Solvent-Free, One-Pot Conjugate Addition of Benzyl Bromides to β-Nitroalkenes Mediated by Magnesium Powder

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Received 30 June 2008; revised 16 October 2008

Abstract: A convenient and efficient methodology for conjugate addition of benzyl bromides to β-nitrostyrenes mediated by magnesium powder in one pot under solvent-free conditions at 0 °C has been developed. Advantages of this method are excellent yields, short reaction times, operational simplicity, and avoidance of the use of organic solvents.

Key words: β-nitrostyrenes, benzyl bromide, conjugate addition, solvent-free, magnesium powder

Conjugate addition of organometallic reagents to powerful Michael acceptors has a vital function in the formation of C–C bonds.[1] Among good acceptors for conjugate addition, β-nitrostyrenes, due to their strongly electron-withdrawing group,[2] can be easily transformed into a variety of valuable functionalities such as amines, ketoximes, hydroxylamines, and nitroalkanes.[3] Therefore, conjugate addition to β-nitrostyrenes has received much attention in recent years.

There have been many reports on the conjugate addition of β-nitrostyrenes mediated by organometallics including Grignard reagents,[4] alkyllithiums,[5] and organoaluminums.[6] However, most of them were not satisfactory due to undesirable side reactions and poor conversion.[7] Moreover, the organometallic reagents needed to be prepared beforehand and the process was rigorous. Researchers have also focused their works on catalytic 1,4-conjugate addition to nitrostyrenes using, for example, copper metal or copper salts.[8] Later, these reactions were promoted by metallic indium,[9] samarium,[10] and zinc[11] in organic solvent in the absence of a catalyst. The progress of these approaches is gratifying, but one of the drawbacks is chemical pollution caused by the use of organic solvents. Hence, we should make an effort to explore more efficient, environmentally benign, handier procedures.

Much research work on 1,4-conjugate addition reactions conducted by organozinc halides has been performed in our laboratory. We have studied the smooth conjugate addition between β-nitrostyrenes and functionalized organozinc halides using copper(II) acetate[12] as a catalyst instead of copper(I) cyanide–bis(lithium chloride),[13,14] and nickel(II) catalyst.[15] In addition, we have successfully achieved the solvent-free conjugate addition of organozinc halides to β-nitrostyrenes in the absence of a catalyst;[16] polyfunctional nitro compounds were obtained in two to three steps from the β-nitrostyrenes. To make the application of nitroalkenes even more attractive, we have focused our attempts on the development of more convenient, rapid, and 'green' reactions mediated by inexpensive metals, instead of organometallics, as reaction substrates.

Herein, we report our improvements: a handy and low-cost conjugate addition, mediated by magnesium powder, of benzyl bromide reagents to β-nitrostyrenes in one pot under solvent-free and catalyst-free conditions to give the corresponding 1,2-diaryl-2-nitropropanes in high to excellent yields.

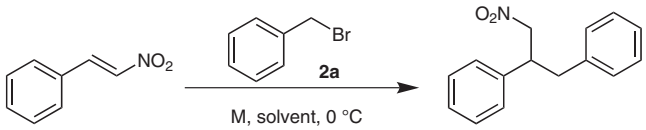
In order to investigate the effects of different metals and solvents on the yields of the reaction, a mixture of β-nitrostyrene (**1a**), benzyl bromide (**2a**), solvent, and metal was stirred at 0 °C (Table 1).

We first examined various metals for the mediation of the reaction. From Table 1, it can be seen that most of the metals examined, such as tin, iron, aluminum, and zinc, did not give rise to the expected products even after prolonged reaction times (Table 1, entries 1–4), only magnesium powder gave the desired product **3a** after 1.5 hours (Table 1, entry 5).

Next we explored the conjugate addition of benzyl bromide (**2a**) to β-nitrostyrene (**1a**) mediated by magnesium using different solvents. We found that the desired product **3a** was not observed after prolonged reaction times when distilled water or dimethyl sulfoxide was used as solvent (Table 1, entries 6 and 7). When the solvent was diethyl ether, ethanol, or *N*,*N*-dimethylformamide (Table 1, entries 8–10), β-nitrostyrene (**1a**) could be benzylated to give 1-nitro-2,3-diphenylpropane (**3a**) in low yields. Even the use of magnesium in tetrahydrofuran, which was very efficient for the conjugate addition of β-nitrostyrene (**1a**), did not improve our results and gave moderate yields (Table 1, entry 11). It is noteworthy that the product yield was higher (72%) in the absence of solvent in comparison to that in tetrahydrofuran (56%). Hence, solvent-free conditions were necessary for successful conjugate addition to β-nitrostyrenes, which is a great improvement in reducing chemical pollution.

SYNTHESIS 2009, No. 4, pp 0597–0601
Advanced online publication: 27.01.2009
DOI: 10.1055/s-0028-1083329; Art ID: F14708SS

Table 1 Conjugate Addition of Benzyl Bromide (**2a**) to β-Nitrostyrene (**1a**) Mediated by Different Metals in Different Solvents[a]



1a **3a**

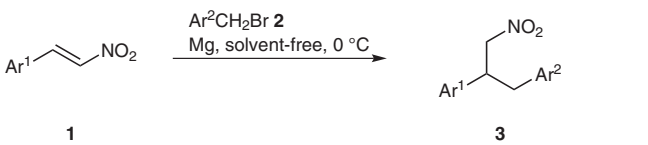
Entry	Mediator	Solvent	Time (h)	Yield[b,c] (%) of **3a**
1	Sn	–	10	n.r.
2	Fe	–	10	n.r.
3	Al	–	10	n.r.
4	Zn	–	10	n.r.
5	Mg	–	1.5	72
6	Mg	H_2O	26	n.r.
7	Mg	DMSO	18	n.r.
8	Mg	Et_2O	5	42
9	Mg	EtOH	5	33
10	Mg	DMF	5	37
11	Mg	THF	4.5	56

[a] Reaction conditions: Mg powder or other metals (4 mmol), BnBr (**2a**, 4 mmol), β-nitrostyrene (**1a**, 2 mmol), solvent (2 mL), 0 °C.
[b] Isolated yields.
[c] n.r. = no reaction; almost all of the β-nitrostyrene was recycled.

In order to explore the applications of this reaction, we performed it using benzyl bromide (**2a**) and substituted benzyl bromides **2** and nitroalkenes **1** under solvent-free conditions directly mediated by magnesium at 0 °C (Table 2). The results in Table 2 reveal that the nature of the substitution pattern on the phenyl ring of the nitroalkene **1** 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 **1** bearing electron-donating groups or moderate electron-withdrawing groups on the phenyl ring Ar^1. However, β-nitrostyrenes **1** bearing strong electron-withdrawing groups, such as the nitro group, on phenyl ring Ar^1 did not give products **3** even after prolonged reaction times. The heterocyclic nitroalkenes also gave adducts **3j** and **3k** in moderate yields and short times (Table 2, entries 10 and 11).

In conclusion, we have developed a new and convenient procedure for the conjugate addition of benzyl bromides to β-nitroalkenes mediated by magnesium powder in one pot under solvent-free and catalyst-free conditions. Compared with previously reported methods,[12–14,16b] the advantages of the present method are: (a) excellent yields when magnesium powder is used as medium (the yields increased to 72–85% from 66–81%); (b) the reaction time is shortened to 1.5–3 hours from 3–5 hours; and (c) the simplicity of the operation.

Table 2 Addition Reactions of Benzyl Bromide to Nitroalkenes Mediated by Magnesium in One Pot under Solvent-Free Conditions[a]



1 **3**

Entry	Ar^1	Ar^2	Product	Time (h)	Yield[b,c,d] (%)
1	Ph	Ph	**3a**	1.5	72 (66)
2	4-ClC_6H_4	Ph	**3b**	2	78 (67)
3	4-$MeOC_6H_4$	Ph	**3c**	2	85 (81)
4	4-MeC_6H_4	Ph	**3d**	1.5	84
5	2-$MeOC_6H_4$	Ph	**3e**	2	77 (70)
6	2-ClC_6H_4	Ph	**3f**	2	83 (76)
7	2,4-$Cl_2C_6H_3$	Ph	**3g**	2	80
8	3,4-$(MeO)_2C_6H_3$	Ph	**3h**	2	77
9	3-BrC_6H_4	Ph	**3i**	2	72
10	2-furyl	Ph	**3j**	1.5	75 (72)
11	2-thienyl	Ph	**3k**	1.5	80 (78)
12	Ph	4-ClC_6H_4	**3l**	3	75 (73)
13	4-$MeOC_6H_4$	4-ClC_6H_4	**3m**	3	71
14	4-MeC_6H_4	4-ClC_6H_4	**3n**	3	78
15	Ph	4-BrC_6H_4	**3o**	3	67
16	4-ClC_6H_4	4-BrC_6H_4	**3p**	3	65

[a] All reactions were performed with Ar^2CH_2Br **2** (4 mmol), Mg powder (4 mmol), β-nitroalkenes **1** (2 mmol), 0 °C, solvent-free conditions.
[b] Isolated yields.
[c] All products were characterized by IR, ^1H NMR, ^{13}C NMR, MS.
[d] Values in brackets are from the reaction of organozinc reagents without solvent.[16b]

All chemicals were obtained from commercial sources. Melting points were measured on an X-4 electrothermal micro melting point apparatus and are uncorrected. IR spectra were measured using an Alpha Centauri FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra (400 MHz and 100 MHz, respectively) were recorded on Bruker AC-E 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were performed on QP-1000A GC-MS spectrometer by EI ionization at 70 eV. Elemental analyses were performed on a Perkin-Elmer PE 2400 instrument. Purification of products was performed by flash chromatography on 200–300 mesh silica gel (petroleum ether–EtOAc, 15:1). All the isolated products were characterized by IR, ^1H and ^{13}C NMR, and MS, and elemental analysis for all the new compounds.

1,2-Diaryl-3-nitropropanes 3; General Procedure

Mg powder (4 mmol) and nitroalkene **1** (2 mmol) were placed in a dried round-bottom flask. Then benzyl bromide **2** (4 mmol) was added slowly. The resulting mixture was stirred at 0 °C and the re-

action was monitored (TLC). After complete conversion, sat. NH_4Cl soln (10 mL) was poured into the mixture. The mixture was extracted with Et_2O (3 × 10 mL) and the organic layer was separated, dried (anhyd $MgSO_4$), and evaporated. The crude mixture was subjected to column chromatography (silica gel, PE–EtOAc) to give the pure product.

1-Nitro-2,3-diphenylpropane (3a)
Yellow oil.[16a]

IR (KBr): 3063, 3030, 2923, 2825, 1601, 1551, 1496, 1500 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.04 (m, 10 H, H_{arom}), 4.65–4.52 (m, 2 H, CH_2), 3.81–3.74 (m, 1 H, CH), 3.07–2.93 (m, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0, 137.7, 129.0, 128.8, 128.6, 127.7, 127.5, 126.8, 79.5, 46.0, 40.0.

MS (EI, 70 eV): *m*/*z* = 241 (M^+), 211, 104, 91, 77.

2-(4-Chlorophenyl)-1-nitro-3-phenylpropane (3b)
Pale yellow solid; mp 105–107 °C (Lit.[16a] 104–106 °C).

IR (KBr): 3027, 2915, 2858, 1549, 1487, 1435 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.21 (m, 5 H, H_{arom}), 7.10–7.04 (m, 4 H, H_{arom}), 4.58 (d, *J* = 8.0 Hz, 2 H, CH_2), 3.77–3.73 (m, 1 H, CH), 2.96 (dd, *J* = 8.0, 4.4 Hz, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 137.3, 133.5, 129.0, 129.0, 128.8, 128.7, 126.9, 79.3, 45.4, 40.0.

MS (EI, 70 eV): *m*/*z* = 275 (M^+), 244, 228, 214, 178, 138, 91, 77.

2-(4-Methoxyphenyl)-1-nitro-3-phenylpropane (3c)
White solid; mp 81 °C (Lit.[16b] 78–79 °C).

IR (KBr): 3020, 2921, 2841, 1550, 1511, 1438 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.18 (m, 3 H, H_{arom}), 7.09–7.06 (m, 4 H, H_{arom}), 6.83 (d, *J* = 8.8 Hz, 2 H, H_{arom}), 4.56 (d, *J* = 7.2 Hz, 2 H, CH_2), 3.78 (s, 3 H, OCH_3), 3.75–3.69 (m, 1 H, CH), 3.08–2.90 (m, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 137.9, 130.9, 129.0, 128.5, 128.5, 126.7, 114.2, 79.8, 55.2, 45.3, 40.1.

MS (EI, 70 eV): *m*/*z* = 271 (M^+), 224, 180, 134, 91, 77.

2-(4-Methylphenyl)-1-nitro-3-phenylpropane (3d)
White solid; mp 33 °C.

