Selective Cyclotrimerization of Acetylenes *via* Tantalum-Alkyne Complexes

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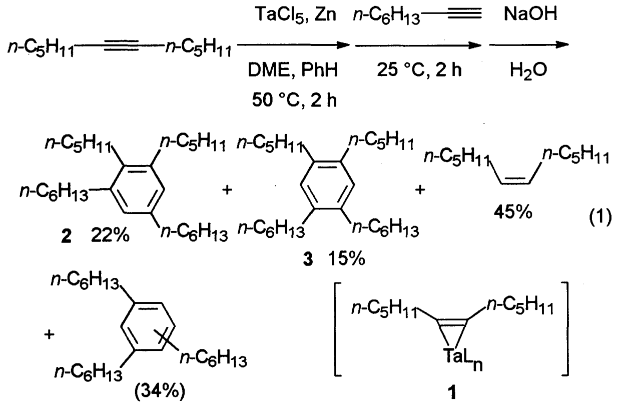
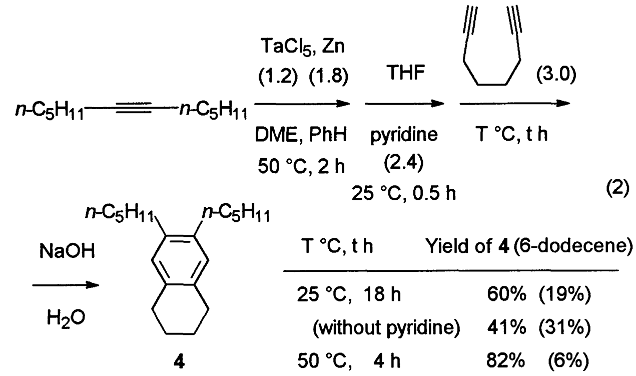
Tantalum-alkyne complexes prepared from internal acetylenes and low-valent tantalum ($\mathrm{TaCl_5}$ and Zn) in DME and benzene react with terminal diynes in the presence of THF and pyridine to give tetrasubstituted benzene derivatives in good to excellent yields.

Cyclotrimerization of acetylenes leading to benzene derivatives can be accomplished with a variety of transition metal catalysts, such as cobalt, rhodium, zirconium, and tantalum complexes.[1,2] During the research of tantalum-alkyne complexes,[3] we noticed that reactivity of the low-valent tantalum derived from $\mathrm{TaCl_5}$ and zinc toward acetylenes depends upon the solvent system and the substituents of acetylenes. For example, treatment of 6-dodecyne with the low-valent tantalum prepared in a mixed solvent of DME and benzene (1:1) at 25 °C produced smoothly a tantalum-6-dodecyne complex (**1**), and no cyclotrimerization was observed. In contrast, cyclotrimerization of 6-dodecyne took place with the low-valent tantalum prepared in benzene and pyridine (2.0 equiv of $\mathrm{TaCl_5}$) to furnish hexapentylbenzene in 87% yield. In the case of a terminal acetylene, cyclotrimerization took place even in a mixed solvent of DME and benzene (1:1). Addition of terminal acetylene, 1-octyne, to the reaction mixture of a tantalum-6-dodecyne complex (**1**) in DME-benzene (1:1) gave tetrasubstituted benzene **2** and **3** in 22% and 15% yields, respectively, along with 6-dodecene in 45% yield (eq. 1). Two regioisomeric trimers of 1-octyne were also produced in 34% combined yields based on 1-octyne. Under the same reaction conditions, internal acetylene, 7-tetradecyne, did not react with the tantalum complex **1**, and 7-tetradecyne was recovered in 84% yield.



(1)

Regioselective cyclotrimerization could be achieved by using terminal 1,ω-diynes (eq. 2). Treatment of a tantalum-6-dodecyne complex **1** with 1,7-octadiyne in a mixed solvent of DME-benzene-THF (1:1:1)[4] afforded tetrasubstituted benzene **4** in 41% yield. Yield of **4** depended on the reaction temperature, the period of addition of the diyne, and the amount of pyridine. When the diyne was added to the tantalum complex **1** at 50 °C over a period of 3 h in the presence of pyridine (2.4 equiv), the yield of the desired compound **4** was improved to 82%.

