Bromination of carbon–carbon double bonds involving oxidation of NaBr in an ionic liquid

Taokei Ying[b], Weiliang Bao[a]* and Yongmin Zhang[a]

[a]Zhejiang University, Xixi Campus, Department of Chemistry, Hangzhou, Zhejiang 310028, P. R. China

[b]Zhejiang Normal University, College of Chemistry and life Science, Jinghua, Zhejiang 321004, P. R. China

Bromination of alkenes has been conducted in a room temperature ionic liquid {[bmim]$^+$ CCl_3COO^- (1–butyl–3–methylimidazolium trichloroacetate)} involving the oxidation of NaBr by hydrogen peroxide with no catalyst. Comparatively fast reactions, good yields and the atom economic nature make this environmentally benign reaction an appealing procedure for alkene and alkyne bromination.

Keywords: Bromination of alkenes, ionic liquid, NaBr

The development of practical processes, reaction media, conditions and/or utility of materials based on the ideas of green chemistry is one of the most challenging issues for chemical research.[1]

Conventional halogenation methods[2] typically use elemental halogens (X_2), which are pollutants, dangerous and generate hazardous HX as byproducts. Recently, the oxidative halogenation of olefins by metal halides has emerged as an important alternative for the synthesis of such halo derivatives.[3] Usually H_2O_2 is used as a green oxidising agent, because it is environmentally friendly, yielding water and oxygen upon decomposition. However, although thermodynamically powerful, H_2O_2 is kinetically a slow oxidant for the halide salts,[4] and halogenations must typically be catalysed for halogenation reactions to occur on a useful time scale[5]. There are other drawbacks such as poor yields and selectivity.

Room temperature ionic liquids (RTILs) are the subject of current interest as novel reaction media. This is mainly due to their unique physical properties, which makes them attractive solvents and catalysts for organic synthesis and organometallic catalysis as well as for biotransformations. Many organic reactions have been carried out in ionic liquids and usually good results have been found, such as improved selectivity, shortened reaction times, and raised yields. Examples are Friedel–Crafts reactions,[6] Diels–Alder reactions,[7] Heck reactions,[8] and Beckmann rearrangements.[9]

In conducting other room temperature ionic liquid mediated reactions we found that hydrogen peroxide would oxidise the bromide anion rapidly [See caution in Experimental section]. As a test we carried out a bromination of a carbon–carbon double bond involving oxidation of NaBr with H_2O_2 in a room temperature ionic liquid. We used [bmim]$^+$ CCl_3COO^- (1–butyl 3–methylimidazolium trichloroacetate) as the reaction medium. The procedure is simple. When NaBr, alkene and H_2O_2 were mixed in the RTIL, H_2SO_4 (60%) was introduced via a small tube slowly at room temperature. The dropping speed should be controlled so that just a very light red–brown bromine colour appears or no colour appears at all in the reaction mixture. When the bromine's colour does not disappear the reaction has ended. No bromine vapour or hydrogen bromide gas escaped in the entire reaction course. The results are summarised in the Table 1.

From Table 1 we can see that all the representative alkenes including isolated and electron–deficient carbon–carbon double bonds give satisfactory yields. The reaction proceeds quickly even with no special catalyst present compared with

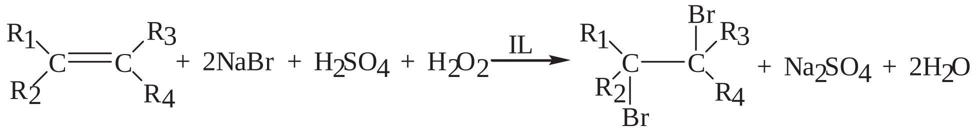
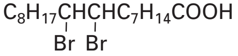
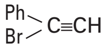
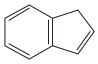
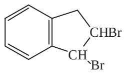
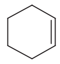
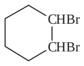


