

Indium Mediated Conjugate Addition of Allyl Bromide to Nitroalkenes in DMF-H₂O Media

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Allylindium bromide prepared by metallic indium and allyl bromide was added to nitroalkenes to give conjugate addition compounds in moderate to good yields in an aqueous media.

Keywords allylindium bromide, indium, nitroalkenes, conjugate addition, aqueous media

Among versatile metal-mediated organic transformations, syntheses involving indium are of current interest because of their distinctive mediatory ability for many organic reactions in aqueous media.¹ Such reactions can proceed in the absence of a dry organic solvent and have significant advantages that a conventional reaction does not exhibit. The metal-mediated addition of an allylic moiety to a carbon framework is particularly interesting.² Nitroalkenes can serve as important synthetic intermediates in organic synthesis.³ Initial reports⁴ of attempted 1,4-addition reaction between monosubstituted nitroalkenes and Grignard reagents does not sound encouraging as the reaction worked poorly because of the polymerization of nitroalkenes and the 1,2-addition reaction leading to very poor yields. However, there have been some positive reports on 1,4-addition reaction initiated by organometallics such as Grignard reagents,⁵ alkyllithium derivatives⁶ and triorganoalanes.⁷ Recently, Bao and Zhang⁸ applied allyl samarium bromide to the conjugate addition of monosubstituted nitroalkenes and got satisfactory results. But the reaction proceeded in anhydrous organic solvents. As metallic indium is a good metallic reagent in aqueous media, we tried to apply metallic in-

dium to mediate above reaction in aqueous media. In this paper, we wish to report the results of indium mediated conjugate addition of allyl bromide with nitroalkenes to give 4,5-unsaturated nitro compounds in aqueous media (as shown in Scheme 1).

Scheme 1

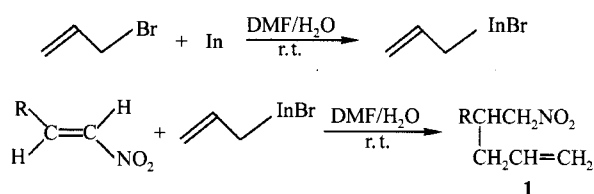


Table 1 summarized the results of the 1,4-addition of allyl bromide with substituted nitroalkenes mediated by metallic indium. The reaction proceeded smoothly and gave the products in satisfactory yields. For all the reactions, the 1,4-addition products, rather than 1,2-addition products, were obtained. Compared with the electron-donating groups, the electron-withdrawing groups, such as 4-NO₂C₆H₄ substituted nitroalkene, gave a much lower yield (Entry 7). The yield of addition of alkyl nitroalkene with allyl indium bromide was relatively lower (Entry 9).

Possible mechanism in this case could be that an allylindium reagent⁹ generated *in situ* readily undergoes 1,4-addition to the C=C bond of nitroalkenes in a

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DMF-H₂O medium (as shown in Scheme 1).

Table 1 Products and yields of indium mediated conjugate addition of allyl bromide with mononitroalkenes

Entry	R	Product	<i>t</i> (h)	Yield (%)
1	C ₆ H ₅	1a	3	87
2	3-BrC ₆ H ₄	1b	3	89
3	4-MeOC ₆ H ₄	1c	3	80
4	4-ClC ₆ H ₄	1d	3	86
5	4-MeC ₆ H ₄	1e	3	75
6	2,6-Cl ₂ C ₆ H ₃	1f	3	77
7	4-NO ₂ C ₆ H ₄	1g	5	51
8	C ₄ H ₃ O (2-Furyl)	1h	3	81
9	Me ₂ CHCH ₂	1i	5	56

In conclusion, it was found that indium was able to mediate conjugate addition of allyl bromide to mononitroalkenes to give 4,5-unsaturated nitro compounds in an aqueous media. The notable advantages of the reaction include mild conditions, short reaction time, simple operation and good yields.

Experimental

DMF was redistilled prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points were uncorrected. Infrared spectra were recorded on an IR-408 spectrometer with absorptions in cm⁻¹. ¹H NMR spectra were recorded on a Bruker AC-80 spectrometer using CDCl₃ as solvent. Chemical shifts are downfield from internal tetramethylsilane. Mass spectra were recorded on an HP 5989B MS spectrometer. Microanalysis was carried out on a Carlo-Erba 1106 instrument.