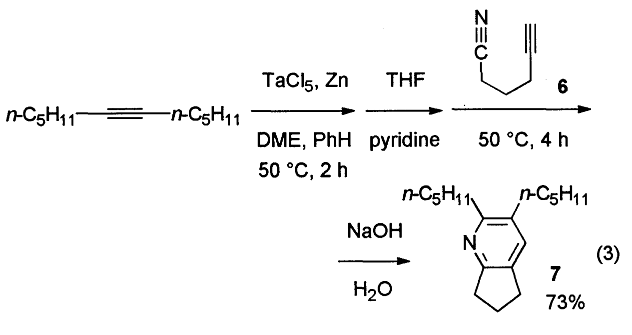


(2)

T °C, t h	Yield of **4** (6-dodecene)
25 °C, 18 h	60% (19%)
(without pyridine)	41% (31%)
50 °C, 4 h	82% (6%)

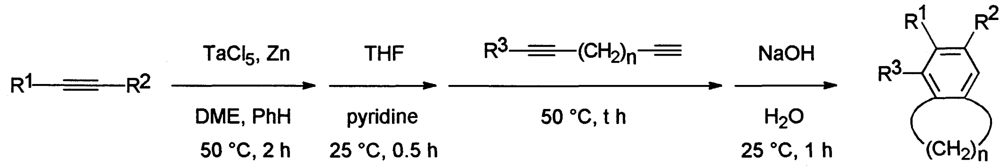
The results of the preparation of benzene derivatives from internal acetylenes and terminal diynes are shown in Table 1.[5] Cyclohexyl and phenyl substituted acetylenes also reacted with 1,7-octadiyne to give the corresponding 1,2,3,4-tetrahydronaphthalene derivatives in 80% and 76% yields, respectively (runs 2 and 3). As a diyne component, 1,6-heptadiyne and even 1,5-hexadiyne could be employed (runs 4 and 5). In the latter case, strained benzocyclobutane derivative was isolated in 75% yield.[2a,6] Oxygen and nitrogen atoms in the diyne tether did not disturb the formation of benzene derivatives (runs 6 and 7). The cyclotrimerization was found to proceed at least one of the acetylenes of the diyne was a terminal one. Tantalum-6-dodecyne complex reacted with mono terminal diynes under the same conditions to give the desired benzene derivatives in 78% and 71% yield, respectively (runs 8 and 9).

Functionalized acetylenes were also examined under the same conditions. In the case of 1-trimethylsilyl-1-dodecyne (**5**), the desired cyclized products were obtained in 61 and 56% yield, respectively (runs 10 and 11). Uncoordination of 1-trimethylsilyl acetylene **5** from the tantalum complex also takes place upon addition of the diynes, and the starting acetylene **5** was recovered over 22% yields. Reaction with methylthio acetylene[3b] took place under the same conditions, and a methylthio-substituted benzenes were prepared in 69 and 64% yield, respectively (runs 12 and 13). On the contrary, tantalum complexes of acetylenic esters and amides[3b] did not produce the desired aromatic compounds, and many byproducts were produced.



(3)

Table 1. Formation of benzene derivatives from acetylenes and diynes[a]



Run	R^1	R^2	R^3	$-(CH_2)_n-$	Time / h	Yield / %[b]
1	n-C_5H_{11}	n-C_5H_{11}	H	$-(CH_2)_4-$	4	82 (4)
2	n-C_6H_{13}	c-C_6H_{11}	H	$-(CH_2)_4-$	4	80
3	n-C_6H_{13}	Ph	H	$-(CH_2)_4-$	6	76[c]
4	n-C_5H_{11}	n-C_5H_{11}	H	$-(CH_2)_3-$	4	74
5			H	$-(CH_2)_2-$	4	75
6			H	$-CH_2OCH_2-$	4	76
7			H	$-CH_2N(CH_2Ph)CH_2-$	4	57
8			n-C_6H_{13}	$-(CH_2)_4-$	4	78
9			Et	$-(CH_2)_2OCH_2-$	4	71[d]
10	Me_3Si	n-$C_{10}H_{21}$ (5)	H	$-(CH_2)_3-$	4	61[e]
11			H	$-CH_2OCH_2-$	4	56[f]
12	MeS	n-$C_{10}H_{21}$	H	$-(CH_2)_3-$	6	69[g]
13			H	$-(CH_2)_4-$	6	64[g]

