		89	11
23	 (*trans*)	2·5		92	12
24	 (*trans, erythro*)	2·5		85	13
25	 (*trans*)	2·5		87	14

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

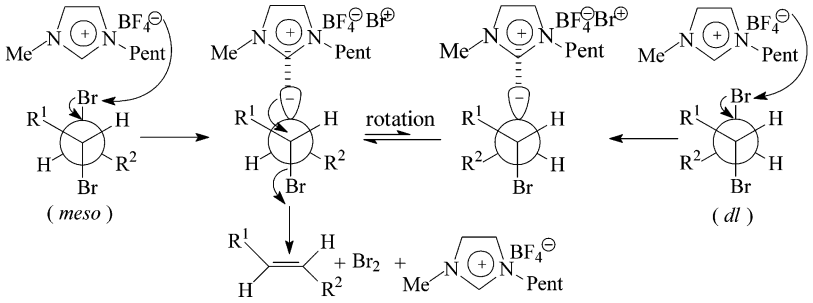
dibromides. The cyclic dibromides also underwent debrominations by this reagent. The sensitive molecules such as furan and thiophene derivatives are acceptable under the reaction conditions (entries 16 and 17). Several structurally diverse *vic*-dibromoalkenes were also subjected to this procedure to provide the corresponding alkynes (entries 20−25). The formation of one C=C and one C≡C bond in one stroke is successfully achieved from the corresponding tetrabromide substrate (entry 24) under the present reaction conditions.

It has been observed that this reaction does not proceed at all at room temperature or under conventional heating (90 °C for 12 h). Without ionic liquid also the reaction does not proceed by microwave irradiation only. The other ionic liquid, [pmIm]Br, is also not very successful in catalyzing the reaction effectively. Thus, this particular ionic liquid, [pmIm]BF_4, plays a vital role in catalyzing this reaction under microwave irradiation. It has been observed that, with the progress of the reaction bromine, gas that has been trapped by cyclooctene in CCl_4 is liberated. The 1,2-dibromocyclooctane has subsequently been isolated and characterized. Thus, it may be speculated that the reaction proceeds through an ionic mechanism as outlined in Scheme 2. The ionic liquid remained intact (^{1}H NMR) and was used for subsequent runs without any difficulty. This also supports the depicted mechanism. Regarding formation of (*E*)-alkenes from all acyclic substrates, it may be assumed that the anion formed from the *dl/threo*-dibromides underwent rapid inversions to the thermodynamically more stable one leading to trans products. This hypothesis gained support when it was observed that the formation of cis product was not detected at any stage of the debromination reaction. The cis alkene also remained unchanged when treated under similar reaction conditions, indicating no isomerization of pure cis alkenes during the reaction.

In general, debrominations by this procedure are very clean, high-yielding, and very fast. This reaction is also very general, being applicable to aryl- as well as alkyl-substituted dibromides. There is no chance of over reduction of the C=C and C≡C bonds formed in this process, unlike in procedures using metals such as Sm[4a] and Mg.[4c]

In conclusion, this procedure using an ionic liquid demonstrates a novel and efficient protocol for debromination of *vicinal* dibromides to (*E*)-alkenes and alkynes. To the best of our knowledge, we are not aware of any such use of ionic liquid. The significant advantages

SCHEME 2. Plausible Mechanism for Stereoselective Debromination



offered by this method are operational simplicity, very fast reaction, high yields of products, excellent stereoselectivity, general applicability to a wide variety of substrates, no over reduction of C=C and C≡C bonds, greenness of procedure by avoiding toxic catalysts and hazardous organic solvent during the reaction, and recyclability of the catalyst. Thus, it provides a better and practical alternative to the existing procedures[4,5] and provides great promise toward further useful applications.

Experimental Section

General Experimental Procedure for the Debromination of *vicinal* Dibromides to (*E*)-Alkenes. Representative Procedure for Debromination of *erythro*-1-Benzoyl-2-Phenyl-1,2-Dibromoethane (Entry 13). A mixture of *erythro*-1-benzoyl-2-phenyl-1,2-dibromoethane (368 mg, 1 mmol) and [pmIm]BF_4 (400 mg, 1.6 mmol) was subjected to heating by microwave irradiation (20% power, 240 W, 130−135 °C as measured by a thermometer placed inside) in a domestic microwave oven (manufactured by BPL, India) for 2 min (TLC). The reaction mixture was allowed to cool and extracted with ether (3 × 5 mL). The ether extract was washed with brine and dried (Na_2SO_4). Evaporation of solvent left the crude product, which was purified by column chromatography to provide the pure product, *trans*-1-benzoyl-2-phenylethene (191 mg, 92%), mp 56 °C; IR(KBr) 1664, 1606, 1573, 1448, 1336 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.01−8.04 (m, 2H), 7.82 (d, J = 15.6 Hz, 1H), 7.63−7.66 (m, 2H), 7.50−7.59 (m, 4H), 7.41−7.43 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 144.9, 138.2, 134.8, 132.8, 130.5, 129.0 (2C), 128.6 (2C), 128.5 (2C), 128.4 (2C), 122.0. These values were in good agreement with the reported ones.[4b]

This procedure was followed for all the reactions listed in Table 1. The products obtained were all known compounds and were identified by comparison of their spectroscopic data (IR, ^1H and ^{13}C NMR) with those reported (references in Table 1).

The ionic liquid remaining in the flask was rinsed with ether and dried under vacuum at 80 °C to be used for subsequent reactions. This can be used for reactions up to five runs without any appreciable loss of efficiency. After five runs, about 50% fresh ionic liquid was added to it, and the mixture was found to be good for several reactions.

Although the representative procedure is based on a milligram scale, it has been scaled up to multigram level without any difficulty.

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Supporting Information Available: Spectroscopic (IR, ^1H and ^{13}C NMR) data of products listed in entries 14−25 and ^{13}C NMR spectra of all the products listed in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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