Synthesis of vinyl bromides from the reaction of α, β-unsaturated carboxylic acids with ionic liquid [bmim][Br$_3$]/[bmim]Br

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Reaction of aryl α, β-unsaturated carboxylic acids with ionic liquid [bmim][Br3]/[bmim]Br affords vinyl bromides in a short reaction time and in good to excellent yields.

Keywords: vinyl bromides, α, β-unsaturated carboxylic acids

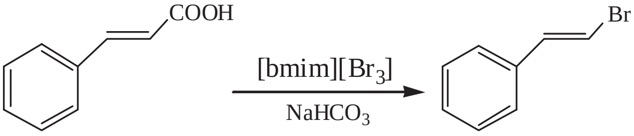
Vinyl bromides are important intermediates in organic synthesis.[1] The Hunsdiecker reaction is an useful transformation in organic chemistry for the synthesis of halogenated organic substrates.[2] However, this reaction and later improvements have major limitations, such as the toxicity and hazard in using Ag(I), Hg(II), Tl(I), Pb(IV) as the catalysts. With α, β-unsaturated carboxylic acids, the yields of the halogenated products in Hunsdiecker reaction are very poor.[3] The decarboxylation of α, β-unsaturated carboxylic acids accompanied by a simultaneous replacement by a halogen is an extremely useful and selective methodology in organic synthesis.[4] Recently, S. Roy reported a halodecarboxylation of α, β-unsaturated carboxylic acids using NBS and lithium acetate; later M. Tokuda improved Roy's method by microwave irradiation to reduce the reaction time and get a better yield. In 2004, Choudary *et al*. reported the formation of β-bromostyrenes by using the molybdate-exchanged Mg-Al-LDH catalyst using 30% H_2O_2 in aqueous media. However, these methods still have drawbacks: (a) the reaction time is longer; (b) the substrate and the catalyst are hard to dissolve in environmentally desirable solvents; (c) the preparation of the catalyst is difficult.

Recently various organic reactions have been performed in environmentally benign ionic liquids.[5] This is attributed to some intriguing properties of ionic liquids, such as high thermal stability, negligible vapour pressure and lack of flammability, recyclability, high loading capacity and tunable polarity. As the ionic liquid can be designed, many different task-specific ionic liquids have been prepared to achieve the anticipated targets.[6] Here, we report the use of the ionic liquid [bmim][Br$_3$]/[bmim]Br as the solvent and the bromine source for the synthesis of vinyl bromides (bmim=1-*n*-butyl-3-methylimidazolium).

The ionic liquid [bmim][Br$_3$] is easy to prepare, by mixing the bromide with the ionic liquid [bmim][Br] in a round-bottomed flask and stirred for 1h at the room temperature. As the pure ionic liquid [bmim][Br$_3$] is solid, the molar ratio of ionic liquid to Br_2 was set to be 1:0.8 and obtained a system composed of a [bmim][Br$_3$]/[bmim]Br mixture.

The reaction of cinnamic acid (2 mM) and $NaHCO_3$ (2 mM) in the [bmim][Br$_3$]/[bmim]Br (3 mM) at 40–50°C needs only 0.5 h, yielding the corresponding β-bromo-styrene in as high as 93% yield (Scheme 1). The results are summarised in Table 1.

From Table 1 we can see that the yields are good to excellent.[8] From the high yield we can deduce that the addition of Br_2 to carbon–carbon double bond is rare and the activity of the bromine can be depressed by forming [bmim][Br$_3$]. But when using the analogous dienoic acid 11 as the substrate, the yield is comparatively low. In addition to the bromodecarboxylation compounds, we also found a byproduct of bromine addition. The selectivity of the reagent is not so good for this substrate. The aromatic acids bearing electron-donating substituents are particularly reactive compared to those having an electron-withdrawing groups. The methodology is also suitable for aliphatic α, β-unsaturated carboxylic acids. In this experiment, the influence of the temperature is important. The reaction does not occur at room temperature and after 24 h, only a little product was formed. However, the product was formed rapidly and the yield was quite good if the temperature was raised to 40–50°C. At 60–70°C, the product was formed more rapidly, but the change was not very distinct.