Table 1 Products and yields

Entry[a]	Substrate	Product	Time /h	Yield %[b]	*Trans*/ *cis*
1	$C_6H_5CH{=}CH_2$	$C_6H_5CHBrCH_2Br$	1	95	
2	*p*-$CH_3OC_6H_4CH{=}CH_2$	*p*-$CH_3OC_6H_4CHBrCH_2Br$	2	80	
3	$C_6H_5CH{=}CHCOCH3$	$C_6H_5CHBrCHBrCOCH_3$	4	88	99:1
4	*p*-Br-$C_6H_4CH{=}CHCOC_6H_5$	*p*-$BrC_6H_4CHBrCHBrCOC_6H_5$	8	82	99:1
5	$C_6H_5CH{=}CHCO_2CH_3$	$C_6H_5CHBrCHBrCO_2CH_3$	6	86	99:1
6	$C_{12}H_{25}CH{=}CH_2$	$C_{12}H_{25}CHBrCH_2Br$	8	90	
7	$C_8H_{17}CH{=}CHC_7H_{14}COOH$	 $C_8H_{17}\underset{Br}{C}H\underset{Br}{C}HC_7H_{14}COOH$	8	85	99:1
8	$C_6H_5C{\equiv}CH$	 $\begin{matrix}Ph\\Br\end{matrix}>C{\equiv}CH$	4	85	80/20
9			2	80	99:1
10			2.5	70	99:1

[a]Reactions were carried out at room temperature
[b]Isolated yield.

---

* Correspondence. E-mail: wbao@hzcnc.com

some reports (for example, in the absence of a catalyst, the half–life of bromination of 4–pentenoic acid with 1.0M NaBr and 1.0 M H_2O_2 in a two–phase mixture of ether and pH=6 phosphate buffer was >72h at 296 K.[5] Bromination of 4–penten–1–ol to get 4,5–dibromopentan–1–ol via benzeneseleninic acid catalysis needs 24h). Another characteristic of the reaction is the stereochemistry. The stereochemistry of the addition is good. For non–terminal alkenes the erythro–threo ratios (*trans*–*cis* addition products) are larger than 99:1 at 10–20°C (from GC–MS and/or NMR); but fall to 5:1 at 40 °C for 3,4–dibromo–4– phenyl–butan–2–one and at 65:35 at 60 °C. In fact, the selectivities observed from this reaction are almost the same as with conventional bromination with elemental bromine.[14] For phenylacetylene 1,2–dibromo–1–phenyl ethylene is the main product (*trans*/*cis* ratio: 80/20, total yield: 85%) even when 4 mole of NaBr was added (1,1,2,2–tetrabromo–1–phenyl ethane yield: <10%).

Another merit of this reaction lies in the recycling of the solvent. Ionic liquids could be almost quantitatively recovered and the recovering procedure is simple. After the product was extracted with ether and the inorganic salts were filtered off, the filtrate was recovered ionic liquid which was treated as described in the Experimental section and can be reused. Other RTILs such as $[bmim]^+$ CF_3COO^- and $[emim][BF_4]^-$ (1–ethyl–3–methylimidazolium tetrafluoroborate) can be used as the medium. When $[emim][BF_4]^-$ is used a methoxy group on a benzene ring will be cleaved.

In conclusion alkene bromination in RTILs involving oxidation of NaBr with H_2O_2 is a procedure with the merits of comparatively rapid reaction, good yields, and atom economy, and is environmentally benign.

Experimental

Reactions were carried out in a 25ml flask equipped with a magnetic stirrer bar with no special precaution in the fume cupboard. All products were characterised by NMR and IR. Melting points are in good agreement with literature data.

CAUTION: As the method involved only 30% H_2O_2 on a small scale and there was no heat or impact involved no danger of explosion was anticipated. However, experiments were conducted in a fume cupboard with safe glass.

Typical procedure The reaction is conducted as follows. To $[bmim]^+$ CCl_3COO^- (1–butyl 3–methyl imidazolium trichloroacetate) ionic liquid (3 ml), NaBr (0.42 g, 4 mmol), alkene (styrene, 0.208 g, 2 mmol) and H_2O_2 (30%, ~0.23 ml) were added. Then H_2SO_4 (60%, ~0.3ml) was introduced via a small tube slowly at room temperature. The dropping speed should be controlled so that just a very light red–brown bromine colour appears or no colour appears at all in the reaction mixture. When the bromine colour does not disappear the reaction has ended. The reaction mixture was extracted with ether (3×10ml). The ether layer was separated. The lower ionic liquid phase can be treated with a little $Na_2S_2O_3$ or $FeSO_4$ to decompose the excess of H_2O_2 and vacuum distillation on a rotatory evaporator to remove the water. The inorganic salts can be filtered off. The resulting ionic liquid can be washed with acetone and then be used again. The product was further purified by column chromatography (10:1, petroleum ether/ethyl acetate), yield: 0.45g (85%).

