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Solvent-controlled chemoselective palladium-catalyzed oligomerization of *tert*-butyl acetylene

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Abstract

A solvent-controlled chemoselective palladium-catalyzed oligomerization of *tert*-butyl acetylene was reported in this paper. The reaction was carried out smoothly in benzene/*n*-BuOH binary solvents system. When benzene, unpolar aprotic solvent, became preponderating in the binary solvents system, a cyclotrimerization process occurred to produce 1,3,5-tri-*tert*-butylbenzene via a mechanism of three acetylene molecular to insert step by step forming σ-butadienyl-Pd and σ-hexatrienyl-Pd intermediates, etc., while when the polar protic component *n*-BuOH, which dissolves more CuX_2 than benzene in the process, was increased to a certain extent in the binary solvents system, the reaction proceed readily to give (3*Z*, 5*Z*)-2,2,7,7-tetramethyl-3,6-dichloro-3,5-octadiene or (3*Z*, 5*Z*)-2,2,7,7-tetramethyl-3,6-dibromo-3,5-octadiene, respectively. Meanwhile, a coupling product 2,2,7,7-tetramethyl-3,5-octadiyne was given exclusively when the reaction was conducted in singular polar H_2O. Influences of the solvents, catalysts, as well as possible mechanisms in the reaction were discussed in this paper.

Keywords: Solvent-controlled; Oligomerization; *tert*-Butyl acetylene; Palladium-catalyzed; Chemoselectivity

1. Introduction

The development of novel palladium-catalyzed oligomerization of alkyne transformations to selectively construct benzene derivatives or conjugated diene skeletons is a promising area for exploration. Moreover, few reports on solvent-controlled chemoselective oligomerization of alkyne to substituted benzene or diene derivatives have been demonstrated [1,2]. We have recently reported the palladium-catalyzed [2 + 2 + 2] and [2 + 2 + 1] oligomerization of alkynes to form benzenes or cyclopentadiene products in different reaction medias (supercritical carbon dioxide or ionic liquids, etc.) [3,7], the reaction medias were found to influence reaction chemoseletivity to some extent.

Experimental results showed that traditional solvent could also influence the chemoselectivity of palladium-catalyzed oligomerization of alkynes. This finding was expected to have a broad impact on the studies of palladium-catalyzed organic reactions leading to new methodology [5,8].

tert-Butyl acetylene (3,3-dimethyl-1-butyne), typical terminal alkyne with bulky *tert*-butyl substituent, possesses some unique characteristics in the palladium-catalyzed oligomerization reaction. Ian P. Rothwell and his co-workers had developed a series titanium catalysts, which could controlled the chemoselectivity of the oligomerization reaction of *tert*-butyl acetylene to a certain degree, 1,3,5-tri-*tert*-butylbenzene, 1,3,6-tri(*tert*-butyl)fulvene or other oligomer were given in a controllable manner (Scheme 1) [4].

It has been reported that $Pd(PhCN)_2Cl_2$ mediated cyclotrimerization of *tert*-butyl acetylene at 20 °C [6]: (1) in acetone only a trimer product 1,3,5-tri-*tert*-butylbenzene was given and (2) while in C_6H_6 or CH_2Cl_2, a complicated palladic complex was obtained. These results indicated that besides catalysts, solvents could also affect the chemoselectivity in some cases. Herein, we report another example of solvent-controlled chemoselective palladium-catalyzed oligomerization of *tert*-butyl acetylene.

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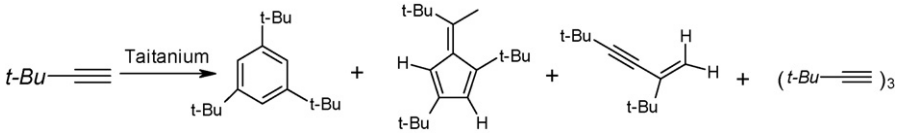


Scheme 1.

