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Communication

The cross-coupling reaction of vinylindiums generated via hydroindation of terminal alkynes with diaryliodoniums salts

Zhao Xue, DeYu Yang *, ChunYan Wang

Department of Chemistry, Zhejiang University (Xi-xi Campus), Tianmushan Road, Hangzhou, Zhejiang 310028, PR China

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Abstract

In $InCl_3$–$NaBH_4$–MeCN system, vinylindiums generated by hydroindation of aryl terminal alkynes can undergo cross-coupling reaction with diaryliodonium salts high regio- and stereoselectively. But under the same conditions, the aliphatic terminal alkynes do not react very well.

Keywords: Terminal alkynes; Diaryliodonium salts; (*E*)-disubstituted alkenes; Cross-coupling; Vinylindiums

1. Introduction

The cross-coupling reaction of organometallic reagents with organic halides has been proven to be an extremely powerful tool in organic synthesis for the selective formation of C–C bond [1,2]. Compared to aryl halides, aryliodonium salts showed high electrophilicity in the reaction with nucleophiles [3], in which the highly electron withdrawing nature of the ArI^+ moiety activated the carbon–iodine bond towards various reactions [4]. So lots of efforts have been devoted in the cross-coupling reaction of hypervalent iodine with alkenylmetallic reagents, such as alkenylcopper(I) [5], alkenylboron [6,8], alkenystannane [7,8] and alkenylzirconium [9]. However, up to now, the cross-coupling reaction of alkenylindium with diaryliodonium salts has not been reported.

Since dichloroindium hydride (Cl_2InH) was first generated using the transmetalation between indium trichloride and tributylstannane at −78 °C [10], it has received more and more attentions. Recently, it has been applied in organic synthesis widely, such as dehalogenation of alkyl halides and other radical cyclizations [11], cross-coupling reaction of terminal alkynes with iodides [12], dimerization of terminal alkynes [13] and reduction of alkynylphosphonates [14]. Our previous work showed that vinylindiums could be easily generated in situ by hydroindation of terminal alkynes in $InCl_3$–$NaBH_4$–MeCN system [13]. Now, this paper wants to report a regio- and stereoselective synthesis of (*E*)-disubstituted alkenes by vinylindiums coupling with diaryliodonium salts.

2. Results and discussion

To determine the optimum reaction conditions, we treated the di(*p*-methylphenyl)iodonium bromide with 4-bromophenylacetylene under different conditions. After a series of experiments, it was found that the preferable mole ratio of $InCl_3$, $NaBH_4$ and alkyne was 3:10:2. With this ratio, reaction occurred at −15 °C to give a quantitative yield of (*E*)-disubstituted alkene (**a**). The products were purified by silica gel column chromatography. The conversion and ratio of (*E*)-4-bromo-4′-methylstilbene (*E*-$\mathbf{I_a}$), (*Z*)-4-bromo-4′-methylstilbene (*Z*-$\mathbf{II_a}$) and 1-bromo-4-[1-(4-methylphenyl)ethenyl]benzene ($\mathbf{III_a}$) were detected by ^1H NMR

* Corresponding author. Tel.: +86 571 88739652; fax: +86 571 88212853.
E-mail address: deyu18@hotmail.com (D. Yang).

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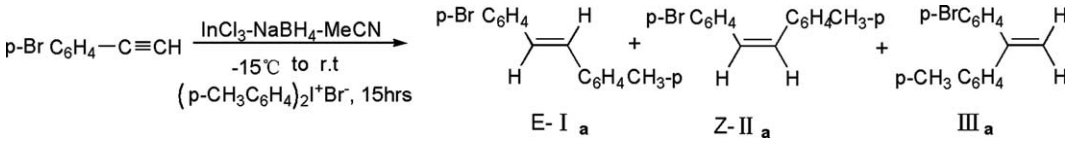
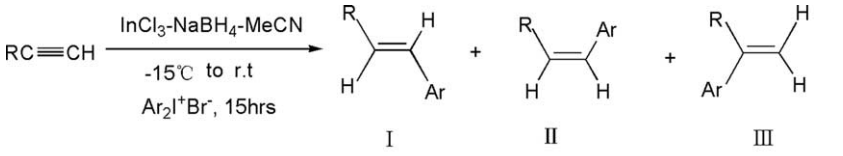


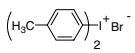
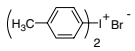
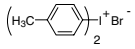
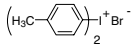
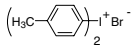
Scheme 1.