Scheme 1

Recycling is one of the important characteristics of ionic liquids.[7] In this experiment, the ionic liquid can be reused more than four times. The results are given in Table 2. We found that the decrease in yield was not evident. Recycling the ionic liquid for the fourth time, the yield was still quite good. When the reaction was finished, some acetone was added, and the ionic liquid was dissolved. The NaBr was filtered, the acetone and H_2O was distilled, we added Br_2(2mM), stirring for a while, and the ionic liquid [bmim][Br$_3$]/[bmim]Br is formed again.

In conclusion, this synthetic procedure is straightforward and simple, and the reaction conditions are mild. We provide an alternative method to obtain β-bromostyrenes from α,β-unsaturated carboxylic acids by using [bmim][Br$_3$]/[bmim]Br without any catalyst in a short reaction time and good to excellent yields.

Experimental

Typical procedure for the bromodecarboxylation of α,β-*unsaturated carboxylic acids*

Cinnamic acid (2 mM) and $NaHCO_3$ (2 mM) were added into the [bmim][Br$_3$]/[bmim]Br (3 mM), stirring for 0.5 h at 40–50°C. After the reaction was complete, the reaction mixture was extracted with 5 ml diethyl ether 3 times. The corresponding β-bromostyrene was separated by column chromatography in a good yield.

*(E)-*β-*bromostyrene* **(1)**: B.p. 220.7–221°C (lit.[8] 220.9°C); IR: ν_{max} 1609, 1575, 941cm^{-1}; ^{1}H NMR: 6.77(1H, d, J = 13.9Hz), 7.11(1H, d, J = 13.9), 7.23–7.32(5H, m).

*(E)-*β-*bromo-4-methylstyrene* **(2)**: M.p. 46.0–46.8°C (lit.[9] 46.0–46.5°C); IR: ν_{max} 1605, 1511, 931 cm^{-1}; ^{1}H NMR: 2.32(3H, s), 6.70(1H, d, J = 13.9Hz), 7.06(1H, d, J = 13.9Hz), 7.12(2H, d, J = 8.3Hz), 7.19(2H, d, J = 8.3Hz).

*(E)-*β-*bromo-4-methoxystyrene* **(3)**: M.p. 58–59°C (lit.[10] 58–59°C); IR: ν_{max} 1607, 1513, 950 cm^{-1}; ^{1}H NMR: 3.81(3H, s), 6.61(1H, d, J = 13.9Hz), 6.85(2H, d, J = 8.9Hz), 7.04(1H, d, J = 13.9Hz), 7.23(2H, d, J = 8.9Hz).

*(E)-*β-*bromo-4-chlorostyrene* **(4)**: M.p. 47–48°C (lit.[11] 47–48°C); IR: ν_{max} 1604, 1586, 945 cm^{-1}; ^{1}H NMR: 6.75(1H, d, J = 13.9Hz), 7.05(1H, d, J = 13.9Hz), 7.21(2H, d, J = 8.6Hz), 7.29(2H, d, J = 8.6Hz).

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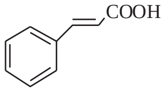
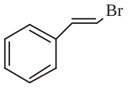
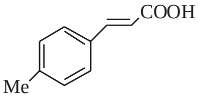
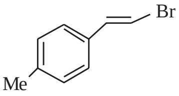
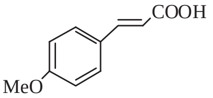
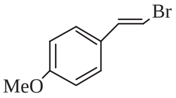
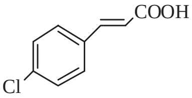
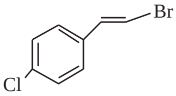
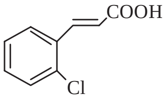
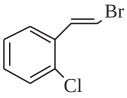
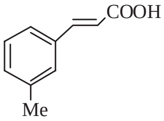
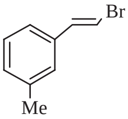
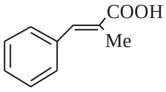
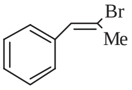
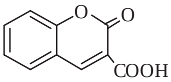
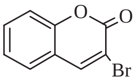
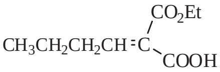
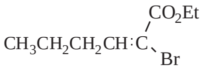
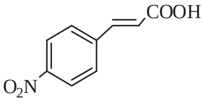
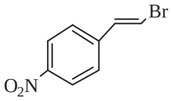
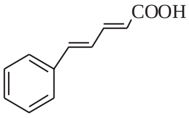
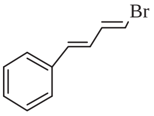
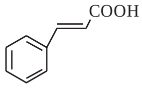
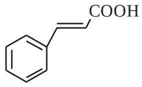
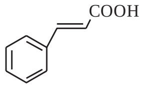
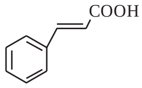
Table 1 Transformation of α,β-unsaturated carboxylic acids into β-bromostyrenes by the using of ionic liquid [bmim][Br_3]/[bmim]Br

