Magnesium powder promoted conjugate addition of allyl bromide to ß-nitroalkenes under solvent-free conditions

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Polyfunctional nitro-compounds were obtained in high yield by a convenient and efficient methodology involving the conjugate addition of allyl bromide to nitrostyrenes in one pot under solvent- and catalyst-free conditions at 0°C.

Keywords: β-nitrostyrenes, allyl bromide, solvent-free, magnesium powder

The conjugate addition of organometallic reagents to powerful Michael acceptors has a useful function in carbon–carbon bond formation.[1,2] There have been many reports of conjugate addition to nitrostyrenes involving organometallic compounds including Grignard reagents,[3,4] alkyllithium[5] and organoaluminium compounds.[6] However most were not satisfactory due to undesirable side reactions and poor conversions.[7,8] Moreover the organometallic reagents needed to be prepared beforehand and the process was vigorous. Research on 1,4-conjugate addition reactions involving organozinc halides has been performed in our laboratory. We have shown that the conjugate addition reaction between β-nitrostyrenes and functionalised organozinc halides occurs smoothly using $Cu(OAc)_2$[9] as a catalyst instead of CuCN•2LiCl[10-11] and nickel(II) catalysts.[12,13] In addition, we have successfully achieved the solvent-free conjugate addition of organozinc halides to β-nitrostyrenes in the absence of catalyst.[14] However, polyfunctional nitro-compounds were prepared in two to three steps from the β-nitrostyrenes.

We report our improvement on a convenient, green and low-cost conjugate addition mediated by magnesium powder of allyl bromide to nitrostyrenes in one pot under solvent- and catalyst-free conditions to give the corresponding nitrostyrenes in high to excellent yields (Scheme 1).

In order to investigate the effect of different metals and solvents on the yields of the reaction, a mixture of nitrostyrenes, allyl bromide, solvent and metal was stirred at 0°C. We examined different metals to mediate the reaction. It was apparent that most metals such as Co, Pb, W, Sn, Fe, Ni, Cd, Mn, Ti, Al and Zn did not give rise to expected products even after prolonging the reaction time.

Then we explored the conjugate addition to β-nitrostyrene mediated by Mg in different solvents. The desired products were not formed after prolonged stirring when distilled water, dichloromethane or dimethyl sulfoxide were used as solvents (Table 1, entries 2–4). When the solvent was diethyl ether, ethanol or N,N-dimethylformamide (Table 1, entries 5–7), nitrostyrenes could be allylated to give the corresponding substituted nitrostyrenes in low yields. Even the use of Mg in tetrahydrofuran, which was very efficient with conjugate addition of β-nitrostyrene, did not improve our results and gave moderate yield (Table 1, entry 8). When the reaction under solvent-free conditions was carried out, the allylation of nitrostyrene proceeded smoothly at zero temperature and satisfactory yields were obtained (Table 1, entry 1). Hence the solvent-free conditions were necessary for the successful conjugate addition to nitrostyrenes, which is a great improvement in reducing chemical pollution.

Table 1 Conjugate addition to β-nitrostyrene mediated by Mg in different solvents[a]

Entry	Mediator	Solvent	Time/h	Yield/%[b]
1	Mg	-	0.67	80
2	Mg	H_2O	37	NR[c]
3	Mg	CH_2Cl_2	16	NR[c]
4	Mg	DMSO	18	NR[c]
5	Mg	Et_2O	4	46
6	Mg	EtOH	5	34
7	Mg	DMF	6	40
8	Mg	THF	4	61

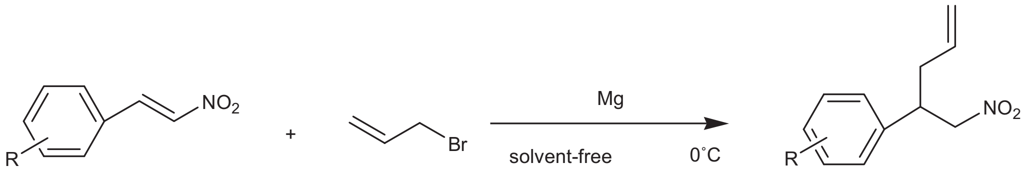
[a]Reaction conditions: magnesium powder or other metals (3 mmol), allyl bromide (3 mmol), β-nitrostyrene (2 mmol) and solvent (2 ml), 0°C.

