# **Application of Iodanes to the Dimerization of Terminal Alkynes**

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**Abstract:** The dimerization of terminal acetylenes was studied using iodanes as oxidants under palladium-catalyzed conditions. It was found that a number of iodanes were useful in the reaction, with (diacetoxyiodo)benzene and iodosylbenzene being the best oxidants. Diynes were prepared in the dimerization in good yields in a short period of time at room temperature.



PdCl<sub>2</sub>, Cul. Et<sub>3</sub>N, THF

Key words: dimerization, diyne, iodane, (diacetoxyiodo)benzene, iodosylbenzene

Diynes are very important compounds in terms of their chemistry and the solid state properties of their homopolymers.<sup>1</sup> This type of compound can be synthesized by the traditional Glaser oxidative dimerization of terminal acetylenes<sup>2</sup> and can also can be formed by Pd(0)–Cu(I)catalyzed self-coupling of terminal alkynes in the presence of chloroacetone,<sup>3</sup> ethyl bromoacetate,<sup>4</sup> ally bromide<sup>5</sup> and iodine.<sup>6</sup> The dimerization of terminal alkynyl halides with terminal alkynes is another route to diynes under palladium-catalyzed conditions.<sup>7</sup> Fairlamb et al. reported the preparation of diynes under standard Sonogashira cross-coupling conditions in the absence of an obvious oxidant.<sup>8</sup> Because palladium-catalyzed homocoupling of alkynes is quick, simple, mild and environmentally more benign, research towards exploring the scope of its use is still required.

Our recent interest has been in the development of new synthetic methods using hypervalent iodine compounds because their chemical properties and reactivity are similar to those of Hg(II), Tl(III) and Pb(IV), but without the toxic and environmental problems associated with such heavy metal congeners. (Diacetoxyiodo)benzene (DIB) is one of the most important, well-studied and practically useful, commercially available hypervalent iodine compounds.<sup>9</sup> As a general, universal oxidizing reagent, DIB has been widely used for the oxidation of, for example, phenols, enolizable ketones, alkenes and alkoxyallenes.<sup>10</sup> Recently, we investigated the dimerization of terminal acetylenes using DIB as an oxidant and found that this reaction could be conveniently carried out in the presence of catalytic amounts of palladium(II) chloride and copper(I) iodide in tetrahydrofuran (Scheme 1).<sup>11</sup>

SYNTHESIS 2007, No. 9, pp 1301–1303 Advanced online publication: 05.04.2007 DOI: 10.1055/s-2007-966008; Art ID: P00207SS © Georg Thieme Verlag Stuttgart · New York In order to extend the scope of the dimerization and to find more mild, efficient oxidants, we investigated other hypervalent iodine compounds as oxidants in the dimerization of phenylacetylene. It was found that a number of iodanes were useful oxidants in the dimerization under the following reaction conditions:<sup>11</sup> phenylacetylene (1.0 mmol), iodane (0.6 mmol), triethylamine (1.1 mmol), palladium(II) chloride (2.0 mol%) and copper(I) iodide (2.0 mol%) stirred for 30 minutes in tetrahydrofuran (3 mL). When catalytic amounts of triphenylphosphine was added to the mixture in a triphenylphosphine-to-palladium(II) chloride ratio of 3:1, the yields of the dimerization were almost quantitative when DIB or iodosylbenzene were used. Under the optimum conditions, the dimerization of phenylacetylene with a range of iodanes is shown in Scheme 2 and the results are summarized in Table 1.

$$Ph \longrightarrow \frac{PdCl_2, Cul, PPh_3, Et_3N}{iodane THF} Ph \longrightarrow Ph \longrightarrow Ph$$

#### Scheme 2

Fable 1	Dimerization	of Phenylacet	tylene with Iodanes
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Entry	Iodane	Yield (%) <sup>a</sup>	
1	PhI(OAc) <sub>2</sub>	96	
2	PhI=O	96	
3	p-ClC <sub>6</sub> H <sub>4</sub> I(OAc) <sub>2</sub>	92	
4	Ph-I OTs	72	
5	OH C C C C C C	68	
6	PhI(CO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	58	

<sup>a</sup> Isolated yields.

As can be seen in Table 1, yields were almost quantitative when DIB or iodosylbenzene were used as oxidants (entries 1 and 2), while when (diacetoxyiodo)-4-chlorobenzene was used, the yield of 92% was somewhat lower (entry 3). Only a moderate yield of 58% was obtained using [bis(trifluoroacetoxy)iodo]benzene as oxidant due to partial decomposition of the reagent during the reaction (entry 6). Two further iodanes used in the reaction gave the product diphenylbutadiyne in good yields.

The excellent yields obtained confirmed that iodosylbenzene was comparable to DIB as an oxidizing agent for the palladium-catalyzed dimerization of terminal alkynes. Under the optimum conditions described above, we studied the dimerization of a series of terminal alkynes using iodosylbenzene as an oxidant (Table 2). It can be seen that the dimerization 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). The reduction in the yields and increased reaction times required for the dimerization of aliphatic, compared with aromatic alkynes, presumably stems from the lower acidity of the acetylinic proton.<sup>12</sup>

 Table 2
 Dimerization of Terminal Alkynes using Iodosylbenzene as Oxidant

R	PdCl <sub>2</sub> , Cul, PPh <sub>3</sub> , Et <sub>3</sub> N PhI=O, THF	- R- <u>-</u>	R	
Entry	Alkyne	Diyne	Time (h)	Yield (%) <sup>a</sup>
1	Ph	2a	0.5	96
2	<b>1а</b> <i>р</i> -МеС <sub>6</sub> Н <sub>4</sub>	2b	1.0	82
3	1b <i>p</i> -EtC <sub>6</sub> H <sub>4</sub>	2c	1.0	84
4	1c n-Bu	2d	2.0	80
5	1d <i>n</i> -C <sub>5</sub> H <sub>11</sub>	2e	2.0	70
6	1e <i>n</i> -C <sub>6</sub> H <sub>13</sub>	2f	2.0	72
	1f			

<sup>a</sup> Isolated yields.

The proposed mechanism for the dimerization of alkynes is shown in Scheme 3, using DIB as a representative iodane. Firstly, the terminal alkyne reacted with palladium(II) chloride to form the dialkynylpalladium, in the presence of copper(I) iodide and triethylamine, which is then transformed to the diyne via a reductive elimination. DIB then regenerates the Pd(II) catalyst by oxidative addition of the Pd(0) formed in the catalytic cycle, making further reductive elimination possible.



Scheme 3

In conclusion, the dimerization of terminal acetylenes was studied, using iodanes as oxidants, under palladium-catalyzed conditions. (Diacetoxyiodo)benzene and iodosylbenzene were found to be the best oxidants. Following this protocol, diynes were prepared in good to excellent yields rapidly, at room temperature, using iodosylbenzene as oxidant.

IR spectra were recorded on a FT-170 SX instrument. <sup>1</sup>H NMR spectra (400 MHz) were measured on a Bruker AM-400 FT-NMR spectrometer. Mass spectra were determined on a HP5989A mass spectrometer. Iodanes were prepared according to literature procedures.<sup>13-17</sup> All terminal alkynes are commercially available.

#### **Terminal Alkyne Dimerization; General Procedure**

To a mixture of alkyne **1** (1.0 mmol), iodane (0.6 mmol), Et<sub>3</sub>N (1.1 mmol), PdCl<sub>2</sub> (2.0 mol%), CuI (2.0 mol%) and PPh<sub>3</sub> (6.0 mol%), THF (3mL) was added. The mixture was stirred at r.t. for 0.5–2.0 h and then separated on a silica gel plate using petroleum ether as solvent. Diyne **2** was afforded in good to excellent yield.

# Diphenylbutadiyne (2a)<sup>6</sup>

IR (film): 3049, 2978, 2145, 1261, 730 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.32–7.36 (m, 6 H), 7.50–7.55 (m, 4 H). MS (EI, 70 eV): *m*/*z* (%) = 202 (100) [M<sup>+</sup>].

# Bis(4-methylphenyl)butadiyne (2b)<sup>18</sup>

IR (film): 3060, 2988, 2133, 1267, 751 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.39 (s, 6 H), 7.25 (d, *J* = 11.0 Hz, 4 H), 7.42 (d, *J* = 11.0 Hz, 4 H). MS (EI, 70 eV): *m/z* (%) = 230 (100) [M<sup>+</sup>].

# Bis(4-ethylphenyl)butadiyne (2c)<sup>4</sup>

IR (film): 3051, 2991, 2152, 1268, 743 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.23 (t, *J* = 7.6 Hz, 6 H), 2.65 (q, *J* = 7.6 Hz, 4 H), 7.14 (d, *J* = 8.0 Hz, 4 H), 7.42 (d, *J* = 8.0 Hz, 4 H). MS (EI, 75 eV): *m*/*z* (%) = 258 (100) [M<sup>+</sup>].

# 5,7-Dodecadiyne (2d)<sup>18</sup>

IR (film): 2966, 2140, 1259, 736 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.90$  (t, J = 7.2 Hz, 6 H), 1.36–1.44 (m, 4 H), 1.45–1.54 (m, 4 H), 2.24 (t, J = 6.8 Hz, 4 H).

MS (EI, 70 eV): m/z (%) = 162 (100) [M<sup>+</sup>].

#### 6,8-Tetradecadiyne (2e)<sup>18</sup>

IR (film): 2971, 2152, 1256, 744 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.89$  (t, J = 7.2 Hz, 6 H), 1.24–1.40 (m, 8 H), 1.48–1.55 (m, 4 H), 2.24 (t, J = 7.2 Hz, 4 H). MS (EI, 70 eV): m/z (%) = 190 (100) [M<sup>+</sup>].

#### 7,9-Hexadecadiyne (2f)<sup>19</sup>

IR (film): 2982, 2133, 1263, 741 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.89$  (t, J = 7.2 Hz, 6 H), 1.18–1.40 (m, 12 H), 1.45–1.56 (m, 4 H), 2.22 (t, J = 6.8 Hz, 4 H). MS (EI, 70 eV): m/z (%) = 218 (100) [M<sup>+</sup>].

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