IR (KBr): 3024, 2932, 2856, 1549, 1444, 1381 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.20 (m, 3 H, H_{arom}), 7.13–7.05 (m, 6 H, H_{arom}), 4.60–4.55 (m, 2 H, CH_2), 3.76–3.72 (m, 1 H, CH), 3.05–2.91 (m, 2 H, CH_2), 2.32 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9, 137.3, 136.0, 129.5, 129.0, 128.5, 127.3, 126.7, 79.7, 45.6, 40.0, 21.0.

MS (EI, 70 eV): *m*/*z* = 255 (M^+), 208, 194, 118, 105, 91, 77.

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.58; H, 7.05; N, 5.06.

2-(2-Methoxyphenyl)-1-nitro-3-phenylpropane (3e)
Yellow oil.[16b]

IR (KBr): 3067, 3026, 2936, 2841, 1551, 1493, 1458 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.22 (m, 4 H, H_{arom}), 7.21–7.01 (m, 3 H, H_{arom}), 6.83 (d, *J* = 8.0 Hz, 2 H, H_{arom}), 4.76 (q, *J* = 7.6 Hz, 1 H, CH_2), 4.61 (q, *J* = 7.2 Hz, 1 H, CH_2), 4.05–4.08 (m, 1 H, CH), 3.83 (s, 3 H, OCH_3), 3.11–2.97 (m, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 138.6, 129.1, 128.9, 128.6, 128.4, 126.9, 126.5, 120.7, 110.9, 77.9, 55.3, 41.6, 37.8.

MS (EI, 70 eV): *m*/*z* = 271 (M^+), 224, 210, 180, 134, 91, 77.

2-(2-Chlorophenyl)-1-nitro-3-phenylpropane (3f)
Pale yellow oil.[16b]

IR (KBr): 3064, 3029, 2922, 2860, 1552, 1478, 1438 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.37 (m, 1 H, H_{arom}), 7.29–7.12 (m, 8 H, H_{arom}), 4.74–4.69 (m, 1 H, CH_2), 4.61–4.57 (m, 1 H, CH_2), 4.39–4.35 (m, 1 H, CH), 3.13–3.07 (m, 1 H, CH_2), 2.97–2.92 (m, 1 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.4, 136.4, 134.0, 130.2, 129.1, 128.6, 127.8, 127.2, 126.9, 77.4, 41.8, 38.4.

MS (EI, 70 eV): *m*/*z* = 275 (M^+), 245, 227, 214, 178, 138, 91, 77.

2-(2,4-Dichlorophenyl)-1-nitro-3-phenylpropane (3g)
White solid; mp 69 °C.

IR (KBr): 3079, 3025, 2957, 2916, 1587, 1549, 14734, 1442 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.40 (s, 1 H, H_{arom}), 7.30–7.21 (m, 4 H, H_{arom}), 7.11 (d, *J* = 8.0 Hz, 3 H, H_{arom}), 4.71–4.57 (m, 2 H, CH_2), 4.36–4.29 (m, 1 H, CH), 3.09–2.92 (m, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6, 137.2, 135.8, 133.9, 130.5, 129.9, 129.2, 128.4, 127.5, 78.7, 42.2, 39.2.

MS (EI, 70 eV): *m*/*z* = 309 (M^+), 263, 248, 178, 91, 75.

Anal. Calcd for $C_{15}H_{13}Cl_2NO_2$: C, 58.08; H, 4.22; N, 4.52. Found: C, 58.00; H, 4.56; N, 4.08.

2-(3,4-Dimethoxyphenyl)-1-nitro-3-phenylpropane (3h)
White solid; mp 75–77 °C.

IR (KBr): 3056, 3005, 2939, 2837, 1593, 1548, 1517, 1460, 1425 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.18 (m, 3 H, H_{arom}), 7.07–7.05 (m, 2 H, H_{arom}), 6.81–6.73 (m, 1 H, H_{arom}), 6.70 (d, *J* = 8.0 Hz, 1 H, H_{arom}), 6.58 (s, 1 H, H_{arom}), 4.57 (d, *J* = 6.8 Hz, 2 H, CH_2), 3.85 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 3.72–3.69 (m, 1 H, CH), 3.03–2.91 (m, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 148.4, 137.8, 131.4, 129.1, 128.5, 126.7, 119.3, 111.3, 110.8, 79.7, 55.9, 55.8, 45.6, 40.1.