Entry	Acid	Product	Reaction time/h	Yield /%[a]
1			0.5	93
2			0.25	90
3			0.2	96
4			1	86
5			1.5	70
6			1.5	88
7			0.5	91
8			2	98
9	 $CH_3CH_2CH_2CH{=}C(CO_2Et)(COOH)$	 $CH_3CH_2CH_2CH{=}C(CO_2Et)(Br)$	2	71[b]
10			3	0
11			3	10

[a]Isolated yield, except entry 6, *E:Z*=70:30 (vide GC). [b]*E:Z*=15:85 (vide GC).

Table 2 Recycling the ionic liquid

Recycled	Acid	Time/h	Yield/%
1		0.5	93
2		0.5	90
3		0.5	85
4		0.5	80

(E)-β-bromo-2-chlorostyrene **(5)**: B.p. 261.0–261.5°C (lit.[12] 261.1°C); IR: ν_{max} 1605, 1470, 1440, 945 cm^{-1}; ^1H NMR: 6.80(1H, d, $J = 13.9$Hz), 7.21–7.25(2H, m), 7.3–7.4(2H, m), 7.47(1H, d, $J = 13.9$Hz).

(E)-β-bromo-4-methylstyrene **(6)**: B.p. 240.3–241°C (lit.[13] 240.8°C); IR: ν_{max} 1600, 1614, 1581, 1197cm^{-1}; ^1H NMR: 2.30(3H, s), 6.67 (1H, d, $J = 14.1$Hz), 6.95–7.24(5H, m).

(E)-2-bromo-1-propenyl-benzene **(7)**: B.p. 231.3–231.9°C (lit.[14] 231.6°C); IR: ν_{max} 3050, 3020, 2960, 2930, 2860, 1640, 1600, 1495, 1442, 1380, 1280, 1200, 1088, 1070, 920, 845, 755, 700, 670 cm^{-1}; ^1H NMR: 2.46(3H, s), 6.70(1H, s), 7.20–7.70(5H, m).

(E)-3-bromo-2H-1-benzopyran-2-one **(8)**: M.p. 108.3–109.2°C (lit.[15] 110°C); IR: ν_{max} 1735, 1606 cm^{-1}; ^1H NMR: 8.10(1H, s), 7.57(1H, t, $J = 7.6$Hz), 7.46(1H, d, $J = 7.6$Hz), 7.36(1H, d, $J = 8.4$Hz), 7.32(1H, t, $J = 7.6$Hz).

Ethyl (Z)-2-bromo-2-hexenate **(9)**: B.p. 228.1–228.7°C (lit.[16] 228.4°C); IR: ν_{max} 1692, 1303, 1214 cm^{-1}; ^1H NMR: 0.86(6H, d, J = 6.0Hz), 1.30(3H, t), 1.86(1H, m), 4.37(2H, q, J = 6.8Hz), 7.46 (1H, t).

(E/Z)-1-bromo-4-phenylbuta-1,3-diene **(11)**: IR: ν_{max} 1691, 1448, 974, 741 cm^{-1}; ^{1}H NMR: 6.23(0.27H, d, *J* = 6.9Hz, (Z)), 6.42(0.73H, d, *J* = 13.2Hz), (E)), 6.5-6.8(2H, m), 6.87(0.73H, dd, *J* = 10.2 and 13.5Hz), (E)), 7.11(0.27H, ddd, *J* = 1.0, 9.9 and 13.5Hz), (Z)), 7.2–7.5(5H, m).

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