1,2-Dibromo-1-phenylethane: m.p. 74–75°C (lit.[3a] 74–76°C); ^{1}H NMR: 8.09 (d, 2H, J = 8.0Hz), 7.65 (t, 1H, J = 7.0Hz), 7.54–7.50(m,2H), 6.80 (d, 0.13H, J = 1.2Hz), 6.75 (d, 0.87H, J = 1.2Hz). IR: 3029, 1631, 1493, 1454, 1432, 1232, 1155, 907 cm^{-1}.

1,2-Dibromo-1-(4′-methoxyphenyl)ethane: m.p. 79–80°C (lit.[10] 80–81°C); ^{1}H NMR: 7.23 (d, 2H, J = 8.4Hz); 6.85 (d, 2H, J = 8.4Hz); 4.79 (dd, 1H, J = 4.0Hz, 8.0Hz); 3.75 (s, 3H); 3.53–3.44 (m, 2H); IR: 3002, 2959, 2836, 1610, 1513, 1462, 1441, 1249, 833cm^{-1}.

3,4-Dibromo-4-phenylbutan-2-one: m.p. 118–120°C (lit.[3a] 118–120°C); ^{1}H NMR: 7.41–7.35(m, 5H), 5.31 (d, 1H, J=11.6H), 4.93 (d, 1H, J=11.6Hz), 2.48 (s, 3H); IR: 3060, 3002, 2991, 1722, 1631, 1492, 1454, 1359, 1207, 1140 cm^{-1}.

1-Benzoyl-1,2-dibromo-2-(4-bromophenyl)ethane: m.p. 175–179°C (lit.[13] 179.5°C); ^{1}H NMR: 8.02–7.98 (m, 2H); 7.59–7.56 (m, 2H); 7.48–7.19 (m, 5H); 5.43 (s, 2H); IR: 3054, 3011, 1684, 1594, 1474, 1264, 891, 796 cm^{-1}. $C_{10}H_9Br_3O$ requires: C, 31.21; H, 2.36%. Found: C, 31.40; H, 2.33%.

Methyl 2,3-Dibromo-3-phenylpropanoate: m.p. 112–114°C(lit.[3a] 114–116°C); ^{1}H NMR: 7.39–7.35 (m, 5H); 5.33 (d, 1H, J = 12.0Hz); 4.82 (d, 1H, J = 12.0Hz); 3.90 (s, 3H); IR: 3063, 3003, 2939, 1734, 1498, 1453, 1277, 1236, 1149, 844 cm^{-1}.

1,2-Dibromotetradecane: m.p.: 0°C (lit.[11] 0°C); ^{1}H NMR: 4.18–4.13 (m, 1H); 3.84 (dd, 1H, J = 4.2Hz, 10.2Hz); 3.62 (t, 1H, J = 10.2Hz); 2.16–2.10 (m, 1H); 1.81–1.73 (m, 1H); 1.57–1.55 (m, 1H); 1.43–1.39 (m, 1H); 1.268 (m, 18H); 0.87 (t, 3H, J = 6.4Hz); IR: 2959, 2837, 1610, 1513, 1462, 1441, 1250, 834 cm^{-1}.

9,10-Dibromooctadecanoic acid: m.p. 27–29°C(lit.[12] 28.5–29.5°C); ^{1}H NMR: 4.22–4.19 (m, 2H); 2.35–2.31 (m, 2H); 2.03–1.94 (m, 2H); 1.85–1.79 (m, 2H); 1.61–1.57 (m, 2H); 1.39–1.19 (m, 18H); 0.86 (t, 3H, J = 6.8Hz); IR: 2927, 2855, 1710, 1461, 1413, 1282, 933 cm^{-1}.

trans-1,2-Dibromo-1-phenylethlene: pale yellow oil[3d]; ^{1}H NMR: 8.10–8.07 (m, 2H), 7.67–7.63 (m, 1H), 7.53–7.50 (m, 2H), 6.70 (s, 1H); *cis*–1,2–Dibromo–1–phenylethlene: 7.49–7.44 (m, 2H); 7.36–7.30 (m, 2H); 7.00 (s, 1H).

1,2-Dibromoindane: m.p. 31–32°C(lit.[10] 32°C); ^{1}H NMR: 7.44 (d, 1H, J = 7.2Hz); 7.32–7.26 (m, 3H); 5.462 (s, 1H); 4.66–4.65 (m, 1H); 3.77 (dd, 1H, J = 5.8Hz, 16.8Hz); 3.26 (d, 1H, J = 16.8Hz); IR: 3040, 2960, 2849, 1608, 1463, 1439, 1345, 1192, 1066, 850cm^{-1}.

1,2-Dibromocyclohexane:[3a] viscous oil; ^{1}H NMR: 4.46 (s, 2H, br); 2.46–2.43 (m, 2H); 1.91–1.79 (m, 4H); 1.53–1.51 (m, 2H); 2925, 2854, 1462, 1375, 1145, 897cm^{-1}.

Received 18 May 2004; accepted 22 October 2004
Paper 04/2534

References

1 P. Tundo and P.T. Anastas, *Green Chemistry: Challenging Perspectives*, Oxford Science, Oxford, 1999.

2 (a) *Comprehensive Organic Transformation*: *A Guide to Functional Group Preparation*, 2nd ed.; R.C. Larock, Ed.; Wiley-VCH: New York, 1999; pp. 629–640; (b) B. Damin, J. Garapon and B. Silion, *Synthesis* 1981, 362; (c) J.H. Rolston and K. Yates, *J. Am. Chem. Soc*. 1969, **91**, 1469; (d) D.R. Dalton, V.P. Dutta and D.C. Jones, *J. Am. Chem. Soc.*, 1968, **90**, 5498.

3 (a) N. Vijay, B.P. Sreeletha, A. Anu, G.G. Tesmot, T. Siji and M. Vairamani, *Tetrahedron*, 2001, **57**, 7417; (b) G.W. Kabalka, K. Yang, N.K. Reddy and C. Narayan, *Synth. Commun.*, 1998, **28**, 925; (c) R.K. Dieter, L.E. Nice and E.V. Sadanandan, *Tetrahedron Lett*., 1996, **37**, 2377; (d) N.B. Barhate, A.S. Gajare, R.D. Wakharkar and A.V. Bedekar, *Tetrahedron*, 1999, **55**, 11127.

4 (a) A. Leulier, *Bull. Soc. Chim. Fr.* 1924, **35**, 1325; (b) A. Mohammed and H.A. Liebhafsky, *J. Am. Chem. Soc.* **1934**, 56, 1680.

5 (a) M. D. Drake, M. A. Bateman and M. R. Detty, *Organometallics*, 2003, **22**, 4158; (b) C. Francavilla, M.D. Drake, F.V. Bright and M.R. Detty, *J. Am. Chem. Soc.* 2001, **123**, 57.

6 (a) C. J. Adams, M. J. Earle, G. Roberts and K. R. Seddon, *Chem. Commun*., 1998, 2097; (b) A. Stark, B. L. Maclean and R. D. Singer, *J. Chem. Soc., Dalton Trans.*, 1999, 63.

7 (a) T. Fischer, A. Sethi, T. Welton and T. Woolf, *Tetrahedron Lett*., 1999, **40**, 793; (b) C. W. Lee, *Tetrahedron Lett*., 1999, **40**, 2461; (c) P. Ludley and N. Karodia, *Tetrahedron Lett.*, 2001, **42**, 2011.

8 (a) T. Jeffery, *Tetrahedron Lett*., 1994, **35**, 3051; (b) V. Calò, A. Nacci, L. Lopez and N. Mannarini, *Tetrahedron Lett.*, 2000, **41**, 8973.

9 (a) R. X. Ren, L. D. Zueva and W. Ou, *Tetrahedron Lett.*, 2001, **42**, 8441; (b) J. Peng and Y. Deng, *Tetrahedron Lett.*, 2001, **42**, 403.

10 Beil., 6, 473.

11 Beil., 1, 171.

12 *Dictionary of Organic Compounds*, Mack Printing Com., Easton, Pennsylvania, J. Buckingham, fifth ed., 1982.

13 Beil., 7, II, 382.

14 *Organic syntheses*. 1951, Collective V. 2, 270–271.