[a]Reaction was conducted in a 1.0 mmol scale. See typical procedure. [b]Isolated yields. [c]Four and a half mmol of 1,7-octadiyne were employed. [d]See reference 8. [e]Trimethylsilyl acetylene 5 was recovered in 22% yield. [f]The acetylene 5 was recovered in 36% yield. [g]Six mmol of 1,7-octadiyne were employed.

When acetylenic nitrile **6** was employed as a diyne component, pyridine ring was formed in 73% yield (eq. 3).[7]

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References and Notes

1 For rewiews, see: E. Müller, *Synthesis*, **1974**, 761; N. E. Schore, *Chem. Rev.*, **88**, 1081 (1988).

2 For some representative example with early transition metals, see: a) Ti: A. J. Hubert and J. Dale, *J. Chem. Soc.*, **1965**, 3160; b) Zr: T. Takahashi, M. Kotora, and Z. Xi, *J. Chem. Soc., Chem. Commun.*, **1995**, 361; c) Nb and Ta: T. Masuda, T. Mori, and T. Higashimura, *Bull. Chem. Soc. Jpn.*, **53**, 1152 (1980); F. A. Cotton, W. T. Hall, K. J. Cann, and F. J. Karol, *Macromolecules*, **14**, 233 (1981); T. Masuda, Y.-X. Deng, and T. Higashimura, *Bull. Chem. Soc. Jpn.*, **56**, 2798 (1983); d) Nb: A. C. Williams, P. Sheffels, D. Sheehan, and T. Livinghouse, *Organometallics*, **8**, 1566 (1989); e) Ta: J. R. Strickler, M. A. Bruck, and D. E. Wigley, *J. Am. Chem. Soc.*, **112**, 2814 (1990); D. P. Smith, J. R. Strickler, S. G. Gray, M. A. Bruck, R. S. Holmes, and D. E. Wigley, *Organometallics*, **11**, 1275 (1992).

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4 Addition of THF increased solubility of the complex **1**.

5 *Typical procedure* (Table 1, run 1): To a mixture of a tantalum-6-dodecyne complex **1**[3a] prepared from 6-dodecyne (0.17 g, 1.0 mmol), $TaCl_5$ (0.43 g, 1.2 mmol) and zinc (0.12 g, 1.8 mmol) in DME and benzene (1:1, 7 mL) were added at 25 °C THF (3.5 mL) and pyridine (0.19 g, 2.4 mmol) successively. After 30 min, a solution of 1,7-octadiyne (0.32 g, 3.0 mmol) in THF (7.5 mL) was added to the mixture at 50 °C over a period of 3 h. The resulting mixture was stirred at 50 °C for an additional 1 h. Aqueous NaOH solution (15%, 1.2 mL) was added, and the mixture was stirred at 25 °C for 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel^R and washed well with ethyl acetate (5x5 mL). Organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the crude product by column chromatography on silica gel gave 0.22 g (82%) of 6,7-dipentyl-1,2,3,4-tetrahydronaphthalene (**4**): bp 78 °C (bath temp, 0.7 Torr); IR (neat): 2922, 2950, 2924, 2856, 1500, 1459, 1438, 1378, 919, 869 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.91 (t, $J = 7.1$ Hz, 6H), 1.3-1.5 (m, 8H), 1.5-1.7 (m, 4H), 1.7-1.9 (m, 4H), 2.5-2.6 (m, 4H), 2.7-2.8 (m, 4H), 6.84 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 23.4, 29.1, 31.3, 32.1, 32.3, 129.7, 134.3, 137.8; MS m/z (%): 272 (M^+, 13), 271 (39), 160 (14), 159 (100), 145 (14), 41 (13). Found: C, 88.00; H, 11.86%; Calcd for $C_{20}H_{32}$: C, 88.16; H, 11.84%.

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7 D. J. Brien, A. Naiman, and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*, **1982**, 133.

8 Product: