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Tetrahedron Letters 46 (2005) 8411–8413

Tetrahedron Letters

Zn/[bmim]PF_6-mediated Markovnikov allylation of unactivated terminal alkynes☆

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Received 19 April 2005; revised 12 September 2005; accepted 23 September 2005
Available online 13 October 2005

Abstract—A simple and highly regioselective method has been developed for the allylation of unactivated terminal alkynes with allyl bromide using Zn/[bmim]PF_6 as an inexpensive, readily available and recyclable reagent system. High conversions and enhanced selectivity together with the environmentally benign nature of the Zn/[bmim]PF_6 reagent system makes this method an attractive alternative to established methods.

Metal mediated processes play a significant role in many C–C bond forming reactions.[1] In continuation of our work on the use of metals such as zinc, indium and magnesium for various transformations,[2] we describe a Zn/[bmim]PF_6 reagent system for the allylation of unactivated terminal alkynes with allyl bromide. Only a few methods have been developed for the allylation of terminal alkynes with allyl halides using group III metals such as indium and gallium. The disadvantage of previous procedures is the formation of anti-Markovnikov by-products.[3] Recently, Lee et al.[4] reported the Markovnikov allylation of unactivated alkynes with allyl bromide using gallium metal. However, this method is also limited due to the difficulty in handling and the high cost of gallium.

The use of solvents like water, supercritical fluids and ionic liquids, has recently received a great deal of attention in different areas of organic chemistry. Particularly, ionic liquids are being used as 'green solvents' with unique properties such as good solvating ability, wide liquid range, tunable polarity, high thermal stability, immiscibility with a number of organic solvents, negligible vapour pressure and ease of recyclability (Fig. 1).[5]

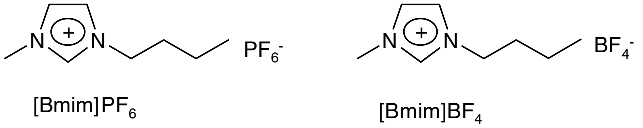


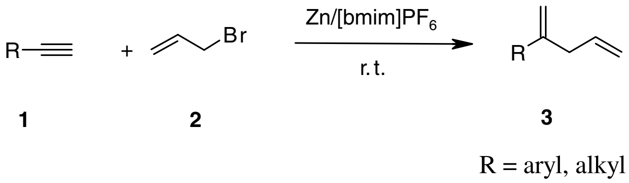
Figure 1. Chemical structures of some ionic liquids (ILs).

Due to stabilization of charged intermediates by ionic liquids, they can promote unprecedented selectivities and increase reaction rates over conventional solvents. Because of their advantages, ionic liquids can make a contribution to green chemistry.[6] This is the first report of the allylation of unactivated terminal alkynes with allyl bromide using Zn/[bmim]PF_6.

Treatment of terminal alkynes **1** with allyl bromide **2** in the presence of Zn/[bmim]PF_6 afforded the products **3** in 70–91% yields (Scheme 1).

The scope and generality of this process is illustrated with respect to various alkynes and the results are presented in Table 1.

In all cases, the reaction proceeded smoothly at room temperature with high selectivity. The reaction did not



Scheme 1.

Keywords: Terminal alkynes; Zinc; Allyl bromide; Ionic liquids.

☆ IICT Communication No. 051001.

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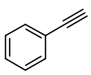
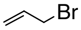
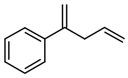
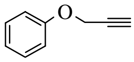
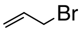
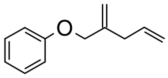
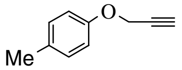
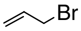
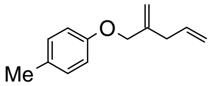
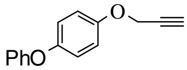
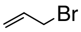
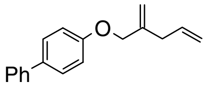
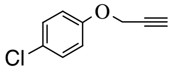
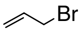
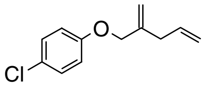
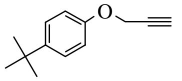
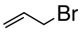
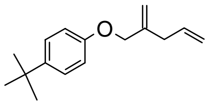
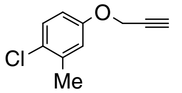
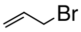
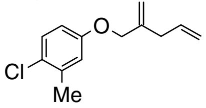
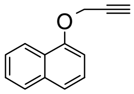
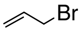
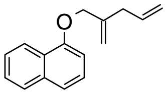
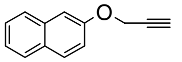
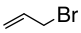
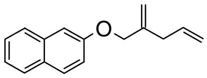
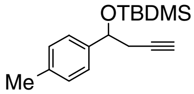
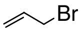
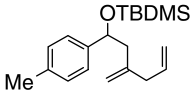
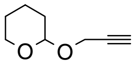
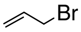
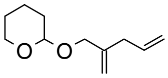
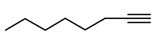
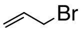
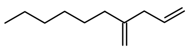
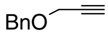
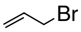
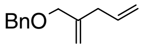
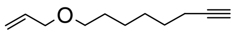
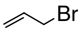
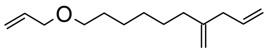
doi:10.1016/j.tetlet.2005.09.147

Table 1. Zn/[bmim]PF_6-mediated allylation of terminal alkynes with allyl bromide

Entry	Terminal alkynes **1**	Allyl bromide **2**	Product[a] **3**	Time (h)	Yield (%)[b]
a				3.0	88
b				2.5	85
c				2.5	89
d				3.0	90
e				3.0	82
f				3.0	80
g				3.0	91
h				2.5	90
i				3.5	85
j				4.0	82
k				4.5	70
l				3.5	85
m				4.0	82
n				4.5	70

[a] All products were characterized by ^{1}H NMR, IR spectroscopy and mass spectrometry.

[b] Yield refers to the isolated pure products after column chromatography.

take place in the absence of either zinc or the ionic liquid, even after long reaction times.

In summary, we have described a simple, convenient and efficient protocol for the allylation of unactivated terminal alkynes with allyl bromide using the Zn/[bmim]PF_6, recyclable reagent system.[7]

Acknowledgements

B.V.S., M.K.G. thank CSIR, New Delhi, and P.M.R. thanks UGC, New Delhi, for the award of fellowships.

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7. General procedure: A mixture of terminal alkyne (1 mmol) and allyl bromide (1.2 mmol) in Zn[bmim]PF_6 (2 mL) was stirred at 27 °C for the appropriate time (Table 1). After completion of the reaction, as indicated by TLC, the reaction mixture was extracted with diethyl ether (3×10 mL). The combined organic extracts were washed with brine solution, dried, then concentrated in vacuo and the resulting product was directly charged onto a small silica gel column and eluted with a mixture of ethyl acetate–*n*-hexane (1:9) to afford pure products. The remaining [bmim]PF_6 ionic liquid was washed with saturated brine solution, (4×5 mL) and dried under vacuum ($\sim$5 h) for the next run. Spectral data for products: compound **3a**: Liquid, IR (KBr): ν_{max}: 2981, 1635, 1494, 1445, 1017, 909, 759, 702 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.46–7.23 (m, 5H), 6.08–5.84 (m, 1H), 5.43 (s, 1H), 5.24–5.04 (m, 3H), 3.25 (d, $J = 6.3$ Hz, 2H). EI-MS: *m*/*z* (%): 144 (M^+, 15), 128 (20), 115 (80), 103 (10), 91 (5), 77 (8), 63 (7), 39 (5). HRMS calcd for $C_{11}H_{12}$: 144.0939. Found: 144.0932. Compound **3b**: Liquid, IR (KBr): ν_{max}: 2928, 2984, 1696, 1354, 1296, 1218, 1094, 968, 771, 670 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.38–7.21 (m, 2H), 7.02–6.90 (m, 3H), 6.42–6.38 (m, 1H), 5.14–4.99 (m, 4H), 4.40 (s, 2H), 2.90 (d, $J = 6.4$ Hz, 2H). EI-MS: *m*/*z* (%): 174 (M^+, 100), 134 (30), 94 (20), 79 (20), 39 (20). HRMS calcd for $C_{12}H_{14}O$: 174.1044. Found: 174.1040. Compound **3k**: Liquid, IR (KBr): ν_{max} 2925, 2875, 1683, 1442, 1376, 1251, 996, 913 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.90–5.64 (m, 2H), 5.11–4.84 (m, 3H), 4.60–4.56 (m, 1H), 4.16–3.76 (m, 3H), 3.50–3.34 (m, 2H), 2.90–2.70 (overlap, 3H), 2.01–1.48 (m, 4H). EI-MS: *m*/*z* (%): 182 (M^+, 5), 146 (5), 132 (5), 120 (20), 86 (100), 41 (45). HRMS calcd for $C_{11}H_{18}O_2$ (Na): 205.1204. Found: 205.1200.