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## Nickel(II) Catalyzed Substitution Reactions of Nitro Group on 1-aryl-2-nitroethenes by Organozinc Halides

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**Abstract**: The nitro group of 1-aryl-2-nitroethenes was readily substituted by the organic moiety of organozinc halides in the presence of a catalytic amount of Ni $(acac)_2$  and tertiary amine to give 1-aryl-1-alkenes in excellent yields.

Organozinc reagents (R2Zn and RZnX) have proved to be versatile synthetic reagents in the last decades<sup>1</sup>. Complex functionalized organozinc reagents have great potential for natural-product synthesis<sup>2</sup>. Unfortunately they are relatively poor nucleophiles and do not react directly with most useful electrophiles such as aldehydes, ketones and organic halides. In 1978, Mukaiyama first reported that Et<sub>2</sub>Zn could add smoothly to benzaldehyde in the presence of aminoalcohols<sup>3</sup>. After this report, much attention has been given to the reaction<sup>4</sup>, especially the enantioselective addition reaction<sup>5</sup> of dialkylzinc compounds with aldehydes and ketones. In 1988, P. Knochel showed<sup>6</sup> that functional organozinc iodides R-ZnI could be transmetallized into organozinccopper reagents R-Cu(CN)ZnI with THF soluble copper salt CuCN · 2LiCl, and then coupled with acyl chlorides or conducted 1,4addition reaction with enones. This report greatly extended the application range of organozinc reagents in organic synthesis. Now these reagents have been successfully used in coupling reactions with organic halides, 1,2-addition reactions with aldehydes or ketones and 1,4-addition reactions with β-unsaturated carbonyl compound or nitro olefins<sup>1,4,7</sup>. However, stoichiometric CuCN · 2LiCl must be used in most of their reactions. In our previous report<sup>8</sup>, we used  $Cu(OAc)_2$  / LiCl as copper salt to carried out the 1,4-addition reaction with enones. Although the method avoided the use of toxic CN<sup>-</sup> ion in the reaction, the amount of Cu(OAc)<sub>2</sub> used was still stoichiometric. In this paper, we report that the nitro group of 1-aryl-2-nitroethenes can be substituted by organozinc halides under the catalysis of Ni(acac)<sub>2</sub> and a tertiary amine to give 1-aryl-1-alkenes in excellent yields (Scheme 1, Table I). A survey of the literature shows that a nitro group on an aromatic ring can be readily substituted by many organic nucleophiles<sup>9</sup>, and the nitro group of 1-aryl-2-nitroethenes can be replaced by dialkylzincs<sup>10</sup>.



Scheme 1

The organozinc reagents were obtained following P. Knochels procedure<sup>6</sup>, and then added into a mixture of  $Ni(acac)_2$  and tertiary amine at room temperature. The substitution reactions were carried out

at -18°C to room temperature. In the course of the reactions, the reaction mixture would become slightly brown from milky white. In the experiment, we find that the structure of nitro compounds have great influence on the reaction. When the nitro group is attached to an aromatic ring or a saturated carbon atom, the reactions are absolutely prohibited. For example, using nitrobenzene or 1-nitro-2-phenylheptane as substrate, over 95% will be recovered after reacting with R-ZnI for 20 hours. This indicates that the nitro group is not reduced in the course of the reaction. In the absence of Ni(acac)<sub>2</sub> and tertiary amine, the reaction was not successful. For example, no product was isolated after the reaction of 1-nitro-2-phenylethene and n-C<sub>5</sub>H<sub>11</sub>ZnI without Ni(acac)<sub>2</sub> and tertiary amine.

Compared with the similar reaction of dialkylzincs<sup>10</sup>, the reaction reported here has the following advantages: easier availability of organozinc iodides than dialkylzincs and higher yields of products.

Table I: Ni(II) catalyzed reaction of nitro olefins with organozinc iodides

Entry	R	Ri	L	Product <sup>a</sup>	Yield(%) <sup>b</sup>
1	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -	Н	Α	3a	88
2	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -	Н	В	3a	86
3	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -	Н	С	3a	91
4	Cl(CH <sub>2</sub> ) <sub>4</sub> -	Н	Α	3b	82
5	Cl(CH <sub>2</sub> ) <sub>4</sub> -	Н	С	3b	85
6	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -	o-Cl-	Α	3c	89
7	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -	o-Cl-	С	3c	90
8	Cl(CH <sub>2</sub> ) <sub>4</sub> -	o-Cl-	Α	3d	85
9	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -	o-CH <sub>3</sub> -	Α	3e	81
10	CH <sub>3</sub> CH <sub>2</sub> -	Н	А	3f	87
11	CH <sub>3</sub> CH <sub>2</sub> -	o-Cl-	Α	3g	82

a: The structures were determined by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and MS. b: Isolated yield.

## **Experimental Section**

General procedure: Under nitrogen atmosphere, a mixture of zinc (0.013 mol), 1,2-dibromoethane (0.04ml) and THF (2ml) in a three-neck flask was heated to  $60-70^{\circ}$ C for a minute and then cooled to room temperature. Chlorotrimethylsilane (0.05ml) was added, and the mixture was stirred at room temperature for 15 minutes. A solution of R-I (0.012mol) in THF (10ml) was then added, and the mixture was stirred for 12h at 35-40°C. The resulting solution of R-ZnI in THF was ready to use.

In another three neck flask, Ni $(acac)_2 (0.0012mol)$ , L (0.0024 mol for A and B, 0.0048 mol for C) and THF (10 mL) were added and heated at 60°C for 10 minutes. The solution of R-ZnI in THF obtained as above was added at room temperature, and the resulting mixture was cooled to -15°C. A solution of nitro olefin (0.01 mol) was added dropwise and the

temperature was allowed to rise to room temperature. After stirring for 18 hours, saturated NH<sub>4</sub>Cl solution (15 mL) and Et<sub>2</sub>O(15 mL) were added and the mixture was stirred for 20 minutes. The organic layer was separated, dried over anhydrous MgSO<sub>4</sub> and concentrated. The product was isolated from the crude reaction mixture by chromatography on silica gel ( petroleum/dichloromethane or diethyl ether).

 $\begin{array}{l} \textbf{3a Colorless liquid, IR } \upsilon_{max}(neat)/cm^{-1} 3057, 3026, 2959, 2928, 2856, \\ 1655, 1599, 1493, 1462, 962, 740, 692; {}^{1}\text{H NMR } \delta_{\text{H}}(80\text{MHz; CDCl}_3) \\ 7.35\text{-}7.19 \ (m, 5\text{H}), \ 6.51\text{-}6.19(m, 2\text{H}), \ 2.16(q, 2\text{H}, J=5.5\text{Hz}), \ 1.58\text{-}1.21(m, 6\text{H}), \ 0.90(t, 3\text{H}); {}^{13}\text{C NMR } \delta_c(100\text{Mhz; CDCl}_3) \ 137.9, \ 131.2, \\ 129.9, \ 1128.4(2\text{C}), \ 126.7, \ 125.9(2\text{C}), \ 33.0, \ 31.2, \ 29.1, \ 22.6, \ 14.1; \ \text{EI-MS } m/z \ 174(\text{M}^+, 58\%), \ 117(100), \ 104(99), \ 103(98), 91(78), \ 77(14) \end{array}$ 

**3b** Colorless liquid, IR  $\upsilon_{max}(neat)/cm^{-1}$  3080, 3026, 2955, 2933, 2864, 1651, 1597, 1577, 1493, 1446, 966, 742, 694, 650; <sup>1</sup>H NMR  $\delta_{H}(80MHz; CDCl_{3})$  7.36-7.04(m, 5H), 6.53-6.00(m, 2H), 3.54(t, 2H, J=6.2Hz), 2.37(q, 2H, J=6.8Hz), 2.36-1.49(m, 4H); EI-MS m/z 194(M<sup>+</sup>, 77%), 117(100), 104(68), 103(31), 91(94), 77(17)

 $\begin{array}{l} \textbf{3c} \mbox{ Colorless liquid, IR } \upsilon_{max}(neat)/cm^{-1} \ 3060, \ 3028, \ 2965, \ 2928, \ 2872, \\ 1648, \ 1596, \ 1567, \ 1468, \ 1437, \ 964, \ 745, \ 691; \ ^1H \ NMR \ \delta_H(80MHz; \\ CDCl_3) \ \ 7.56-7.13(m, \ 4H), \ \ 6.86-6.01(m, \ 2H), \ \ 2.03-3.13(q, \ 2H, \\ J=6.4Hz), \ 1.66-1.27(m, \ 6H), \ 0.91(t, \ 3H, \ J=5.5Hz); \ EI-MS \ m/z \ 208(M^+, \ 99\%), \ 173(19), \ 165(27), \ 151(100), \ 138(98), \ 125(97), \ 89(95), \ 77(8) \end{array}$ 

**3d** Colorless liquid, IR  $\nu_{max}(neat)/cm^{-1}$  3061, 3038, 2937, 2864, 2841, 1649, 1591, 1556, 1469, 1441, 966, 750, 694, 651; <sup>1</sup>H NMR  $\delta_{H}(80MHz; CDCl_{3})$  7.54-7.14(m, 4H), 6.68-6.05(m, 2H), 3.56(t, 2H, J=6.18Hz), 2.42-2.16(q, 2H, J=7.02Hz), 1.93-1.62(m, 4H); EI-MS m/z 230(M<sup>+</sup>, 40%), 195(5), 151(100), 150(99), 138(98), 125(71), 115(97), 77(10)

 $\begin{array}{l} \textbf{3e} \mbox{ Colorless liquid, IR } \upsilon_{max}(neat)/cm^{-1} \ 3030, \ 3001, \ 2937, \ 2928, \ 2856, \\ 2835, \ 1610, \ 1574, \ 1512, \ 1464, \ 1441, \ 1248, \ 964, \ 798; \ ^1H \ NMR \\ \delta_H(80MHz; \ CDCl_3) \ 7.32\ -6.84(m, \ 4H), \ 6.45\ -5.80(m, \ 2H), \ 3.78(s, \ 3H), \\ 2.21\ -2.13(m, \ 2H), \ 1.50\ -1.98(m, \ 6H), \ 0.90(t, \ 3H); \ EI\ MS \ m/z \ 204(M^+, \ 99\%), \ 147(100), \ 134(66), \ 121(65), \ 91(95), \ 90(53), \ 77(11) \end{array}$ 

**3f** Colorless liquid, IR  $v_{max}$ (neat)/cm<sup>-1</sup> 3028, 2967, 2930, 2874, 1651, 1599, 1493, 1452, 964, 742, 692; <sup>1</sup>H NMR  $\delta_{H}$ (80MHz; CDCl<sub>3</sub>) 7.41-7.10(m, 5H), 6.53-6.24(m, 2H), 2.40-2.07(m, 2H), 1.09(t, 3H),

J=7.35Hz); EI-MS m/z 132(M<sup>+</sup>, 99%), 117(100), 104(33), 103(35), 91(98), 77(76)

**3g** Colorless liquid, IR  $v_{max}$ (neat)/cm<sup>-1</sup> 3065, 2966, 2930, 2874, 1647, 1591, 1566, 1469, 1437, 964, 746, 690; <sup>1</sup>H NMR δ<sub>H</sub>(80MHz; CDCl<sub>3</sub>) 7.60-7.13(m, 4H), 6.88-6.05(m, 2H), 2.48-2.14(m, 2H), 1.11(t, 3H, J=7.43Hz); <sup>13</sup>C NMR δ<sub>c</sub>(100MHz; CDCl<sub>3</sub>) 135.9, 135.5, 132.5, 129.5, 127.8, 126.7, 126.5, 125.1, 26.3, 13.5; EI-MS m/z 166(M<sup>+</sup>, 99%), 151(100), 138(12), 131(97), 116(99), 91(73), 77(21)

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