

An efficient synthesis of diynes using (diacetoxyiodo)benzene

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Abstract

A novel and facile method for synthesis of symmetrical conjugated diynes, using (diacetoxyiodo)benzene as oxidant under palladium-catalyzed conditions is presented, in which diynes are prepared in good yields in a short period of time at room temperature.

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1. Introduction

Diynes are very important compounds in terms of their chemistry and the solid state properties of their homopolymers [1]. The synthesis of diynes, in addition to the traditional Glaser oxidative dimerization of terminal acetylenes [2], they can be achieved by Pd(0)–Cu(I) catalyzed self-coupling of terminal alkynes in the presence of chloroacetone [3], ethyl bromoacetate [4], allyl bromide [5] and iodine [6], diynes were also prepared under standard Sonogashira cross-coupling conditions in the absence of an obvious oxidant [7]. Because palladium-catalyzed homocoupling of alkynes is quick, simple, mild and environmentally more benign, the research in exploring the scope of it is still a much-sought process.

(Diacetoxyiodo)benzene (DIB) is a most important, well investigated, and practically useful organic derivatives of iodine (III) [8]. As a general, universal oxidizing reagent, DIB has been widely used for the oxidation of phenols, enolizable ketones, alkenes, alkoxyallenes and so on [9]. We investigated the oxidative coupling of isopropylidene 5-alkylmalonates using (diacetoxyiodo)benzene [10] and now we wish to report a novel and facile method for the synthesis of symmetrical conjugated diynes by the reaction

of 1-alkynes with DIB in the presence of catalytic amounts of PdCl₂ and CuI, the good result is in agreement with that DIB is a good oxidizing reagent for the palladium-catalyzed homocoupling of alkynes.

2. Results and discussion

2.1. The homocoupling of phenylacetylene

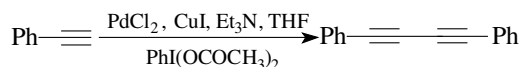
Initially, we mixed phenylacetylene with DIB and Et₃N in THF in the presence of catalytic amounts of PdCl₂ and CuI under N₂ at room temperature, we found that the homocoupling occurred easily and the product of diphenylbutadiyne was obtained in good yield in a short period of time. Then, we investigated the reaction in air, and found that reaction was also carried out fluently and the same result was achieved. In order to determine the optimum reaction conditions, a series of experiments were performed on the homocoupling of phenylacetylene using DIB as an oxidizing reagent, the results are summarized in Table 1.

It is shown from Table 1 that yield of the diyne depended on the amount of DIB used in the reaction: if DIB was not presented or only in catalytic amounts, the yields were poor (entries 1 and 15); however, when the amount was raised to 0.5 molar ratio of phenylacetylene or more, diyne was obtained in excellent yields (entries

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Table 1
The results of the homocoupling of phenylacetylene^a



Entry	DIB (equiv.)	Catalyst (2%)	Base (1.1 equiv.)	Solvent	Time (h)	Yield (%) ^b	
1	0.10	PdCl ₂	CuI	Et ₃ N	THF	0.5	33
2	0.35	PdCl ₂	CuI	Et ₃ N	THF	0.5	73
3	0.5	PdCl ₂	CuI	Et ₃ N	THF	0.5	88
4	1.0	PdCl ₂	CuI	Et ₃ N	THF	0.5	91
5	0.6	PdCl ₂	CuI	Et ₃ N	THF	0.5	90
6	0.6	PdCl ₂	CuI	Et ₃ N	DMF	0.5	82
7	0.6	PdCl ₂	CuI	Et ₃ N	CH ₃ CN	0.5	72
8	0.6	PdCl ₂	CuI	Et ₃ N	H ₂ O	0.5	67
9	0.6	PdCl ₂	CuI	Et ₂ NH	THF	0.5	88
10	0.6	PdCl ₂	CuI	<i>i</i> -Pr ₂ NH	THF	0.5	90
11	0.6	PdCl ₂	CuI	NaHCO ₃	THF	0.5	65
12	0.6	PdCl ₂	CuI	Na ₂ CO ₃	THF	0.5	71
13	0.6	PdCl ₂		Et ₃ N	THF	20	27
14	0.6		CuI	Et ₃ N	THF	0.5	12
15	0	PdCl ₂	CuI	Et ₃ N	THF	2.5	37

^a Reaction conditions: 1.0 mmol of phenylacetylene, 0.6 mmol of DIB, 1.1 mmol of Et₃N, PdCl₂ (2.0 mol%), CuI (2.0 mol%), THF (3 mL) at RT.

^b Isolate yields.

3–5). As a suitable solvent, THF was the most preferred (entries 5–8). Organic bases were better than inorganic bases, and the bases Et₃N, Et₂NH and *i*-Pr₂NH were almost effective (entries 5, 9 and 10). Without CuI, the homocoupling occurred slowly and a poor yield of diyne was afforded (entry 13). In the absence of PdCl₂, the reaction also yielded a small amount of diyne (entry 14). We also investigated the coupling reaction using Pd(OAc)₂ instead of PdCl₂, the same result was got; when PdCl₂(PPh₃)₂ was used, the reaction was somewhat slower and the yield in 0.5 h was lower compared with PdCl₂.

2.2. The homocoupling of terminal alkynes

Under the optimum reaction conditions, the homocoupling of a series of terminal alkynes using DIB as oxidizing reagent and Et₃N as a base in the presence of catalytic amounts of PdCl₂ and CuI was investigated, the good results are summarized in Table 2. It is shown that the homocoupling of terminal aromatic alkynes gave diynes in excellent yields (entries 1–3); while when aliphatic alkynes were used, the yields were somewhat lower (entries 4–6) compared with aromatic alkynes and the homocoupling needed to prolong the reaction time due to the weaker acidity of the acetylenic proton [11]. Using this protocol, the dimerization of 2-methyl-3-butyne-2-nol **1g** gave diyne **2g** in 62% yield after 3 h. However, switching to ethyl propionate resulted in no reaction [7].

2.3. Mechanistic consideration

Scheme 1 illustrates the proposed mechanism for the homocoupling of alkynes *via* a reductive elimination

from the dialkynylpalladium, which was derived from 1-alkyne and PdCl₂ in the presence of CuI and Et₃N. DIB was used to regenerate the Pd(II) catalyst by oxidative addition from the Pd(0) formed in the catalytic cycle, making the second reductive elimination possible and eventually converting all alkynes to the corresponding diynes.

In conclusion, we have successfully developed a novel and facile method for synthesis of symmetrical conjugated diynes by palladium-catalyzed homocoupling of terminal alkynes, using DIB to initiate the reaction. It has some advantages such as mild reaction conditions, simple procedure and good yields. Furthermore, the scope of palladium-catalyzed homocoupling of alkynes could be extended. Further investigation of the reactions will be reported in due course.

3. Experimental

3.1. General

IR spectra were recorded on a FT-170 SX instrument, ¹H NMR spectra were measured on a Broker AM-400 FT-NMR spectrometer, and Mass spectra were determined on HP5989A mass spectrometer. All terminal alkynes are commercially available.

3.2. The homocoupling of terminal alkynes

A typical reaction procedure: to a mixture of phenylacetylene (1.0 mmol), DIB (0.6 mmol), Et₃N (1.1 mmol), PdCl₂ (2.0 mol%) and CuI (2.0 mol%), THF (3 mL) was added. The mixture was stirred at room temperature for

Table 2
The results of the homocoupling of alkynes^a

Entry	Alkyne	Diyne	Time (h)	Yield (%) ^b
1	Ph—C≡C— 1a	2a	0.5	90
2	<i>p</i> -CH ₃ -C ₆ H ₄ —C≡C— 1b	2b	0.5	87
3	<i>p</i> -C ₂ H ₅ -C ₆ H ₄ —C≡C— 1c	2c	0.5	88
4	n-C ₄ H ₉ —C≡C— 1d	2d	1.0	70
5	n-C ₅ H ₁₁ —C≡C— 1e	2e	1.0	77
6	n-C ₆ H ₁₃ —C≡C— 1f	2f	1.0	74
7	Me C≡C— Me OH 1g	2g	3.0	62

^a Reaction conditions: 1.0 mmol of alkyne, 0.6 mmol of DIB, 1.1 mmol of Et₃N, PdCl₂ (2.0 mol%), CuI (2.0 mol%), THF (3 mL) at RT.

^b Isolated yields.

3.3. Diphenylbutadiyne (**2a**) [6]

¹H NMR (CDCl₃): δ = 7.32–7.36 (m, 6H), 7.50–7.55 (m, 4H); IR (film): ν = 3049, 2978, 2145, 1261, 730 cm⁻¹; MS (70 eV, EI) *m/z* (%): 202 (M⁺, 100).

3.4. Bis(4-methylphenyl)butadiyne (**2b**) [12]

¹H NMR (CDCl₃): δ = 2.39 (s, 3H), 7.25 (d, *J* = 11.0 Hz, 4H), 7.42 (d, *J* = 11.0 Hz, 4H); IR (film): ν = 3060, 2988, 2133, 1267, 751 cm⁻¹; MS (70 eV, EI) *m/z* (%): 230 (M⁺, 100).

3.5. Bis(4-ethylphenyl)butadiyne (**2c**) [4]

¹H NMR (CDCl₃): δ = 1.23 (t, *J* = 7.6 Hz, 6H), 2.65 (q, *J* = 7.6 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 7.42 (d, *J* = 8.0 Hz, 4H); IR (film): ν = 3051, 2991, 2152, 1268, 743 cm⁻¹; MS (75 eV, EI) *m/z* (%): 258 (M⁺, 100).

3.6. 5,7-Dodecadiyne (**2d**) [12]

¹H NMR (CDCl₃): δ = 0.90 (t, *J* = 7.2 Hz, 6H), 1.36–1.44 (m, 4H), 1.45–1.54 (m, 4H), 2.24 (t, *J* = 6.8 Hz, 4H); IR (film): ν = 2966, 2140, 1259, 736 cm⁻¹; HRMS (EI) calcd. for C₁₂H₁₈ M⁺ 162.1409, found: 162.1401.

3.7. 6,8-Tetradecadiyne (**2e**) [12]

¹H NMR (CDCl₃): δ = 0.89 (t, *J* = 7.2 Hz, 6H), 1.24–1.40 (m, 8H), 1.48–1.55 (m, 4H), 2.24 (t, *J* = 7.2 Hz, 4H); IR (film): ν = 2971, 2152, 1256, 744 cm⁻¹; HRMS (EI) calcd. for C₁₄H₂₂ M⁺ 190.1722, found: 190.1712.

3.8. 7,9-Hexadecadiyne (**2f**) [13]

¹H NMR (CDCl₃): δ = 0.89 (t, *J* = 7.2 Hz, 6H), 1.18–1.40 (m, 12H), 1.45–1.56 (m, 4H), 2.22 (t, *J* = 6.8 Hz, 4H); IR (film): ν = 2982, 2133, 1263, 741 cm⁻¹; HRMS (EI) calcd. for C₁₆H₂₆ M⁺ 218.2035, found: 218.2022.

3.9. 2,7-Dimethylocta-3,5-diyne-2,7-diol (**2g**) [14]

¹H NMR (CDCl₃): δ = 1.37 (s, 12H), 2.52 (s, 2H); IR (film): ν = 3279, 3211, 2924, 2120, 1216, 1170 cm⁻¹; MS (75 eV, EI) *m/z* (%): 166 (M⁺, 1.2), 43 (100).

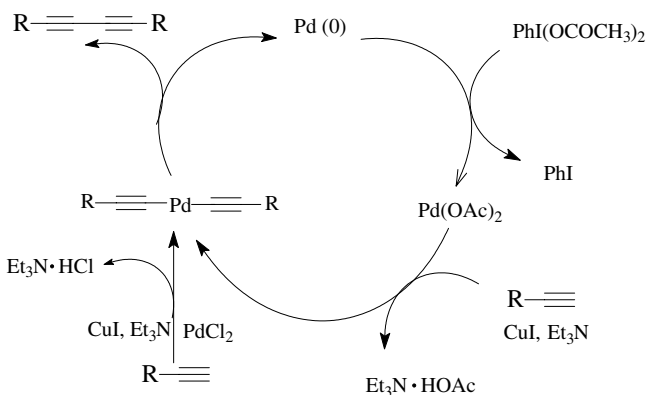
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0.5 h and then separated by a silica gel plate using petroleum ether as developer, the product of diphenylbutadiyne (**2a**) was afforded in 90% yield.



Scheme 1.

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