MS (EI, 70 eV): *m*/*z* = 301 (M^+), 255, 241, 210, 165, 91, 77.

Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.59; H, 6.58; N, 4.34.

2-(3-Bromophenyl)-1-nitro-3-phenylpropane (3i)
White solid; mp 35–36 °C.

IR (KBr): 3060, 3028, 2918, 2855, 1595, 1549, 1478, 1434 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.39 (m, 1 H, H_{arom}), 7.33–7.28 (m, 1 H, H_{arom}), 7.26–7.16 (m, 4 H, H_{arom}), 7.07 (d, *J* = 6.4 Hz, 3 H, H_{arom}), 4.59–4.55 (m, 2 H, CH_2), 3.76–3.72 (m, 1 H, CH), 3.03–2.90 (m, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.4, 137.2, 130.9, 130.5, 130.4, 129.0, 128.7, 127.0, 126.2, 122.9, 79.1, 45.5, 39.8.

MS (EI, 70 eV): *m*/*z* = 319 (M^+), 271, 258, 192, 91, 77.

Anal. Calcd for $C_{15}H_{14}BrNO_2$: C, 56.27; H, 4.41; N, 4.37. Found: C, 56.23; H, 4.70; N, 3.90.

2-(2-Furyl)-1-nitro-3-phenylpropane (3j)
Yellow oil.[16b]

IR (KBr): 3063, 3030, 2924, 2860, 1551, 1501, 1451, 1431 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.37 (dd, *J* = 2.0, 0.8 Hz, 1 H, H_{arom}), 7.30–7.20 (m, 3 H, H_{arom}), 7.08–7.06 (m, 2 H, H_{arom}), 6.27–6.26 (m, 1 H, H_{arom}), 6.04 (d, *J* = 2.4 Hz, 1 H, H_{arom}), 4.61 (dd,

J = 12.8, 8 Hz, 1 H, CH_2), 4.52 (dd, J = 12.8, 6.4 Hz, 1 H, CH_2), 3.92–3.85 (m, 1 H, CH), 3.11 (dd, J = 13.6, 7.6 Hz, 1 H, CH_2), 2.94 (dd, J = 13.6, 7.6 Hz, 1 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 142.2, 137.4, 129.0, 128.6, 127.0, 110.4, 107.5, 77.3, 39.6, 37.3.

MS (EI, 70 eV): m/z = 231 (M^+), 184, 91, 77.

1-Nitro-3-phenyl-2-(2-thienyl)propane (3k)
Yellow oil.[16b]

IR (KBr): 3029, 2922, 1551, 1433 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.20 (m, 4 H, H_{arom}), 7.12 (d, J = 6.8 Hz, 2 H, H_{arom}), 6.91 (dd, J = 4.8, 3.6 Hz, 1 H, H_{arom}), 6.81 (d, J = 3.6 Hz, 1 H, H_{arom}), 4.56 (m, J = 7.2 Hz, 2 H, CH_2), 4.14–4.06 (m, 1 H, CH), 3.10 (dd, J = 13.6, 7.2 Hz, 1 H, CH_2), 3.00 (dd, J = 13.6, 7.2 Hz, 1 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 137.4, 129.0, 128.6, 127.0, 127.0, 125.5, 124.5, 80.0, 41.3, 40.8.

MS (EI, 70 eV): m/z = 247 (M^+), 200, 110, 91, 77, 65.

1-(4-Chlorophenyl)-3-nitro-2-phenylpropane (3l)
Pale yellow solid; mp 54–55 °C (Lit.[16b] 50–52 °C).

IR (KBr): 3030, 2922, 2857, 1555, 1489, 1450 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.26 (m, 3 H, H_{arom}), 7.21 (d, J = 4.8 Hz, 2 H, H_{arom}), 7.20–7.10 (m, 2 H, H_{arom}), 6.95 (d, J = 8.4 Hz, 2 H, H_{arom}), 4.64–4.57 (m, 2 H, CH_2), 3.75–3.68 (m, 1 H, CH), 2.96 (m, J = 8.0 Hz, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 136.2, 132.6, 130.4, 128.9, 128.6, 127.8, 127.5, 79.5, 45.9, 39.1.

MS (EI, 70 eV): m/z = 275 (M^+), 244, 227, 214, 178, 125, 104, 91, 77.

1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-3-nitropropane (3m)
White solid; mp 82–84 °C.

IR (KBr): 3038, 2927, 2846, 1611, 1547, 1436 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, J = 8.8 Hz, 2 H, H_{arom}), 7.02 (d, J = 6.4 Hz, 2 H, H_{arom}), 6.95 (d, J = 8.4 Hz, 2 H, H_{arom}), 6.82 (d, J = 6.8 Hz, 2 H, H_{arom}), 4.56 (d, J = 8.0 Hz, 2 H, CH_2), 3.77 (s, 3 H, OCH_3), 3.68–3.64 (m, 1 H, CH), 2.93 (d, J = 6.4 Hz, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 136.3, 132.5, 130.4, 130.3, 128.6, 128.5, 114.3, 79.8, 55.2, 45.2, 39.2.

MS (EI, 70 eV): m/z = 305 (M^+), 180, 134, 125, 91, 89.

Anal. Calcd for $C_{16}H_{16}ClNO_3$: C, 62.85; H, 5.27; N, 4.58. Found: C, 62.90; H, 5.61; N, 4.16.

1-(4-Chlorophenyl)-2-(4-methylphenyl)-3-nitropropane (3n)
White solid; mp 79–80 °C.

IR (KBr): 3022, 2923, 2859, 1551, 1488, 1435 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, J = 8.4 Hz, 2 H, H_{arom}), 7.09 (d, J = 7.6 Hz, 2 H, H_{arom}), 7.10–6.94 (m, 4 H, H_{arom}), 4.56 (d, J = 6.8 Hz, 2 H, CH_2), 3.70–3.65 (m, 1 H, CH), 2.93 (d, J = 7.2 Hz, 2 H, CH_2), 2.30 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 136.3, 135.3, 132.5, 130.4, 129.6, 128.6, 127.3, 79.7, 45.5, 39.1, 21.0.

MS (EI, 70 eV): m/z = 289 (M^+), 242, 228, 125, 118, 105, 89.

Anal. Calcd for $C_{16}H_{16}ClNO_2$: C, 66.32; H, 6.14; N, 3.97. Found: C, 66.08; H, 6.03; N, 4.15.

1-(4-Bromophenyl)-3-nitro-2-phenylpropane (3o)
White solid; mp 60 °C.

IR (KBr): 3030, 2921, 1558, 1487, 1438, 1384 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.24 (m, 5 H, H_{arom}), 7.11 (d, J = 6.8 Hz, 2 H, H_{arom}), 6.90 (d, J = 8.4 Hz, 2 H, H_{arom}), 4.60 (d, J = 7.2 Hz, 2 H, CH_2), 3.75–3.68 (m, 1 H, CH), 2.94 (d, J = 8.0 Hz, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 136.7, 131.6, 130.7, 128.9, 127.8, 127.5, 120.6, 79.5, 45.8, 39.2.

MS (EI, 70 eV): m/z = 319 (M^+), 273, 259, 169, 104, 90, 77.

Anal. Calcd for $C_{15}H_{14}BrNO_2$: C, 56.27; H, 4.41; N, 4.37. Found: C, 56.23; H, 4.73; N, 4.03.

1-(4-Bromophenyl)-2-(4-chlorophenyl)-3-nitropropane (3p)
White solid; mp 86–87 °C.

IR (KBr): 3025, 2922, 1550, 1487, 1430, 1380 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 2.0 Hz, 2 H, H_{arom}), 7.36 (d, J = 2.0 Hz, 2 H, H_{arom}), 7.04 (d, J = 7.2 Hz, 2 H, H_{arom}), 6.89 (d, J = 8.0 Hz, 2 H, H_{arom}), 4.57 (d, J = 7.2 Hz, 2 H, CH_2), 3.72–3.69 (m, 1 H, CH), 2.95–2.88 (m, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.9, 136.3, 133.7, 131.7, 130.7, 129.1, 128.9, 79.2, 45.2, 39.1.

MS (EI, 70 eV): m/z = 355 (M^+ + 2), 293, 178, 169, 103, 90, 77.

Anal. Calcd for $C_{15}H_{13}BrClNO_2$: C, 50.80; H, 3.69; N, 3.95. Found: C, 51.00; H, 4.18; N, 3.52.

Acknowledgment

The work was supported by the National Natural Science Foundation of China (Grant 20272047, 20572086), the Gansu Natural Science Foundation of China (0308RJZA-100) and Key Laboratory of Eco-Environment-Related Polymer Material (Northwest Normal University), Ministry of the Education of China.

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