2. Results and discussion

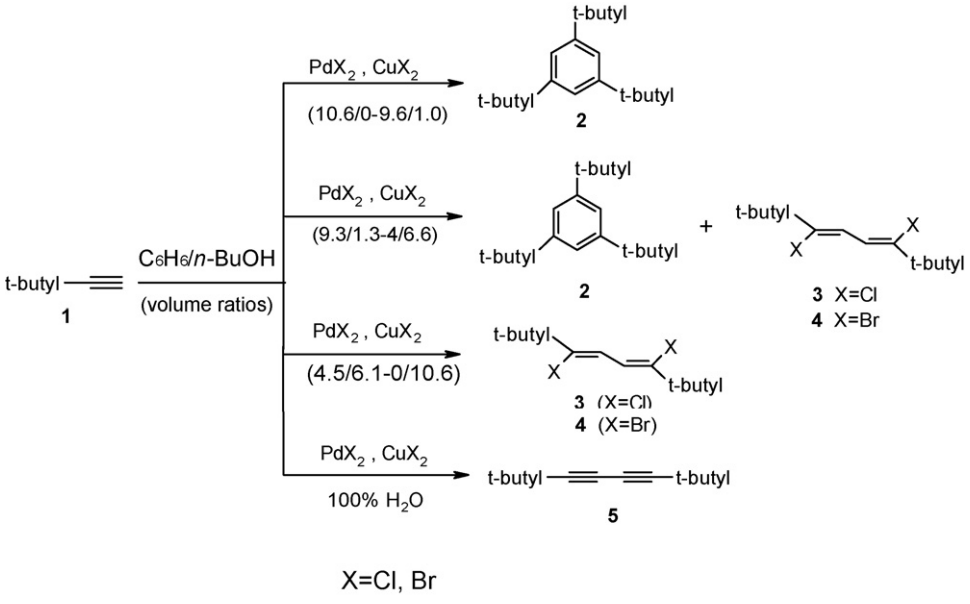
We carried out the oligomerization reaction in the presence of a catalytic amount of the palladium catalyst and 2 equiv. of cupric catalyst, and found that solvent choices play important roles in the palladium-catalyzed oligomerization of *tert*-butyl acetylene (Scheme 2).

We found that in the presence of 5 mol% of PdX_2 and 2 equiv. of CuX_2 (X = Cl, Br), the optimum yield of **2** (1,3,5-tri-*tert*-butylbenzene, Scheme 2) was observed when the volume ratio of benzene/*n*-BuOH was 10/0.6 (100%, entries 3–4, Table 1).

It was interesting that catalyzed by 5 mol% of $PdCl_2$ and 2 equiv. of $CuCl_2$, when the volume ratio of benzene/*n*-BuOH was changed to 3/7.6, 93% yield of **3** ((3*Z*, 5*Z*)-2,2,7,7-tetramethyl-3,6-dichloro-3,5-octadiene, Scheme 2) was given exclusively (entry 17, Table 1). Similarly, catalyzed by $PdBr_2$ and $CuBr_2$, in benzene/*n*-BuOH (with a volume ratio of 3/7.6), the reaction ran smoothly and 90% yield of **4** ((3*Z*, 5*Z*)-2,2,7,7-tetramethyl-3,6-dibromo-3,5-octadiene) was obtained (entry 19, Table 1), no **2** was observed in the above two processes, these results showed that both the catalysts (PdX_2 and CuX_2, X = Cl, Br) and solvents could affect the chemoselectivity of the reactions.

The results of PdX_2 and CuX_2-catalyzed oligomerization of *tert*-butyl acetylene were summarized in Table 1. As shown in Table 1, solvents were crucial for the chemoselectivity of the oligomerization reaction. In the presence of PdX_2 and CuX_2, the yield selectivity to cyclotrimerization product **2** and dimerization product **3** (or **4**) depends upon the volume ratios of C_6H_6/*n*-BuOH: (1) in C_6H_6 alone, 74% yield of **2** was given (entry 1, Table 1), while when the volume ratio was changed to 10/0.6, the yield of **2** increased rapidly to 100% (entries 3, 4, Table 1), (2) in a volume ratio of 9/1.6, the yield of **2** decreased distinctly, some by-products, **3** or **4**, was also observed (entries 8, 9, Table 1), (3) when the ratios of C_6H_6/*n*-BuOH range from 9/1.6 to 3/7.6, with the ratio of *n*-BuOH increased step by step, **3** (or **4**) became dominant product gradually. The structures of **3** and **4** were confirmed through GC–MS, ^{1}H NMR, ^{13}C NMR and IR spectra. Compound **3** was also confirmed by X-ray crystallography (Fig. 1), (4) in a range of 4/6.6–0/10.6 (volume ratio), product **3** (or **4**) was given exclusively. The optimum results were observed when the volume ratio was 3/7.6 (93% of **3** or 90% of **4**, entries 17 and 19, Table 1), (4) in H_2O, **5** (2,2,7,7-tetramethyl-3,5-octadiyne) was obtained for the sole product (entries 20–22, Table 1), (5) ratios 9.3/1.3 (C_6H_6/*n*-BuOH) and 4.5/6.1 were observed for two critical points, in a range of 9.3/1.3–4.5/6.1, a mixture of **2** and **3** (or **2** and **4**) were obtained.