General procedure

A suspension of In powder (2 mmol) and allyl bromide (2 mmol) in 10 mL of DMF-H₂O (7.5:2.5) was stirred under nitrogen atmosphere at room temperature until the metal dissolved completely to form a clear solution. To the allyl indium bromide reagent generated above, a solution of nitroalkene in DMF (3 mL) was added. The reaction mixture was stirred for the duration of the given time (Table 1). After completion (as monitored by TLC), the reaction was quenched with aqueous ammonium chloride (10%, 5 mL) and extracted with

ether (20 mL × 3). The combined ether extracts were washed with saturated brine (15 mL), and dried over anhydrous sodium sulfate. After evaporating the solvent under reduced pressure, the crude product was purified by preparative thin layer chromatography on silica gel using ethyl acetate and cyclohexane (1:4) as the eluent to afford the pure product.

1a oil (lit.⁸); ¹H NMR (CDCl₃, 80 MHz) δ: 2.39 (t, *J* = 6.8 Hz, 2H), 3.42 (q, *J* = 7.0 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 2H), 4.80–5.09 (m, 2H), 5.27–5.95 (m, 1H), 7.15 (s, 5H); IR (film) ν: 3090, 3055, 2940, 1620, 1560, 1390, 910, 770, 690 cm⁻¹.

1b oil (lit.⁸); ¹H NMR (CDCl₃, 80 MHz) δ: 2.35 (t, *J* = 6.7 Hz, 2H), 3.42 (q, *J* = 7.0 Hz, 1H), 4.46 (d, *J* = 7.8 Hz, 2H), 4.80–5.09 (m, 2H), 5.27–5.96 (m, 1H), 7.00–7.63 (m, 4H); IR (film) ν: 3110, 3090, 2940, 1650, 1570, 1390, 1350, 1260, 960, 925, 780 cm⁻¹.

1c oil (lit.⁸); ¹H NMR (CDCl₃, 80 MHz) δ: 2.30 (t, *J* = 6.5 Hz, 2H), 3.35 (q, *J* = 7.0 Hz, 1H), 3.60 (s, 1H), 4.35 (d, *J* = 7.8 Hz, 2H), 4.75–5.05 (m, 2H), 5.25–5.90 (m, 1H), 6.83 (q, *J* = 8.5 Hz, 4H); IR (film) ν: 3090, 3015, 2950, 2850, 1650, 1565, 1390, 1310, 920, 820 cm⁻¹.

1d oil (lit.⁸); ¹H NMR (CDCl₃, 80 MHz) δ: 2.30 (t, *J* = 6.6 Hz, 2H), 3.41 (q, *J* = 7.2 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 2H), 4.75–5.05 (m, 2H), 5.25–5.85 (m, 1H), 7.15 (q, *J* = 7.0 Hz, 4H); IR (film) ν: 3100, 3055, 2940, 1660, 1560, 1390, 1345, 1095, 1020, 910, 785 cm⁻¹.

1e oil; ¹H NMR (CDCl₃, 80 MHz) δ: 2.39 (t, *J* = 6.8 Hz, 2H), 3.41 (q, *J* = 7.0 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 2H), 4.80–5.10 (m, 2H), 5.27–5.95 (m, 1H), 7.15 (s, 5H), 7.10–8.10 (m, 10H); IR (film) ν: 3100, 3060, 2940, 1610, 1550, 1390, 915, 780 cm⁻¹; MS (70 eV) *m/z* (%): 205 (M⁺, 100); Anal. calcd for C₁₂H₁₅NO₂: C 70.24, H 7.32, N 6.83; found C 70.16, H 7.37, N 6.74.

1f oil; ¹H NMR (CDCl₃, 80 MHz) δ: 2.39 (t, *J* = 6.8 Hz, 2H), 3.41 (q, *J* = 7.0 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 2H), 4.80–5.10 (m, 2H), 5.27–5.95 (m, 1H), 7.15 (s, 5H), 7.10–8.10 (m, 10H); IR (film) ν: 3090, 3055, 2940, 1620, 1560, 1390, 910, 780 cm⁻¹; MS (70 eV) *m/z* (%):

260 (M^+ , 100); Anal. calcd for $C_{11}H_{11}Cl_2NO_2$: C 50.77, H 4.23, N 5.38; found C 50.68, H 4.13, N 5.36.

1g oil (lit.⁸); 1H NMR ($CDCl_3$, 80 MHz) δ : 2.40 (t, $J = 6.6$ Hz, 2H), 3.55 (q, $J = 7.0$ Hz, 1H), 4.50 (d, $J = 6.0$ Hz, 2H), 4.80–5.08 (m, 2H), 5.25–5.95 (m, 1H), 7.25 (d, $J = 8.6$ Hz, 2H), 8.10 (d, $J = 8.8$ Hz, 2H); IR (film) ν : 3110, 3055, 2950, 2860, 1650, 1560, 1380, 1110, 920 cm^{-1} .

1h oil (lit.⁸); 1H NMR ($CDCl_3$, 80 MHz) δ : 2.39 (t, $J = 6.4$ Hz, 2H), 3.55 (q, $J = 7.0$ Hz, 1H), 4.40 (d, $J = 7.2$ Hz, 2H), 4.80–5.05 (m, 2H), 5.27–5.85 (m, 1H), 5.90 (d, $J = 3.5$ Hz, 1H), 6.15 (dd, $J = 3.5, 1.5$ Hz, 1H), 7.20 (d, $J = 1.4$ Hz, 1H); IR (film) ν : 3100, 3010, 2945, 1660, 1560, 1385, 1150, 1010, 910, 750 cm^{-1} .

1i oil (lit.⁸); 1H NMR ($CDCl_3$, 80 MHz) δ : 0.88 (d, $J = 6.0$ Hz, 6H), 1.15–1.80 (m, 3H), 1.90–2.55 (m, 3H), 4.20 (d, $J = 6.0$ Hz, 2H), 4.80–5.10 (m, 2H), 5.35–6.05 (m, 1H); IR (film) ν : 3090, 2980, 2950, 2890, 1650, 1560,

1390, 990, 920 cm^{-1} .

References

- Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*, John Wiley & Sons, Inc.: New York, 1997.
- Li, C. J. *Tetrahedron Lett.* **1996**, 37, 5643 and the references cited therein.
- McNulty, J.; Mo, R. *Chem. Commun.* **1998**, 933.
- (a) Kohler, E. P.; Stone, J. F. *J. Am. Chem. Soc.* **1930**, 52, 761.
(b) Buckley, G. D. *J. Chem. Soc.* **1947**, 1494.
- (a) Bowlus, S. B. *Tetrahedron Lett.* **1975**, 16, 3591.
(b) Ashwood, M. S.; Bell, L. A.; Houghton, P. G.; Wright, S. H. B. *Synthesis* **1988**, 379.
(c) Iida, T.; Funabashi, M.; Yoshimura, J. *Bull. Chem. Soc. Jpn.* **1973**, 46, 3202.
- Knochel, P.; Seebach, D. *Tetrahedron Lett.* **1981**, 22, 3223.
- Pecunioso, A.; Menicagli, R. *J. Org. Chem.* **1988**, 53, 45.
- Bao, W.; Zhang, Y. *J. Chem. Res.* **1999**, 732.
- Sampath Kumar, H. M.; Anjaneyulu, S.; Jagan Reddy, E.; Yadav, J. S. *Tetrahedron Lett.* **2000**, 41, 9311.

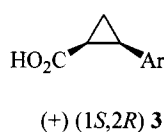
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Addition and Corrections

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FENG, Guo-Qiang (冯国强); **WANG, Mei-Xiang*** (王梅祥). Highly Enantioselective Microbial Hydrolysis of *cis*-2-Arylcyclopropanecarbonitriles.

Page 114, Scheme 1. The structure of (+) (1*S*, 2*R*) **3** should be drawn as follows:



The scheme in the graphic abstract of this paper should be drawn as follows:

