

## The Solvent Effect on the Chemoselectivity of Palladium-catalyzed Oligomerization of 3, 3-Dimethyl-1-butyne

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**Abstract:** The chemoselectivities of PdCl<sub>2</sub> and CuCl<sub>2</sub>-catalyzed oligomerization of 3, 3-dimethyl-1-butyne: 1, 3, 5-*tri-tert*-butylbenzene, 2, 2, 7, 7-tetramethyl-3, 6-dichloro-3, 5-octadiene and 2, 2, 7, 7-tetramethyl-3, 5-octadiyne were obtained, respectively, by regulating the polarity of the solvent.

**Keywords:** Solvent, chemoselectivity, palladium, oligomerization, 3, 3-dimethyl-1-butyne.

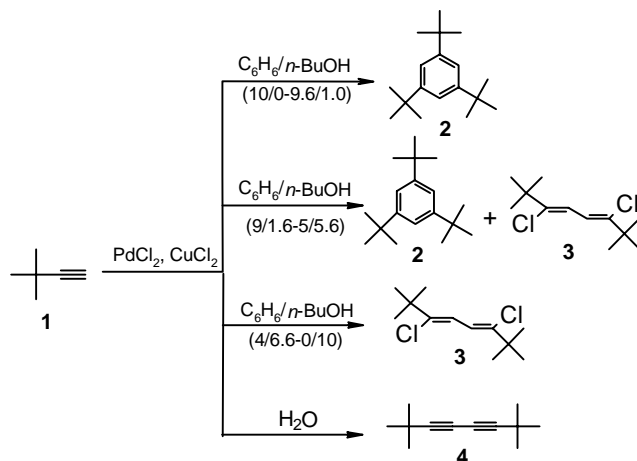
Recently, we found that the solvent plays an important role in the chemoselectivity using Pd (II) as the catalyst. This finding is expected to have a broad impact on studies of Pd (II)-catalyzed organic reactions leading to new methodology<sup>1</sup>. Herein we report another example of solvent effect on the chemoselectivity of palladium-catalyzed oligomerization of 3, 3-dimethyl-1-butyne.

It has been reported that Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> mediated a cyclotrimerization process of 3, 3-dimethyl-1-butyne at 20 °C<sup>2</sup>. The results indicated that the solvent could affect the chemoselectivity. We found that the similar phenomena by using a catalytic amount of PdCl<sub>2</sub> and 2 equiv. of CuCl<sub>2</sub> as the catalyst systems (**Scheme 1**). The results of PdCl<sub>2</sub> and CuCl<sub>2</sub>-catalyzed oligomerization of 3, 3-dimethyl-1-butyne were summarized in **Table 1**. As shown in **Table 1**, the solvents were crucial in the chemoselectivity of the oligomerization: (1) In C<sub>6</sub>H<sub>6</sub> / *n*-BuOH, the yields selectivity to cyclotrimerization product **2** and dimerization product **3** depends upon the C<sub>6</sub>H<sub>6</sub> / *n*-BuOH volumetric ratio: In C<sub>6</sub>H<sub>6</sub> alone (C<sub>6</sub>H<sub>6</sub>: 10.6 mL), 74% of the cyclotrimerization product **2** (1, 3, 5-*tri-tert*-butyl benzene) was obtained as the sole product; while in C<sub>6</sub>H<sub>6</sub> / *n*-BuOH (10 / 0.6), the yield of **2** was 100%. (2) When the C<sub>6</sub>H<sub>6</sub> / *n*-BuOH volumetric ratio was 9 / 1.6, the yield of cyclotrimerization product **2** together with the by-product **3** was 93% (the ratio of 2/3 is 85/15, **Table 1**, entry 6), *i.e.* the dimerization product **3** (2, 2, 7, 7-tetramethyl-3, 6-dichloro-3, 5-octadiene). The dimerization product **3** was dominant in increased C<sub>6</sub>H<sub>6</sub> / *n*-BuOH (≥6 / 4.6). (3) Only **3** was produced when the C<sub>6</sub>H<sub>6</sub> / *n*-BuOH volumetric ratio was not less than 4 / 6.6.

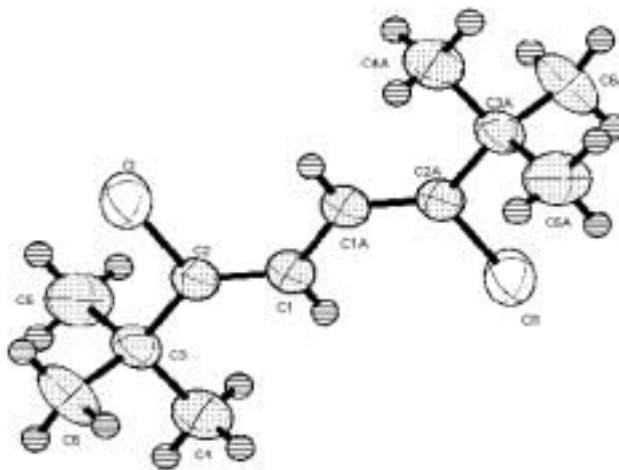
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Scheme 1



The structure of **3** was confirmed through X-ray crystallography (**Figure 1**), GC-MS,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectra<sup>3</sup>. (4) In  $\text{H}_2\text{O}$ , another dimerization product **4** (2, 2, 7, 7-tetramethyl-3, 5-octadiyne) was obtained as the sole product.

Figure 1 Crystal structure of **3**

When water was used as the reaction medium, only dimerization product **4** was obtained (entry 13, 14, **Table 1**).

The reaction temperature could affect the rate and yield of the cyclotrimerization to some extent, as shown in entries 2 and 3, **Table 1**. As the existence of some  $\text{CuCl}$  in  $\text{CuCl}_2$ , product **4** could also be yielded in the absence of  $\text{PdCl}_2$ .<sup>4, 5</sup>

In conclusion, we found that the solvents could control the chemoselectivity in the oligomerization reaction of **3**, 3,3-dimethyl-1-butyne with the catalyst system of  $\text{PdCl}_2$  and  $\text{CuCl}_2$ . It would not only allow us to construct some new reactions, but also let us to reconsider the role of the solvent in the Pd (II)-catalyzed reactions. Further efforts

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**Table 1** PdCl<sub>2</sub> and CuCl<sub>2</sub>-catalyzed oligomerization of 3, 3-dimethyl-1-butyne<sup>a</sup>

Entry	Solvent (ratio)	Time (h)	T (°C)	Isolated Yield (%)	
				<b>2 + 3 (2/3)</b>	<b>4</b>
1	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (10/0)	12	40	74 (100/0)	trace
2	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (10/0.6)	18	r.t.	85 (100/0)	trace
3	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (10/0.6)	12	40	100 (100/0)	0
4 <sup>b</sup>	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (10/0.6)	12	40	35 (100/0)	trace
5	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (9.6/1.0)	12	40	94 (100/0)	trace
6	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (9/1.6)	12	40	93 (85/15)	trace
7	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (8/2.6)	12	40	92 (68/32)	trace
8	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (7/3.6)	12	40	92 (52/48)	trace
9	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (6/4.6)	12	40	93 (39/61)	trace
10	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (5/5.6)	12	40	93 (8/92)	trace
11	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (4/6.6)	12	40	93 (0/100)	trace
12	C <sub>6</sub> H <sub>6</sub> / <i>n</i> -BuOH (3/7.6)	12	40	93 (0/100)	trace
13	H <sub>2</sub> O	12	40	trace(2)	45
14 <sup>c</sup>	H <sub>2</sub> O	12	40	0	17

<sup>a</sup> Reaction conditions<sup>2</sup>: alkyne **1** (1mmol), PdCl<sub>2</sub> (10 mg, 0.056 mmol) and CuCl<sub>2</sub> (2 mmol). <sup>b</sup> In the absence of CuCl<sub>2</sub>, the conversion of alkyne **1** is 41%. <sup>c</sup> In the absence of PdCl<sub>2</sub>, the conversion of alkyne **1** is 19%.

associated with the solvent effect on the chemoselectivity are under progress in our laboratory.

### Acknowledgments

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### References and Notes

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- Spectral data of the products **2**, **3**, and **4**: **2**: white crystal, mp 70~73°C (lit.<sup>6</sup> mp73°C) ; <sup>1</sup>H NMR δ 1.207 (s, 27H), 6.523 (s, 3H); <sup>13</sup>C NMR δ 28.9, 39.2, 117.9, 148.0; MS *m/z* 246 (M<sup>+</sup>), 219, 202, 199, 183, 163, 157, 143, 123, 107, 91, 77, 65, 57, 41, 29; **3**: white crystal, <sup>1</sup>H NMR δ 1.208 (s, 18H), 6.524 (s, 2H); <sup>13</sup>C NMR δ 28.8, 39.2, 76.7, 77.0, 77.3, 117.9, 148.0; MS *m/z* 234 (M<sup>+</sup>), 219, 199, 177, 163, 150, 143, 123, 107, 91, 77, 57, 41, 28. Found: C, 61.56 H, 9.01; Cl, 29.42 calcd. Crystal data: C<sub>6</sub>H<sub>10</sub>Cl, M=117.59, Crystals wre grown from petroleum ether, monoclinic, space group: P2(1)/n, a=6.2780(8), b=10.3432(14), c=10.6927 (15) Å, α=90, β=105.300(3), γ=90°, V=669.72(16) Å<sup>3</sup>, Z=4, D<sub>c</sub>=1.164g cm<sup>-3</sup>, λ=0.71073 Å, T= 293(2)K, μ=0.450mm<sup>-1</sup>, 4037 reflection measured, 1582 unique (R<sub>int</sub>=0.0750) were used in all calculations. Final R=0.0454(obs.), 0.0670(all); wR(F<sup>2</sup>)= 0.1140(obs.), 0.1222(all); **4**: solid, <sup>1</sup>H NMR δ 1.208 (s, 18H), 6.524 (s, 2H); <sup>13</sup>C NMR δ 28.8, 39.2, 76.7, 77.0, 77.3, 117.9, 148.0; MS *m/z* 162 (M<sup>+</sup>), 147, 132, 119, 105, 91, 77, 55, 41, 39.
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