The cage of **3** has a symmetric structure containing two conjugated double bonds, which attached to *tert*-butyl substituent and chlorine atom, respectively. The bond distance of C(1)–C(1A) is 1.444(4) Å, obviously shorter than the bond distance of C(2)–C(3) (1.509(3) Å), this could be explained by hybrid orbital theory: the former can be recognized as sp^2–sp^2, while the latter can be considered as sp^2–sp^3. Both the bond lengths of C(1)–C(1A) and C(2A)–C(3A) (confirmed for C–C bonds) are considerably longer than that of C(1)–C(2) (determined for a



Scheme 2.

Table 1
Solvent-controlled PdX_2 and CuX_2-catalyzed oligomerization of *tert*-butyl acetylene[a]

Entry	Solvent volume ratio[b]	Time (h)	T (°C)	Conversion[c] (%)	Isolated yield (%)	
					(**2/3** or **2/4**)	**5**
1	10.6/0	12	40	79	74 (**2/3**, 100/0)	Trace
2	10/0.6	18	r.t.	90	85 (**2/3**, 100/0)	Trace
3	10/0.6	12	40	100	100 (**2/3**, 100/0)	0
4[d]	10/0.6	12	40	100	100 (**2/3**, 100/0)	0
5[e]	10/0.6	12	40	41	35 (**2/3**, 100/0)	Trace
6	9.6/1.0	12	40	100	94 (**2/3**, 100/0)	Trace
7	9.3/1.3	12	40	100	89 (**2/3**, 93/7)	Trace
8	9/1.6	12	40	100	93 (**2/3**, 85/15)	Trace
9[d]	9/1.6	12	40	100	94 (**2/3**, 85/15)	Trace
10	8/2.6	12	40	100	92 (**2/3**, 68/32)	Trace
11	7/3.6	12	40	100	92 (**2/3**, 52/48)	Trace
12	6/4.6	12	40	100	90 (**2/3**, 52/48)	Trace
13	6.5/4.1	12	40	99	91 (**2/3**, 49/51)	Trace
14	5/5.6	12	40	100	89 (**2/3**, 8/92)	Trace
15	4.5/6.1	12	40	100	89 (**2/3**, 2/98)	Trace
16	4/6.6	12	40	100	92 (**2/3**, 0/100)	Trace
17	3/7.6	12	40	100	93 (**2/3**, 0/100)	Trace
18	0/10.6	12	40	100	78 (**2/3**, 0/100)	Trace
19[d]	3/7.6	12	40	100	90 (**2/4**, 0/100)	Trace
20	–[f]	12	40	45	Trace (**2**)	43
21	–[g]	12	40	19	0	17
22	–[h]	12	40	48	Trace (**2**)	46

[a] Reaction conditions: *tert*-butyl acetylene **1** (1 mmol), $PdCl_2$ (10 mg, 0.056 mmol), $CuCl_2$ (2 mmol), and benzene/*n*-BuOH (10.6 ml, desired volume ratio).
[b] Volume ratio of benzene/*n*-BuOH.
[c] Detected by GC.
[d] Catalyzed by $PdBr_2$ (0.056 mmol) and $CuBr_2$ (2 mmol) instead of $PdCl_2$ and $CuCl_2$.
[e] In the absence of CuX_2.
[f] 100% H_2O as the solvent instead of benzene/*n*-BuOH, $PdCl_2$–$CuCl_2$ was used for catalysts.
[g] 100% H_2O as the solvent instead of benzene/*n*-BuOH, only $CuCl_2$ was used for catalyst.
[h] 100% H_2O as the solvent instead of benzene/*n*-BuOH, $PdBr_2$–$CuBr_2$ was used for catalysts.

C=C bond conjugated with C1A–C2A). And the C–H distances were observed in a anticipated range of 0.92(3)–1.02(3) Å, e.g. bond C(1)–H(1A) 0.880 Å, bond C(4)–H(4A) 0.97 Å, bond C(4)–H(4C) 1.02 Å, etc. For the angles, both C(1)–C(2)–Cl and C(1A)–C(2A)–Cl(A) have a value of 117.95(14)°, while the angles of C(4)–C(3)–C(6) (108.4(4)°) and C(6)–C(3)–C(5) (109.0(4)°) are slightly different.

As a symmetrical molecular, bonds distances and angles in the symmetric parts were observed approximately identical, e.g. bonds lengths of Cl–C(2) (1.7460(19) Å) and ClA–C(2A) (1.7458(19) Å) are nearly identical, and the angles values for C(2)–C(3)–C(6) and C(2A)–C(3A)–C(6A) are equivalent (109.16(18)°).

Reaction temperature could also affect the palladium-catalyzed oligomeriztion of *tert*-butyl acetylene to some extent. At room temperature, 18 h was required and 85% yield of **2** was obtained (entry 2, Table 1). While controlled at 40 °C, only 12 h was needed, the reaction proceeded swimmingly with 100% yield of **2** (entry 3, Table 1).

Based on our previous reports [3,7], we proposed plausible pathways for the solvent-controlled palladium-catalyzed oligomerization of *tert*-butyl acetylene (Scheme 3): cyclotrimerization of *tert*-butyl acetylene would occur via pathway A, which was considered to involve a series of stepwise *cis* insertions of coordinated alkyne **1**. (i) Firstly, alkyne **1** inserts into a Cl–Pd bond giving **6**, (ii) into a vinyl–Pd bond giving a σ-butadienyl-Pd complex **7**, and (iii) then occurs to give a σ-hexatrienyl-Pd complex **8**; which undergoes an successive internal *cis* insertion. Because there is less steric hindrance in **8** (generated from intermediate **7**) than **8′** (generated from intermediate **7′**) during the subsequent ring-closure process [7(b)], intermediates **7** and **8** (instead of **7′** and **8′**) were formed in pathway A, (iv) to give the substitute palladiumcyclohexadiene **9**, with the assistance of CuX_2 [10], the reaction gave 1,3,5-tri-*tert*-butylbenzene **2** and regenerated the active PdX_2 (X = Cl and Br) quickly. Maitlis and his co-workers had laid emphasis on the mechanism induced by $CuCl_2$ [6].

Pathway B was a little different from pathway A, in pathway A, intermediate **7** was formed, with a series *cis* addition of alkyne **1**, product **2** was given in the final step. As state above, **7′** could not be formed in pathway A for steric hindrance reason, while it is interesting that in pathway B, intermediate **7′** was formed readily, with successive reaction with released halogen anion (X^-), product **3** (X = Cl) or **4** (X = Br) was given smoothly.

In the above two processes, the role of CuX_2 as an oxidant not only to cleave the C–Pd σ-bonds but to regenerates the active PdX_2 (X = Cl and Br) species by reoxidize Pd(0) formed in the process for further reaction cycle. It is noteworthy high ratio of

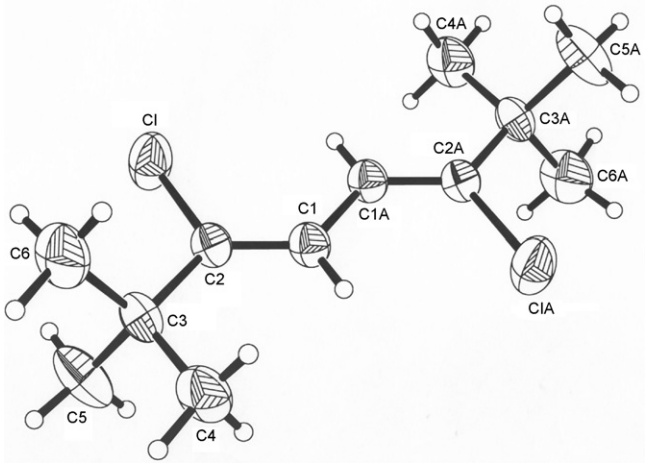


Fig. 1. Crystal structure of **3**. Selected bond lengths (Å) and angles (°) are Cl–C(2) 1.7460(19), ClA–C(2A) 1.7458(19), C(1)–C(2) 1.320(3), C(1A)–C(2A) 1.320(3), C(1)–C(1A) 1.444(4), C(2)–C(3) 1.509(3), C(2A)–C(3A) 1.509(3), C(3)–C(4) 1.513(3), C(3A)–C(4A) 1.513(3), C(3)–C(5) 1.524(3), C(3A)–C(5A) 1.524(3), C(3)–C(6) 1.523(3), C(3A)–C(6A) 1.523(3), C(1)–H(1A) 0.880(18), C(1A)–H(1a) 0.880(18), C(4)–H(4A) 0.97(3), C(4)–H(4B) 0.92(3), C(4)–H(4C) 1.02(3), C(4A)–H(4a) 0.98(3), C(4A)–H(4b) 0.92(3), C(4A)–H(4c) 1.01(3), C(5)–H(5A) 0.95(4), C(5A)–H(5a) 0.96(4), C(6)–H(6A) 0.98(3), C(6A)–H(6a) 0.97(3), C(2)–C(1)–C(1A) 127.5(2), C(2)–C(1)–H(1) 117.9(12), C(2A)–C(1A)–H(1a) 117.9(12), C(1)–C(2)–Cl 117.95(14), C(1A)–C(2A)–Cl(A) 117.95(14), C(2)–C(3)–C(4) 109.16(18), C(2A)–C(3A)–C(4A) 109.16(18), C(2)–C(3)–C(5) 109.16(18), C(2A)–C(3A)–C(5A) 109.16(18), C(2)–C(3)–C(6) 109.16(18), C(2A)–C(3A)–C(6A) 109.16(18), C(4)–C(3)–C(5) 109.8(4), C(4A)–C(3A)–C(5A) 109.7(4), C(4)–C(3)–C(6) 108.4(4), C(4A)–C(3A)–C(6A) 108.4(4), C(6)–C(3)–C(5) 109.0(4), C(6A)–C(3A)–C(5A) 109.0(4), C(3)–C(6)–H(6A) 105.9(16), C(3A)–C(6A)–H(6a) 109.5(16), C(3)–C(6)–H(6B) 105.9(16), C(3A)–C(6A)–H(6b) 109.5(16), C(3)–C(5)–H(5B) 109.5(16), C(3A)–C(5A)–H(5b) 109.5(16).

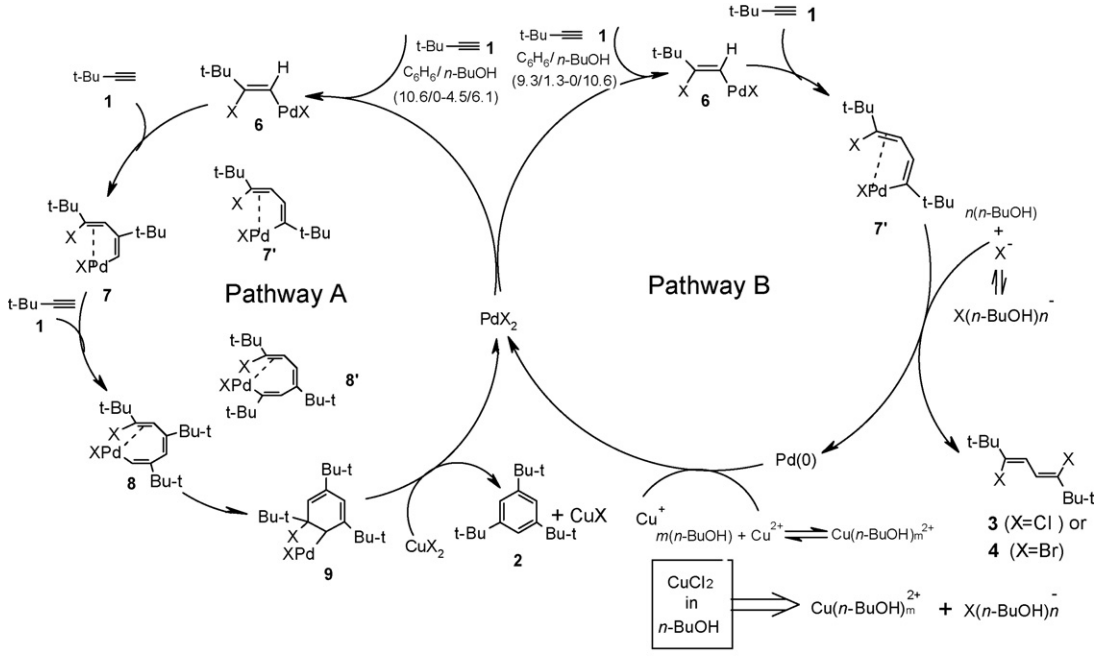
n-BuOH would lead to the formation of **3** or **4**, that is to say, *n*-BuOH, a polar protic solvent, play an important role in pathway B, a much more likely role of *n*-BuOH is that it dissolves more CuX_2 (X = Cl, Br) than benzene (for CuX_2 are typical ionic compounds). When the volume ratio of C_6H_6/*n*-BuOH ranged within (9.6/1.0–0/10.6), pathway B would occur. Higher ratio of *n*-BuOH helped to dissolve more CuX_2 (forming a cation of $Cu(n\text{-BuOH})_n^{2+}$ and solivated halo anion $X(n\text{-BuOH})_n^-$ [9]).

Obviously, CuX_2 ($X(n\text{-BuOH})_n^-$, X = Br, Cl, X^- was released in the reaction) are the halide source of **3** and **4**, and the more solivated halo anion $X(n\text{-BuOH})_n^-$ in solution, the more intermediate **7′** was formed (chemical balance shift right giving **3** or **4** are favorable for the formation of **7′** in pathway B).

Although higher ratio of *n*-BuOH were favorable for pathway B, small amount unpolar unprotic co-solvent benzene was also helpful for pathway B, in like wise, small portion of *n*-BuOH in pathway A was also helpful, these might be explained by component behavior in binary solvent system [9].

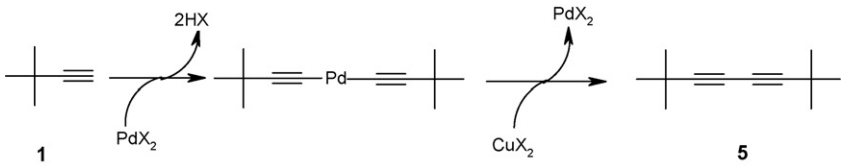
In water, an insertion reaction of PdX_2 with *tert*-butyl acetylene to give the sole dimer product **5** (Scheme 4) occurred. The reason why **5** could be yielded in the absence of PdX_2 is that there might be some CuX in CuX_2 [11].

In summary, we have developed a general solvent-controlled chemoselective PdX_2 and CuX_2-catalyzed oligomerization of *tert*-butyl acetylene. It would not only allow us to construct some new reactions, but also require us to reconsider the role of the solvent in the reported Pd(II)-catalyzed reactions. Further effort associated with solvent effect on the chemoselectivity and mechanistic investigations are currently under progress in our laboratory.



When the volume ratio of C_6H_6/*n*-BuOH vary within the range of (9.3/1.3-4.5/6.1), pathway A and pathway B proceed simultaneously, a complex of **2+3** or **2+4** will be given respectively.

Scheme 3.



Scheme 4.

3. Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 400 spectrometer in $CDCl_3$ with TMS as an internal standard. IR spectra were obtained with WQF-410 FTIR spectrometer. GC–MS were recorded on a HP 6890-5937 mass spectrometer. Elemental analyses were performed on a Heraeus CHN-O Rapid elemental analyzer instrument. HF_{254} plates were used for analytical TLC chromatography.

3.1. General procedure for the oligomerization of tert-butyl acetylene

To a mixture of PdX_2 (0.056 mmol) and CuX_2 (2 mmol) in benzene/*n*-BuOH (10.6 ml, desired volume ratio), *tert*-butyl acetylene (1.0 mmol) was added. Then, the reaction system was stirred at 40 °C for 12 h, after complete conversion of acetylene as monitored by GC analyses, the mixture was filtered, and the solvents was removed by rotary evaporation to give crude products. The products were then purified by flash column chromatography to afford **2**, **3**, **4**, **5**, respectively (hexane).

3.2. 1,3,5-Tri-tert-butylbenzene [7(b)] (2)

Hexane:EtOAc (9:1) was used as the eluent: solid, mp 70–73 °C (lit. mp 73 °C); ^{1}H NMR δ 1.207 (s, 27H), 6.523 (s, 3H); ^{13}C NMR δ 28.9, 39.2, 117.9, 148.0; MS *m/z* 246 (M^+), 219, 202, 199, 183, 163, 157, 143, 123, 107, 91, 77, 65, 57, 41, 29.

3.3. (3Z, 5Z)-2,2,7,7-Tetramethyl-3,6-dichloro-3, 5-dienes (3)

Hexane:EtOAc (3:7) was used as the eluent: white crystal, mp 67–68 °C; ^{1}H NMR (400 MHz) δ 1.208 (s, 18H), 6.524 (s, 2H); ^{13}C NMR (75 MHz) δ 28.8, 39.2, 76.7, 77.0, 77.3, 117.9, 148.0; IR (KBr): 1589, 1421, 896, 738 cm^{-1}; MS *m/z* 236 ($M^+(^{37}Cl)$) 234 ($M^+(^{35}Cl)$), 219, 199, 177, 163, 150, 143, 123, 107, 91, 77, 57, 41, 28. Anal. Found: C, 61.56; H, 9.01; Cl, 29.42.

3.4. Crystal data (3)

$C_6H_{10}Cl$, $M = 117.59$, crystals were grown from petroleum ether, monoclinic, space group: $P2(1)/n$, $a = 6.2780(8)$ Å, $b = 10.3432(14)$ Å, $c = 10.6927(15)$ Å, $\alpha = 90$, $\beta = 105.300(3)$, $\gamma = 90°$, $V = 669.72(16)$ $Å^3$, $Z = 4$, $D_c = 1.164$ g cm^{-3}, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $\mu = 0.450$ mm^{-1}, 4037 reflection measured, 1582 unique ($R_{int} = 0.0750$) were used in all calculations. Final $R = 0.0454$(obs.), 0.0670(all); $wR(F^2) = 0.1140$(obs.), 0.1222(all).

3.5. (3Z, 5Z)-2,2,7,7-Tetramethyl-3,6-dibromo-3, 5-dienes (4)

Hexane:EtOAc (3:7) was used as the eluent: white crystal, mp 74–75 °C; ^{1}H NMR (400 MHz) δ 1.230 (s, 18H), 6.590 (s, 2H); ^{13}C NMR (75 MHz) δ 29.2, 29.6, 31.6, 40.3, 119.4, 123.6, 144.7; IR (KBr): 1605, 1552, 1422, 896, 763 cm^{-1}; MS *m/z* 324 ($M^+(^{81}Br)$), 322 ($M^+(^{79}Br)$), 309, 245, 230, 213, 201, 187, 173, 164, 149, 133, 121, 107, 91, 77, 57, 41, 29. Anal. Found: C, 44.41, H, 6.21; Br, 49.36.

3.6. 2,2,7,7-Tetramethyl-3,5-octadiyne [12] (5)

Hexane:EtOAc (9:1) was used as the eluent: ^{1}H NMR (400 MHz) δ 1.227 (s, 18H); ^{13}C NMR (75 MHz) δ 28.8, 39.2, 76.7, 77.0, 77.3, 117.9, 148.0; IR (KBr): 2967, 1729, 1282, 1076, 881, 414 cm^{-1}; MS *m/z* 162 (M^+), 147, 132, 119, 105, 91, 77, 55, 41, 39.

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