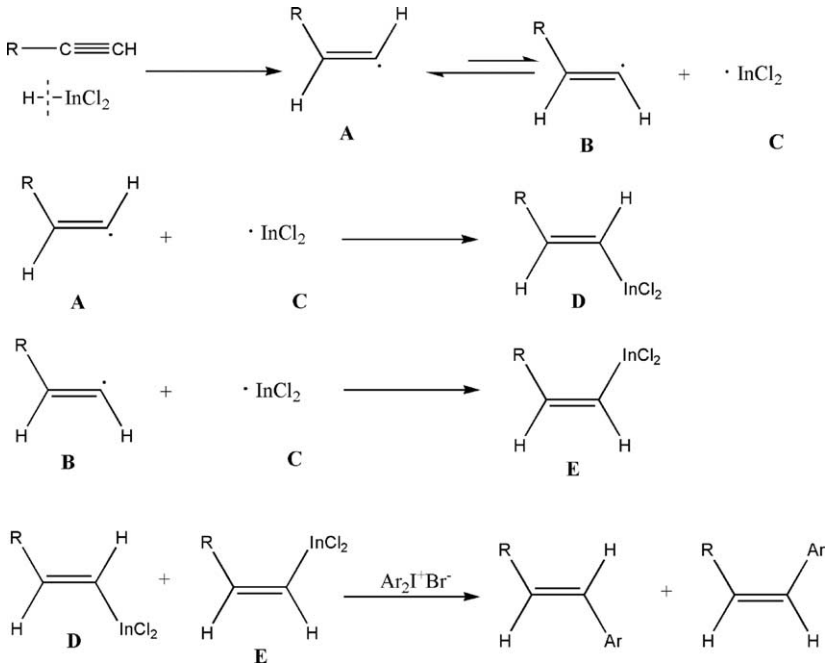
Scheme 2.

(400 MHz) and MS. The stereochemistry in the double bond C=C of the isomer (*E* or *Z*) was assigned on the basis of the value of the ^{1}H NMR coupling constants between the olefinic protons, which was consistent with the literature reported in the references cited [9]. *E*-**I$_a$** was the major product. The ratio of *E*-**I$_a$**, *Z*-**II$_a$** and **III$_a$** was 96:3:1, showing high regio- and stereoselectivity (Scheme 1). Furthermore, the yield of the reaction was satisfactory.

Table 1
The coupling reactions in $InCl_3$-$NaBH_4$-MeCN system

Entry	Terminal alkynes	Diaryliodonium salts	I:II:III[a]	Yield (%)[b]
a	p-BrC_6H_4C≡CH		96:3:1	83
b	PhC≡CH		95:3:2	81
c	p-$CH_3C_6H_4$C≡CH		88:9:3	86
d	p-$CH_3OC_6H_4$C≡CH		89:9:2	81
e			91:9:0	78
f	p-BrC_6H_4C≡CH	$Ph_2I^+Br^-$	96:3:1	81
g	PhC≡CH	$Ph_2I^+Br^-$	100:0:0	84
h	p-$CH_3C_6H_4$C≡CH	$Ph_2I^+Br^-$	94:5:2	83
i	p-$CH_3OC_6H_4$C≡CH	$Ph_2I^+Br^-$	92:8:0	80
j		$Ph_2I^+Br^-$	100:0:0	81
k	p-BrC_6H_4C≡CH		87:10:3	70
l	PhC≡CH		99:1:0	70
m	p-$CH_3C_6H_4$C≡CH		99:1:0	73
n	p-$CH_3OC_6H_4$C≡CH		81:17:2	69
o			91:9:0	61
p		Diaryliodonium[c]	–	–
q	n-$C_8H_{17}OCH_2$C≡CH	Diaryliodonium[c]	–	–
r	i-BuC≡CH	Diaryliodonium[c]	–	–

[a] Determined by ^{1}H NMR (400 MHz).
[b] Isolated yield by terminal alkynes.
[c] The diaryliodonium was $Ar_2I^+Br^-$ (Ar: Ph, *p*-$CH_3C_6H_4$, 2-thienyl).



Scheme 3.

Under the same conditions, a wide array of terminal alkynes were tested (Scheme 2). It was found that when R was the aryl group, such as Ph, *p*-$CH_3C_6H_4$, *p*-BrC_6H_4 or *p*-$CH_3OC_6H_4$, the reaction could take place smoothly (**a**–**d**, **f**–**i**, **k**–**n**). Both the selectivity and the yield were satisfactory. But when R was the aliphatic group, such as *i*-Bu, *n*-$C_8H_{17}OCH_2$ or cyclopropyl, no expected product was obtained (**p**, **q**, **r**). Interestingly, when (1-cyclohexen-1-yl)ethynyl was used as the aliphatic terminal alkyne, the desired cross-coupling product was obtained (**e**, **j**, **o**). In addition, compared with the reactions in which the 2, 2′-dithienyliodonium salts participated, the yields of these reactions in which the diphenyliodonium salts participated were higher. The products were determined by ^{1}H NMR and MS, which were consistent with the previous papers [15]. The results were listed in Table 1.

According to all these results, a plausible mechanism was proposed (Scheme 3) [13,14]. There is an equilibration between two configurations of the alkenyl radical (**A** and **B**). Furthermore, the intermediate **A** is more stable than **B**. A precedent for such an equilibration has been reported in the literature [16]. The radical intermediate in which aryl ring bears an electron-withdrawing group is more stable than the intermediate bearing an electron-releasing group. In this paper, the conjugation of the terminal alkynes could also make the radical intermediate (**A** and **B**) stable, but the radical intermediate generated from the aliphatic terminal alkynes is not stable enough to react with the diaryliodonium salts in our experiments.

In summary, $InCl_3$–$NaBH_4$–MeCN system was first employed in the cross-coupling reaction of vinylindiums with diaryliodonium salts successfully. The results showed that the presented method was efficient and simple to synthesize (*E*)-disubstituted alkenes without using the expensive palladium as catalyst.

3. Experimental

^{1}H NMR spectra were obtained with a Brucker AC-P-400 NMR spectrometer with TMS as an internal standard and $CDCl_3$ as solvent. Mass spectra were determined using a Finnigan Trace DSQ mass spectrometer. The reactions were carried out in pre-dried (150 °C, 4 h) glassware and cooled under a stream of dry nitrogen. Acetonitrile was freshly distilled from phosphorus pentoxide before use. Terminal alkynes [17] and diaryliodonium salts [18] were prepared according to the literature.

A general procedure was as follows: a mixture of $InCl_3$ (3 mmol) and $NaBH_4$ (10 mmol) in dry CH_3CN (10 ml) was stirred for 30 min at −15 °C under nitrogen, and terminal alkyne (2 mmol) was subsequently added. The mixture was stirred another an hour, and then diaryliodonium salts (2 mmol) was added. Followed by warming to room temperature automatically and the mixture was stirred for another 15 h. The reaction was quenched with 5 ml deionized water, filtered and the filtrate was extracted with ether (3 × 10 ml). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuum. Purification by silica gel column (100–200 mesh), using petroleum ether (b.p. 60–90 °C) as eluent could afford the corresponding products.

(*E*)-4-bromo-4′-methylstilbene (**I$_a$**) [15a], (*E*)-4-methylstilbene (**I$_b$**, **I$_h$**) [15b], (*E*)-4,4′-dimethylstilbene (**I$_c$**) [15a], (*E*)-4-methoxy-4′-methylstilbene (**I$_d$**) [15c,15d,15e], (*E*)-4-bromostilbene (**I$_f$**) [15c,15f], (*E*)-stilbene (**I$_g$**) [15b], (*E*)-4-methoxystilbene (**I$_i$**) [15b], (*E*)-1-(2-phenylethenyl)cyclohexene

($\mathbf{I_j}$) [15g], (*E*)-2-[2-(4-bromophenyl)ethenyl]thiophene ($\mathbf{I_k}$) [15h,15i], (*E*)-2-(2-phenylethenyl) thiophene ($\mathbf{I_l}$) [15j], (*E*)-2-[2-(4-methylphenyl)ethenyl]thiophene ($\mathbf{I_m}$) [15j], (*E*)-2-[2-(4-methoxyphenyl)ethenyl]thiophene ($\mathbf{I_n}$) [15h] were characterized comparing their physical properties and ^{1}H NMR spectra with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) data for $\mathbf{I_e}$: $\delta_H = 1.65$ (m, 2 H), $\delta_H = 1.74$ (m, 2 H), $\delta_H = 2.20$ (m, 2 H), $\delta_H = 2.26$ (m, 2 H), $\delta_H = 2.35$ (s, 3 H), $\delta_H = 5.69$ (t, 1 H, $J = 4.4$ Hz), $\delta_H = 6.43$ (d, 1 H, $J = 16.4$ Hz), $\delta_H = 6.74$ (d, 1 H, $J = 16.4$ Hz), $\delta_H = 7.13$ (d, 2 H, $J = 8$ Hz), $\delta_H = 7.31$ (d, 2 H, $J = 8$ Hz); MS (EI): 198 [M^+].

^{1}H NMR (400 MHz, $CDCl_3$) data for $\mathbf{I_o}$: $\delta_H = 1.62$ (m, 2 H), $\delta_H = 1.71$ (m, 2 H), $\delta_H = 2.17$ (m, 2 H), $\delta_H = 2.22$ (m, 2 H), $\delta_H = 5.87$ (t, 1 H, $J = 4$ Hz), $\delta_H = 6.56$ (d, 1 H, $J = 16$ Hz), $\delta_H = 6.61$ (d, 1 H, $J = 16$ Hz), $\delta_H = 6.93$ (m, 2H), $\delta_H = 7.10$ (d, 1 H, $J = 5.2$ Hz); MS (EI): 190 [M^+].

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References

[1] F. Diederich, P.J. Stang, Metal-Catalyzed Cross-Coupling Reactions, Wiley-VCH, Weinheim, 1998;
J. Tsuji, Palladium Reagents and Catalysts, Innovations in Organic Synthesis, Wiley, Chichester, UK, 1996;
N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[2] For example, see: I. Beletskaya, A. Pelter, Tetrahedron 53 (1997) 4957.
[3] M. Ochiai, K. Sumi, Y. Takaoka, M. Kunishima, Y. Nagao, M. Shiro, E. Fujita, Tetraheron 44 (1988) 4095;
M. Ochiai, K. Sumi, Y. Nagao, E. Fujita, Tetraheron Lett. 26 (1985) 2351.
[4] P.J. Stang, V.V. Zhdankin, Chem. Rev. 96 (1996) 1123;
A. Varvoglis, Hyper Valent Iodine in Organic Synthesis, Academic Press, London, 1997;
T. Wirth, U.H. Hirt, Synthesis (1999) 1271.
[5] P.J. Stang, T. Kitamura, J. Am. Chem. Soc. 109 (1987) 7561.
[6] S.K. Kang, H.W. Lee, S.B. Jang, P.S. Ho, J. Org. Chem. 61 (1996) 4720.
[7] S.K. Kang, H.W. Lee, J.S. Kim, S.C. Choi, Tetrahedron Lett. 37 (1996) 3723.
[8] S.K. Kang, T. Yamaguchi, T.-H. Kim, P.-S. Ho, J. Org. Chem. 61 (1996) 9082.
[9] X. Huang, A.M. Sun, Synth.Commun. 28 (1998) 773.
[10] T. Miyai, K. Inoue, M. Yasuda, I. Shibata, A. Baba, Tetrahedron Lett. 39 (1998) 1929.
[11] K. Inoue, A. Sawada, I. Shibata, A. Baba, Tretrahedron Lett. 42 (2001) 4661;
B.C. Ranu, S. Samanta, Tetrahedron 59 (2003) 7901;
K. Inoue, A. Sawada, I. Shibata, A. Baba, J. Am. Chem. Soc. 124 (2002) 906;
B.C. Ranu, S. Samanta, Tretrahedron Lett. 43 (2002) 7405;
B.C. Ranu, S. Samanta, J. Org. Chem. 68 (2003) 7130;
N. Hayashi, I. Shibata, A. Baba, Org. Lett. 6 (2004) 4981;
B.C. Ranu, A. Das, A. Hajra, Synthesis 7 (2003) 1012.
[12] K. Takami, S. Mikami, H. Yorimitsu, H. Shinokubo, K. Oshima, J. Org. Chem. 68 (2003) 6627;
K. Takami, H. Yorimitsu, K. Oshima, Org. Lett. 4 (2002) 2993.
[13] C.Y. Wang, H. Su, D.Y. Yang, Synlett 3 (2004) 0561.
[14] C.Y. Wang, Y.J. Pan, D.Y. Yang, J. Organomet. Chem. 690 (2005) 1705.
[15] (a) P. Warner, R. Sutherland, J. Org. Chem. 57 (1992) 6294;
(b) R.K. Arvela, N.E. Leadbeater, J. Org. Chem. 70 (2005) 1786;
(c) F. Babudri, G.M. Farinola, F. Naso, D. Panessa, J. Org. Chem. 65 (2000) 1554;
(d) S. Younes, G. Tchani, G.B. Mouysset, J.L. Stigliani, M. Payard, R. Bonnafous, J.T. Versailles, Eur. J. Med. Chem. 29 (1994) 87;
(e) J.E. Dubois, M.F. Ruasse, J. Org. Chem. 38 (1973) 493;
(f) N. Kumari, P.S. Kendurkar, R.S. Tewari, J. Organomet. Chem. 96 (1975) 237;
(g) M. Yus, A. Gutiérrez, F. Foubelo, Tetrahedron 57 (2001) 4411;
(h) I.S. Lee, H. Seo, Y.K. Chung, Organometallics 18 (1999) 1091;
(i) I.S. Lee, D.S. Choi, D.M. Shin, Y.K. Chung, C.H. Choi, Organometallics 23 (2004) 1875;
(j) K. Itami, T. Nokami, Y. Ishimura, K. Mitsudo, T. Kamei, J.i. Yoshida, J. Am. Chem. Soc. 123 (2001) 11577.
[16] M. Taniguchi, K. Nozaki, K. Miura, K. Oshima, K. Utimoto, Bull. Chem. Soc. Jpn. 65 (1992) 349.
[17] J.B. Lambert, E.G. Larson, R.J. Bosch, M.L.E. TeVrucht, J. Am. Chem. Soc. 107 (1985) 5443.
[18] F.M. Beringer, M. Drexler, E.M. Gindler, C.C. Lumpkin, J. Am. Chem. Soc. 75 (1953) 2705;
F.M. Beringer, H.E. Bachofner, R.A. Falk, M. Leff, J. Am. Chem. Soc. 80 (1958) 4279.