

Proceeding Paper

# A New Method for the Synthesis of Tetra-Alkyl-Substituted Buta-1,3-dienes Using TaCl<sub>5</sub>-Catalyzed Reaction of Dialkyl-Substituted Alkynes with EtAlCl<sub>2</sub> in the Presence of Metallic Magnesium<sup>†</sup>

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**Abstract:** For the first time, regio- and stereoselective synthesis of tetra-alkyl-substituted buta-1,3-dienes was carried out using the reaction of dialkyl-substituted alkynes with EtAlCl<sub>2</sub> and metallic magnesium in the presence of catalytic amounts of tantalum (V) chloride in a toluene solution. The effect of the solvent and temperature on the process of oxidative coupling of molecules of disubstituted alkynes on low-valent tantalum has been studied. A scheme was proposed for the catalytic conversion of disubstituted alkynes to buta-1,3-dienes under the conditions of organoaluminum synthesis. It was found that the reaction of in situ obtained metallacyclopentadienes with methanesulfonyl chloride leads to the selective formation of tetra-alkyl-substituted 1,4-dichlorobuta-1,3-dienes.

**Keywords:** alkynes; tantalum (V) chloride; magnesium; diethylaluminum chloride; buta-1,3-dienes

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## 1. Introduction

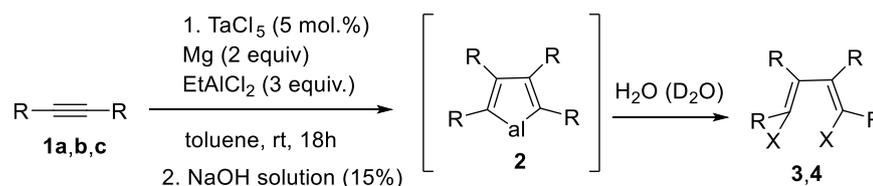
Carboalumination of alkynes is an effective tool for the formation of carbon-carbon bonds. Synthetic transformations of formed alkenylaluminums under the action of electrophilic reagents make it possible to synthesize various classes of organic compounds. Cp<sub>2</sub>ZrCl<sub>2</sub>-Catalyzed methylalumination of alkynes [1] and Cp<sub>2</sub>ZrCl<sub>2</sub>-catalyzed cycloalumination of alkynes [2] are the main methods for the preparation of trisubstituted 1-alkenylaluminums of various structures, the hydrolysis of which leads to the selective production of trisubstituted alkenes. It should be noted that the authors of this work were the first to carry out cycloalumination of such functionally substituted alkynes as 2-alkynylamines, alkynylols [3], 1-alkynylphosphines [4], phosphorsulfides, 1-alkenylselenides [5], and sulfides [6]. In this work, we studied TaCl<sub>5</sub>-catalyzed reaction of alkynes with EtAlCl<sub>2</sub> to develop new catalytic systems for carboalumination of alkynes.

## 2. Results and Discussion

We found that the reaction of dialkyl-substituted alkynes 1 (4-octyne, 5-decyne, 3-hexyne) with 3 equivalents of EtAlCl<sub>2</sub> and 2 equivalents of metallic magnesium in the presence of 5 mol% TaCl<sub>5</sub> in a toluene solution at room temperature with subsequent hydrolysis (or deuteration) leads to the regio- and stereoselective formation of tetra-alkyl-substituted buta-1,3-dienes 3 and 4 with *E*-configuration of the double bond. The structure of the diene derivatives was established using <sup>1</sup>D- and <sup>2</sup>D-NMR spectroscopy of

hydrolysis and deuteroysis products 3 and 4. The reaction is accompanied by a side process of alkynes trimerization with the formation of trimers in an amount of 5–9%. An increase in the concentration of TaCl<sub>5</sub> to 10 mol% is accompanied by an increase in the yield of the trimers up to 20% (Table 1, Entry 2). In the case of the reaction of 5-decyne with 3 equivalents of EtAlCl<sub>2</sub> in the presence of 5 mol% TaCl<sub>5</sub> in a toluene solution in the absence of Mg, the yield of the trimer achieves 77% (Table 1, Entry 3).

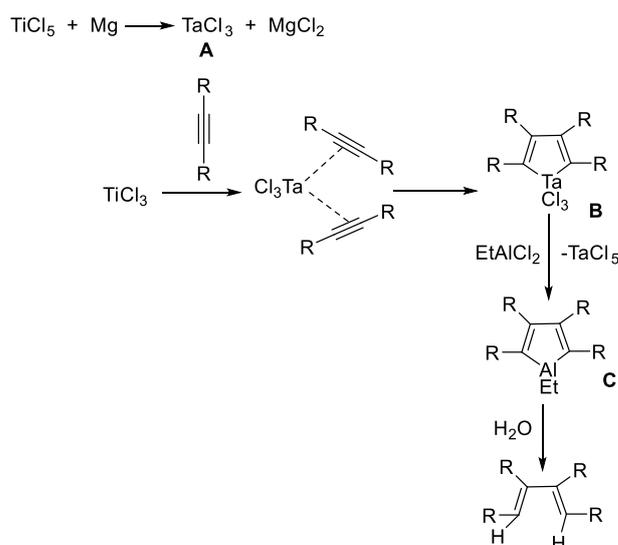
**Table 1.** Ta-catalyzed reaction of disubstituted alkynes with EtAlCl<sub>2</sub>–Mg reagent system.



**3a:** R = Et, X = H, 79%. **3b:** R = Pr, X = H, 70%. **3c:** R = Bu, X = H, 83%, **4c:** R = Bu, X = D, 77%

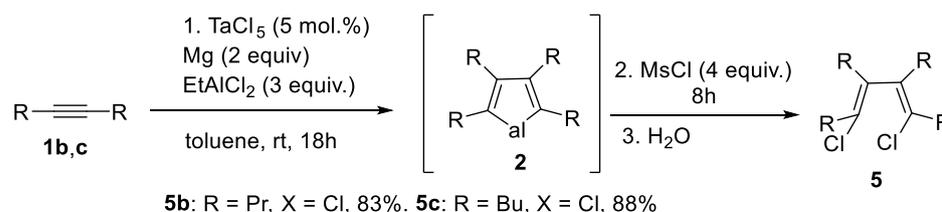
Entry	Catalyst (mol%)	Mg	Time	GC Yield of Dimer 4c (%)	GC Yield of Trimer-1,2,3,4,5,6-hexabutylbenzene (%)
1	5	2 equiv.	18 h	77	9
2	10	2 equiv.	18 h	59	20
3	5	-	18 h	7	77%

We believe that the process of dimerization of alkynes on low-valent tantalum is initiated by TaCl<sub>3</sub>, which is formed as a result of the reduction of TaCl<sub>5</sub> by metallic magnesium. From the literature [7] on the reduction of alkynes using TaCl<sub>5</sub>-Mg reagent system, it is known that the reduction of TaCl<sub>5</sub> by metallic magnesium leads to the formation of tantalum (III) chloride **A**. Further, the oxidative coupling of two acetylene molecules on low-valent tantalum occurs with the formation of tantalacyclopentadiene **B**. Subsequent trans-metallation of complex **B** with EtAlCl<sub>2</sub> leads to the formation of aluminacyclopentadiene **C**, the hydrolysis of which gives tetraalkyl-substituted butadiene derivative (Scheme 1).



**Scheme 1.** The proposed mechanism of the reaction of dialkyl-substituted alkynes with TaCl<sub>5</sub>-Mg reagent system.

We have previously demonstrated that trialkylsilyl esters of sulfonic acids [8], S-methylthiosulfonate [9], as well as sulfonyl halides [10] are effective electrophilic reagents for the functionalization of aluminacyclopent-2-enes. In this work, we carried out the reaction of aluminacyclopentadienes with methanesulfonyl chloride. So, the reaction of dialkyl-substituted alkynes with 2 equivalents of Mg and 3 equivalents of EtAlCl<sub>2</sub> in the presence of 5 mol% TaCl<sub>5</sub> in toluene solution at room temperature followed by the addition of 4 equivalents of methanesulfonyl chloride gives tetraalkyl-substituted 1,4-dichlorobuta-1,3-diene **5** in high yield after 8 h (Scheme 2).



**Scheme 2.** Functionalization of aluminacyclopentenes with methanesulfonyl chloride.

### 3. Conclusions

Thus, we have demonstrated for the first time that the reaction of dialkyl-substituted alkynes with EtAlCl<sub>2</sub> and metallic magnesium in the presence of catalytic amounts of tantalum (V) chloride in a toluene solution leads to the regio- and stereoselective formation of tetraalkyl-substituted buta-1,3-diene. A selective method is proposed for the preparation of tetraalkyl-substituted 1,4-dichlorobuta-1,3-diene based on the reaction of aluminacyclopentadienes (obtained in situ using TaCl<sub>5</sub>-catalyzed reaction of dialkyl-substituted alkynes with EtAlCl<sub>2</sub> in the presence of metallic magnesium) with methanesulfonyl chlorides.

### 4. Experimental Part

The reagents were obtained from Sigma-Aldrich or Acros. Toluene were dried over sodium. Nuclear magnetic resonance spectroscopy was performed on a Bruker Avance 500. The <sup>1</sup>H NMR spectra were recorded at 500 MHz and <sup>13</sup>C-<sup>1</sup>H} NMR spectra at 100 MHz in CDCl<sub>3</sub>. The chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as the internal standard. Elemental analysis was performed using a Carlo-Erba CHN 1106 elemental analyser. Mass spectra were obtained on a Finnigan 4021 instrument.

(*5E,7E*)-6,7-dibutyldodeca-5,7-diene (**3c**); Typical Procedure. To a solution of 276 mg of dec-5-yne (2 mmol), TaCl<sub>5</sub> (35.8 mg, 0.1 mmol) and Mg (96 mg, 4 mmol) was added EtAlCl<sub>2</sub> (0.5 M in hexanes, 0.82 mL, 6 mmol). After 18 h at 23 °C, the reaction mixture was diluted with Et<sub>2</sub>O (5 mL), and 25 wt% KOH solution (3 mL) was added dropwise while the reaction flask was cooled in an ice bath. The aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous CaCl<sub>2</sub>. The reaction mixture was filtered through a filter paper and concentrated in vacuo to give crude product as a yellow oil. The residue was distilled through a micro column at 1.5 mmHg to afford **3c** (463 mg, 83%) as a colourless oil. b.p. 138–140 °C. <sup>1</sup>H: 0.91–0.96 (m, 12H, 4CH<sub>3</sub>), 1.29–1.38 (m, 16H, 8CH<sub>2</sub>), 2.07–2.11 (m, 4H, 2CH<sub>2</sub>), 2.16–2.19 (t, *J* = 7 Hz, 4H, 2CH<sub>2</sub>), 5.35–5.37 (t, *J* = 7 Hz, 2H, 2CH). <sup>13</sup>C: 14.06 (4C), 22.47 (2C), 22.79 (2C), 27.72 (2C), 27.91 (2C), 31.17 (2C), 32.31 (2C), 125.91 (2C), 141.21 (2C) MS (EI): *m/z*, % = 204 (15) [M<sup>+</sup>], 161 (11), 147 (13), 117 (18), 105 (100). Anal. calcd for C<sub>20</sub>H<sub>38</sub>, (%): C, 86.25; H, 13.75; Found, (%): C, 86.28; H, 13.69. (*4E,6E*)-5,6-dipropyldeca-4,6-diene (**3b**) Using the procedure described above 220 mg of oct-4-yne (2 mmol) gave crude product that was distilled through a micro column at 1,6 mmHg to afford **3b** (311 mg, 70%) as a colourless oil. b.p. 98–100 °C (1,6 mmHg). <sup>1</sup>H: 0.88–0.95 (m, 12H, 4CH<sub>3</sub>), 1.31–1.37 (m, 4H, 2CH<sub>2</sub>), 1.39–1.45 (m, 4H, 2CH<sub>2</sub>), 2.05–2.09 (q, *J* = 14 Hz, *J* = 7 Hz, 4H, 2CH<sub>2</sub>), 2.14–2.17 (t, *J* = 7 Hz, 4H, 2CH<sub>2</sub>), 5.36–5.38 (t, *J* = 7 Hz, 2H, 2CH). <sup>13</sup>C: 13.93 (2C), 14.11 (2C), 22.05 (2C), 23.21 (2C),

30.06 (2C), 30.31 (2C), 126.00 (2C), 141.27 (2C). Anal. calcd for  $C_{16}H_{30}$ , (%): C, 86.40; H, 13.60; Found, %: C, 86.53; H, 13.78. (5Z,7Z)-6,7-dibutyl-5,8-dichlorododeca-5,7-diene (**5c**) Using the procedure described above 276 mg of dec-5-yne (2 mmol) and 916 mg, 8 mmol methanesulfonyl chloride (instead of  $H_2O$ ) gave crude product that was distilled through a micro column at 2 mmHg to afford **5c** (611 mg, 88%) as a colourless oil. b.p. 201–203 °C (2 mmHg).  $^1H$ : 0.91–0.97 (m, 12H, 4CH<sub>3</sub>), 1.28–1.41 (m, 12H, 6CH<sub>2</sub>), 1.58–1.63 (m, 4H, 2CH<sub>2</sub>), 2.03–2.09 (m, 2H(A), 2CH<sub>2</sub>), 2.27–2.33 (m, 2H(B), 2CH<sub>2</sub>), 2.39–2.47 (m, 4H, 2CH<sub>2</sub>).  $^{13}C$ : 13.91 (2C), 14.00 (2C), 22.03 (2C), 23.04 (2C), 29.92 (2C), 30.22 (2C), 31.90 (2C), 34.76 (2C), 131.41 (2C), 135.43 (2C). Anal. calcd for  $C_{20}H_{36}Cl_2$ , (%): C, 69.15; H, 10.45. Found, %: C, 69.27; H, 10.51.

**Author Contributions:** Conceptualization, R.N.K.; methodology, R.N.K.; software, O.S.M.; validation, A.K.A.; formal analysis, A.K.A.; investigation, A.K.A.; resources, I.R.R.; data curation, O.S.M.; writing—original draft preparation, R.N.K.; writing—review and editing, I.R.R.; visualization, I.R.R.; supervision, U.M.D.; project administration, U.M.D.; funding acquisition, I.R.R. All authors have read and agreed to the published version of the manuscript.

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