[b]The isolated yields are reported and all of the products were identified by IR, ^{1}H NMR, ^{13}C NMR and MS.

[c]NR: no reaction. Almost all of the β-nitrostyrene was recycled.

In pursuit of better reaction conditions, we conducted conjugate addition to β-nitrostyrene mediated by magnesium powder at different temperatures under solvent-free condition. Running the reaction at higher temperature decreased the yield but lower temperature did not improve the yields. Finally, we established the optimum temperature, at which the corresponding substituted nitrostyrenes were isolated in significant quantities.

In continuation of our research program on solvent-free conjugate addition, we tried the reaction of allyl bromide with nitrostyrenes under solvent-free conditions directly mediated by Mg and obtained satisfactory results. The 1,4-addition products were examined and the results are summarised in Table 2. Analysis of the results of Table 2 reveals that the nature of the substitution pattern on the phenyl ring plays a major role in determining the yields of the reaction. High yields can be achieved with shorter times in the case of many nitrostyrenes bearing electron-donating groups on the phenyl ring. However, no product was obtained with substrates having electron-withdrawing groups or phenyl groups even after prolonging reaction time. The heterocyclic nitroalkenes



Scheme 1

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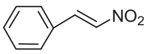
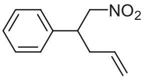
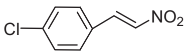
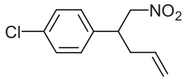
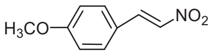
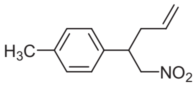
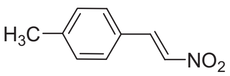
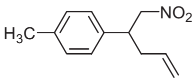
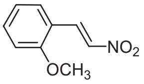
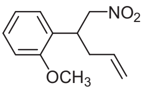
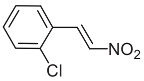
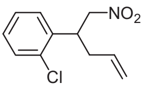
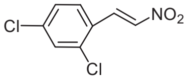
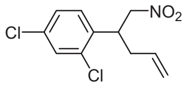
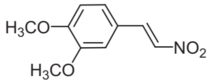
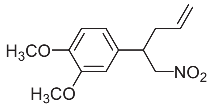
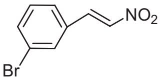
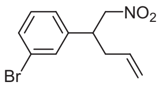
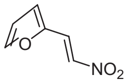
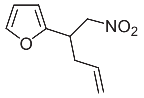
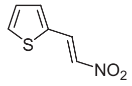
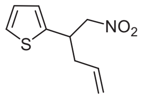
Table 2 Addition reactions of allyl bromide to nitroalkenes mediated by Mg[a]

Entry	β-Nitrostyrene	Product[b]		Time/h	Yield/%[c]
1			**2a**	0.67	80
2			**2b**	1.5	85
3			**2c**	1.5	82
4			**2d**	1	85
5			**2e**	1.5	86
6			**2f**	1.5	87
7			**2g**	1	86
8			**2h**	1.5	83
9			**2i**	1.5	78
10			**2j**	0.67	88
11			**2k**	0.67	86

[a] All reactions were performed with allyl bromide (3 mmol), magnesium powder(3 mmol) and nitroalkenes (2 mmol) at 0°C under solvent-free conditions.
[b] Isolated yield.
[c] All products were characterised by IR, ^{1}H NMR, ^{13}C NMR, MS.

also afforded adducts in high yield and shorter time (Table 2, entries 10 and 11). It is noteworthy that no coupling products were found in our reactions.

In conclusion, we have developed a successful methodology for the conjugate addition of allyl bromide to nitrostyrenes in one pot under solvent- and catalyst-free conditions at 0°C. In contrast to previously reported reaction systems, the reaction here has the following advantages: easy manipulation, short reaction time, environmentally-benign and high yield.

Experimental

General remarks

All manipulations was performed under an atmosphere of dry nitrogen gas. THF were refluxed over sodium/benzophenone before use. β-Nitrostyrene and its derivatives were prepared according to the literature.[17] IR spectra were obtained using an Alpha Centauri FT-IR spectrophotometer. Mass spectra were recorded on an HP 5988A and GC/MS/DS instrument. Melting points were determined with an X-4 apparatus and were not corrected. ^{1}H (400 MHz), and ^{13}C (100 MHz) NMR spectra were obtained for $CDCl_3$ solutions with TMS as an internal standard at room temperature.

General procedure for the reaction

Magnesium powder (3 mmol) and β-nitrostyrene (2 mmol) were placed in a dried round-bottom flask. Then allyl bromide (3 mmol) was added dropwise. The resulting mixture was stirred for the given time (Table 2) at 0°C and the reaction was monitored by TLC. After complete conversion, saturated NH_4Cl (10 ml) solution was poured into the mixture. The mixture was extracted with Et_2O (3 × 10 ml) and the organic layer was separated and dried over anhydrous $MgSO_4$. The solvent was evaporated and the pure product was obtained by column chromatograph of the crude mixture on silica gel using petroleum/ethyl acetate as an eluent.

1-Nitro-2-phenylpent-4-ene (**2a**): Pale yellow oil; [15] IR (KBr) ν_{max} cm^{-1}: 3073, 3030, 2922, 2853, 1641, 1548, 1451, 1434 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.17 (m, 5H), 5.70–5.60 (m, 1H), 5.09–

5.02 (m, 2H), 4.64–4.51 (m, 2H), 3.60–3.52 (m, 1H), 2.56–2.38(m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 134.1, 128.8, 127.6, 127.4, 118.1, 79.8, 43.7, 37.6; EI-MS (*m/z*) 191 (M$^+$), 150, 135, 91, 77.

1-Nitro-2-(4-chlorophenyl)pent-4-ene (**2b**): Pale yellow oil;[15] IR (KBr) ν_{max} cm^{-1}: 3079, 2927, 2853, 1644, 1552, 1492, 1436 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31 (d, 2H, J = 7.0 Hz), 7.14 (d, 2H, J = 7.0 Hz), 5.67–5.57 (m, 1H), 5.08–5.03 (m, 2H), 4.63–4.58 (m, 1H), 4.52–4.47(m,1H), 3.577–3.50 (m, 1H), 2.46–2.39(m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.6, 133.7, 133.5, 129.1, 128.8, 118.7, 79.6, 43.2, 37.6; EI-MS (*m/z*) 225 (M$^+$), 184, 178, 138, 125, 103, 77.

1-Nitro-2-(4-methoxyphenyl)pent-4-ene (**2c**): Pale yellow oil;[15] IR (KBr) ν_{max} cm^{-1}: 3076, 2922, 2841, 1613, 1549, 1514, 1440 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.12 (d, 2H, J = 7 Hz), 6.85 (d, 2H, J = 7 Hz), 5.71–5.61 (m, 1H), 5.10–5.04 (m, 2H), 4.63–4.58 (m, 1H), 4.53–4.47(m,1H), 3.79 (s, 3H), 3.55–3.50 (m, 1H), 2.48–2.39(m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 158.9, 134.3, 131.0, 128.4, 118.1, 114.2, 80.2, 55.2, 43.1, 37.7; EI-MS (*m/z*) 221 (M$^+$), 180, 134, 121, 91, 77.

1-Nitro-2-(4-methylphenyl)pent-4-ene (**2d**): Pale yellow oil;[16] IR (KBr) ν_{max} cm^{-1}:3079, 3022, 2922, 2863, 1642, 1553, 1516, 1432 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.14 (d, 2H, J = 7.6 Hz), 7.08(d, 2H, J = 7.6 Hz), 5.69–5.61 (m, 1H), 5.09–5.04 (m, 2H), 4.63–4.49 (m, 2H), 3.56–3.49 (m, 1H), 2.49–2.38 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz,CDCl$_3$): δ 137.3, 136.1, 134.3, 129.6, 127.3, 118.1, 80.0, 43.4, 37.7, 21.0; EI-MS (*m/z*) 205 (M$^+$), 164,159, 118, 105, 91, 77.

1-Nitro-2-(2-methoxyphenyl)pent-4-ene (**2e**): Pale yellow oil;[14] IR (KBr) ν_{max} cm^{-1}: 3075, 3006, 2921, 2842, 1595, 1550, 1494, 1462, 1438 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.27–7.25 (m, 1H), 7.23–7.10 (m, 1H), 6.94–6.88 (m, 2H), 5.73–5.62 (m, 1H), 5.10–5.01 (m, 2H), 4.73–4.68 (m, 1H), 4.65–4.60 (m,1H), 3.84(s, 3H), 3.90–3.82 (m, 1H), 2.60–2.44(m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 157.2, 135.0, 128.8, 128.6, 127.0, 120.7, 117.6, 111, 78.4, 55.3, 39.1, 35.8; EI-MS (*m/z*) 221 (M$^+$), 180, 134, 119, 91, 77.

1-Nitro-2-(2-chlorophenyl)pent-4-ene (**2f**): Pale yellow oil;[14] IR (KBr) ν_{max} cm^{-1}: 3074, 2920, 2856, 1641, 1551, 1476, 1436 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.40(d, 1H, J = 8.0 Hz), 7.28–7.19 (m, 3H), 5.73–5.63 (m, 1H), 5.11–5.06 (m, 2H), 4.71–4.61 (m, 2H), 4.20–4.13 (m, 1H), 2.57–2.46(m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 134.1, 133.7, 130.2, 128.7, 127.8, 127.2, 118.6, 78.0, 39.6, 36.3; EI-MS (*m/z*) 225 (M$^+$), 184, 177, 138, 125, 103, 77.

1-Nitro-2-(2,4-dichlorophenyl)pent-4-ene (**2g**): Pale yellow oil;[15] IR (KBr) ν_{max} cm^{-1}: 3080, 2979, 2920, 2854, 1640, 1554, 1475, 1437 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43 (s, 1H), 7.2 5(d, 1H, J = 8.0 Hz), 7.14 (d, 1H, J = 8.0 Hz), 5.70–5.61 (m, 1H), 5.19–5.07 (m, 2H), 4.65–4.62 (m, 2H), 4.13–4.10 (m, 1H), 2.52–2.48 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 135.0, 133.9, 133.3, 130.1, 128.7, 127.6, 127.2, 118.9, 78.0, 39.2, 36.2; EI-MS (*m/z*) 259 (M$^+$), 218, 198, 172, 159, 137, 102, 75.

1-Nitro-2-(3,4-methoxyphenyl)pent-4-ene (**2h**): Yellow oil;[16] IR (KBr) ν_{max} cm^{-1}: 3081, 3014, 2967, 2938, 1593, 1550, 1517, 1466 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.83 (d, 1H, J = 8.0 Hz), 6.74 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.4), 6.68 (d, 1H, J = 2.4), 5.72–5.62 (m, 1H), 5.30–5.05 (m, 2H), 4.63–4.50 (m, 2H), 3.86 (s, 3H), 3.87 (s, 3H), 3.55–3.47 (m, 1H), 2.50–2.38 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 149.1, 148.4, 134.3, 131.5, 119.3, 118.1, 111.3, 110.6, 80.1, 55.9, 55.8, 43.4, 37.7; MS (*m/z*) 251 (M$^+$), 210, 205, 164, 151, 106.

1-Nitro-2-(3-bromophenyl)pent-4-ene (**2i**): Pale yellow oil;[15] IR (KBr) ν_{max} cm^{-1}: 3075, 2979, 2922, 2855, 1642, 1553, 1476, 1432 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41(d, 1H, J = 8.0 Hz), 7.35 (s, 1H), 7.21 (t, 1H, J = 8.0 Hz), 7.13 (d, 1H, J = 8.0 Hz), 5.70–5.59 (m, 1H), 5.11–5.07 (m, 2H), 4.65–4.60 (m, 1H), 4.56–4.51 (m, 1H), 3.58–3.50 (m, 1H), 2.50–2.38 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 134.1, 133.7, 130.2, 128.7, 127.8, 127.2, 118.6, 78.0, 39.6, 36.3; EI-MS (*m/z*) 252 (M$^+$-17), 228, 208, 182, 169, 143, 129, 103, 77.

1-Nitro-2-(2-furyl)pent-4-ene (**2j**): Yellow oil;[15] IR (KBr) ν_{max} cm^{-1}: 3123, 3081, 2982, 2922, 2855, 1641, 1554, 1507, 1435 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ7.36 (dd, 1H, J_1 = 2.0 Hz, J_2 = 0.8 Hz), 6.31 (dd, 1H, J_1 = 3.2 Hz, J_2 = 1.6 Hz), 6.15 (d, 1H, J = 3.2 Hz), 5.76–5.66 (m, 1H), 5.14–5.10 (m, 2H), 4.64–4.55 (m, 2H), 3.75–3.68 (m, 1H), 2.58–2.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 152.2, 142.2, 133.6, 118.6, 110.3, 107.0, 77.4, 37.3, 35.3; EI-MS (*m/z*) 181 (M$^+$), 134, 94, 81, 65.

1-Nitro-2-(2-thienyl)pent-4-ene (**2k**): Pale yellow oil;[16] IR (KBr) ν_{max} cm^{-1}: 3078, 2922, 1641, 1553, 1436 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ7.22 (dd, 1H, J_1 = 4.8 Hz, J_2 = 1.6 Hz), 6.95 (dd, 1H, J_1 = 5.2 Hz, J_2 = 3.6 Hz), 6.88 (d, 1H, J = 4.8 Hz), 5.78–5.68 (m, 1H), 5.16–5.10 (m, 2H), 4.66–4.61 (m, 1H), 4.56–4.50 (m, 1H), 3.95–3.88 (m, 1H), 2.58–2.44 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.1, 133.6, 127.0, 125.3, 124.6, 118.77, 80.2, 39.1, 38.5; EI-MS (*m/z*) 180 (M$^+$), 150, 110, 97, 84.

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Reference

1 K. Tomioka and Y. Nagaoka, in *Comprehensive asymmetric catalysis*, eds E. N. Jacobsen, A. Pfaltz, H. Yamamotoe, Springer-Verlag, Berlin/ Heidelberg, 1999, Vol. 3 Chap. 31.1.
2 A. Alexakis, in *Transition metal catalysed Reactions* eds S.-I. Murahashi, S.G. Daviese, IUPAC Blackwell Science, Oxford, 1999, p. 303.
3 C.F. Yao, W.C. Chen and Y.M. Li, *Tetrahedron Lett.*, 1996, **37**, 6339.
4 C.F. Yao, K.H. Kao, J.T. Liu, C.M. Chu and Y. Wang, *Tetrahedron*, 1998, **54**, 791.
5 P. Knochel and D. Seebach, *Tetrahedron Lett.*, 1981, **22**, 3223.
6 A. Pecunioso and R. Menicagli, *J. Org. Chem***.**, 1988, **53**, 45.
7 N. Kornblum, *Angew. Chem. Int. Ed. Engl.*, 1975, **14**, 734.
8 E.W. Colvin, A.D. Robertson, D. Seebach and A.K. Beck, *J. Chem. Soc., Chem. Commun.*, 1981, 952.
9 D.F. Huang, Y.L. Hu, J.-X. Wang and Y.Q. Yin, *Chin. Chem. Lett.*, 2007, **18**, 1040.
10 Y.L. Hu, J.H. Yu, J.-X. Wang and Y.Q. Yin, *Synth. Commun.*, 1998, **28**, 2793.
11 Y. Hu, J. Yu, S. Yang, J.X. Wang and Y. Yin, *Chinese Chem. Lett.,* 1998, **9**, 699.
12 D. Huang, Y. Yang, J.X. Wang and Y. Hu, *J. Chem. Res. (S)*, 2002, 79.
13 Y. Hu, J. Yu, S. Yang, J.X. Wang and Y. Yin, *Synlett.*, 1998, 1213.
14 D.F. Huang, Y.L. Hu and J.-X. Wang, *Synlett.*, 2007, **1**, 1.
15 W.L Bao, Y.F. Zheng and Y.M. Zhang, *J. Chem. Res (S)*, 1999, 732.
16 H.M. Kumar, B.V. Subba, P. Thirupathi and J.S. Yadav, *Terahedron Lett.,* 1999, **40**, 5387.
17 R. Menicagli and S. Samaritani, *Tetrahedron,* 1996, **52**, 1425.