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$TaCl_5$-Catalyzed Homo-Coupling of Disubstituted Alkynes under the Action of $EtAlCl_2$ and Mg [†]

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Abstract: The reaction of homo-coupling of alkynes using zirconium- and titanium-containing reagents is an important basis for the efficient synthesis of polymer, oligomers and macrocycles. It is generally accepted that the homo-coupling takes place through the intermediate formation of “Cp_2Zr” or “Cp_2Ti” species that can be generated by the interaction of Cp_2ZrCl_2 or Cp_2TiCl_2 with alkali and alkaline earth metals, as well as with alkyl derivatives of metals. The most widely used reagents include Negishi reagent (“Cp_2ZrBu_2”), Takahashi reagent (“Cp_2ZrEt_2”), and Rosenthal reagent ($Cp_2Zr(py)TMSC{\equiv}CTMS$). The well-known system of reagents $Ti(O^{i}Pr)_4$–*i*-PrMgBr should also be mentioned. Recently, we have shown the promise of using a reagent based on tantalum ($TaCl_5$–Mg) for the reduction of propargylamines. Continuing these studies, in order to develop new catalytic systems for the homo-coupling of acetylenic compounds, in this work we studied the $TaCl_5$-catalyzed reaction of dialkyl-substituted acetylenes with $EtAlCl_2$ and Mg. We have established for the first time that the reaction of dialkyl-substituted acetylenes with $EtAlCl_2$ and magnesium in the presence of catalytic amounts of tantalum (V) chloride in a toluene solution after hydrolysis gives tetraalkyl-substituted (*E*,*E*)-buta-1,3-dienes in high yield. A plausible scheme for the catalytic conversion has been proposed.

Keywords: acetylenes; homo-coupling; tantalum catalysis; organoaluminums

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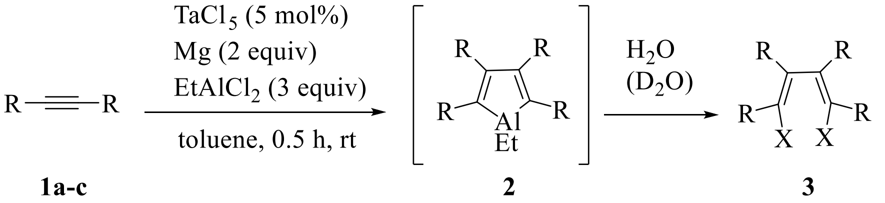
1. Introduction

The reaction of homo-coupling of alkynes using zirconium- and titanium-containing reagents is an important basis for the efficient synthesis of polymer, oligomers and macrocycles [1]. It is generally accepted that the homo-coupling takes place through the intermediate formation of “Cp_2Zr” or “Cp_2Ti” species that can be generated by the interaction of Cp_2ZrCl_2 or Cp_2TiCl_2 with alkali and alkaline earth metals, as well as with alkyl derivatives of metals. The most widely used reagents include Negishi reagent (“Cp_2ZrBu_2”) [2,3], Takahashi reagent (“Cp_2ZrEt_2”) [4], and Rosenthal reagent ($Cp_2Zr(py)TMSC{\equiv}CTMS$) [5–7]. The well-known system of reagents $Ti(O^{i}Pr)_4$–*i*-PrMgBr should also be mentioned [8]. Recently, we have shown the promise of using a reagent based on tantalum ($TaCl_5$–Mg) for the reduction of propargylamines [9]. Continuing these studies, in order to develop new catalytic systems for the homo-coupling of acetylenic compounds, in this work we studied the $TaCl_5$-catalyzed reaction of dialkyl-substituted acetylenes with $EtAlCl_2$ and Mg.

2. Results and Discussion

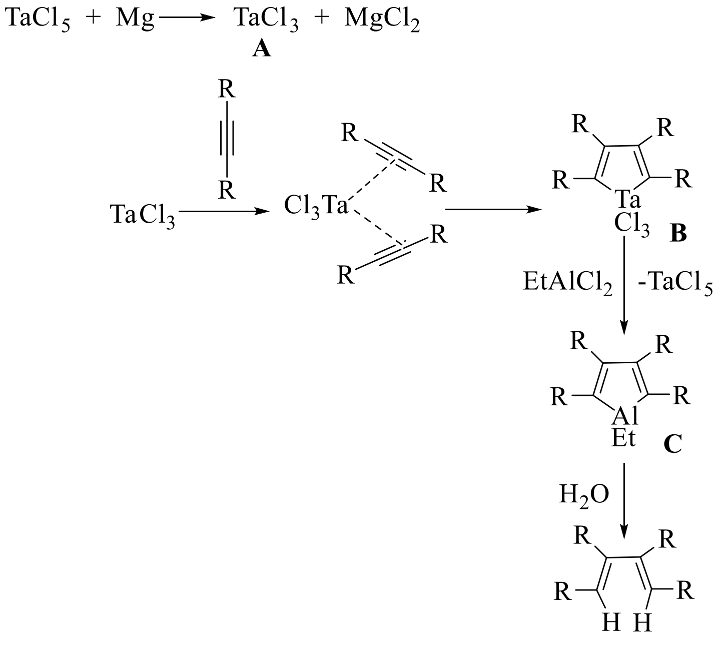
We have found that the reaction of dialkyl-substituted acetylenes **1** (4-octyne, 5-decyne, 3-hexyne) with 3 equiv. of $EtAlCl_2$ and 2 equiv. of magnesium in the presence of 5 mol.% of $TaCl_5$ in a toluene solution at room temperature and subsequent hydrolysis leads to the regio- and stereoselective formation of tetraalkyl-substituted (*E*,*E*)-buta-1,3-dienes **3** (Scheme 1). The reaction is accompanied by a side reaction of alkyne cyclotrimerization to give hexaalkyl substituted benzene in the amount of 5–9%.



3a: R = Et, X = H, 79%.
3b: R = *n*-Pr, X = H, 70%.
3c: R = *n*-Bu, X = H, 83%,

Scheme 1. $TaCl_5$-catalyzed homo-coupling of disubstituted alkynes under the action of $EtAlCl_2$ and Mg.

We assumed that the homocoupling of alkynes is initiated by low-valent $TaCl_3$, which is generated as a result of the reduction of $TaCl_5$ with metallic magnesium (Scheme 2). Next, the coupling of two acetylenic molecules coordinated with $TaCl_3$ occurs to form tantalacyclopentadiene, similarly to the Zr-catalyzed homocoupling of alkynes with $EtAlCl_2$ and Mg. The reaction of tantalacyclopentadiene with $EtAlCl_2$ is accompanied by *trans*-metalation with the formation of aluminacyclopentadiene **2**, the hydrolysis of which gives the target tetraalkyl-substituted butadiene derivative **3**.



Scheme 2. Plausible mechanism of $TaCl_5$-catalyzed homo-coupling of disubstituted alkynes.

3. Experimental Section

3.1. General

Commercial reagents were used (Aldrich). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-II 400 Ascend instrument (400 MHz for 1H and 100 MHz for ^{13}C in $CDCl_3$) and Bruker Avance-III HD 500 Ascend instrument (500 MHz for ^1H and 125 MHz for ^{13}C in $CDCl_3$). Mass spectra were run on a Shimadzu GCMS-QP2010Plus mass spectrometer (SPB-5 capillary column, 30 m × 0.25 mm, helium as the carrier gas, temperature programming from 40 to 300 °C at 8 °C/min, evaporation temperature of 280 °C, ion source temperature of 200 °C, and ionization energy of 70 eV). The elemental composition of the samples was determined on a Carlo Erba 1106 elemental analyzer. The course of the reaction and the purity of the products were monitored by gas liquid chromatography on a Shimadzu GC-9A, GC-2014 instrument [2 m × 3 mm column, SE-30 silicone (5%) on Chromaton N-AW-HMDS as the stationary phase, temperature programming from 50 to 270 °C at 8 °C/min, helium as the carrier gas (47 mL/min)].

3.2. General Procedure for the Ta-Mg-Catalyzed Reaction of Alkynes with $EtAlCl_2$

Alkyne (2 mmol), $TaCl_5$ (35.8 mg, 0.1 mmol), and metallic Mg (96 mg, 4 mmol) were sequentially charged into a glass reactor under a dry argon atmosphere. $EtAlCl_2$ (0.5 M in hexane, 0.82 mL, 6 mmol) was added to the resulting reaction mixture and stirred for 0.5 h at 23 °C. After 0.5 h, the reaction mixture was diluted with diethyl ether (5 mL) and 25% KOH solution (3 mL) was added dropwise at 0 °C. After adding 25% KOH solution, the reaction mixture was stirred at room temperature for 1 h. The aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined extracts were washed with brine (10 mL) and dried over anhydrous $CaCl_2$. The reaction mixture was filtered through a paper filter, concentrated using a rotary evaporator and the residue was purified by distillation to obtain tetraalkyl-substituted (*E*,*E*)-buta-1,3-dienes.

(4E,6E)-5,6-dipropyldeca-4,6-diene ***3b***. Colorless oil, yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88–0.95 (m, 12H), 1.31–1.37 (m, 4H), 1.39–1.45 (m, 4H), 2.05–2.09 (m, 4H), 2.14–2.17 (m, 4H), 5.36–5.38 (t, 2H, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.93, 14.11, 22.05, 23.21, 30.06, 30.31, 126.00, 141.27.

(5E,7E)-6,7-dibutyldodeca-5,7-diene ***3c***. Colorless oil, yield 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91–0.96 (m, 12 H), 1.29–1.38 (m, 16 H), 2.07–2.11 (m, 4H), 2.16–2.19 (m, 4H), 5.35–5.37 (t, 2H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.06, 22.47, 22.79, 27.72, 27.91, 31.17, 32.31, 125.91, 141.21. EIMS (70 eV, *m*/*z*): 204 (15) [M+], 161 (11), 147 (13), 117 (18), 105 (100).

4. Conclusions

It has been established that the reaction of dialkyl-substituted acetylenes with $EtAlCl_2$ and metallic magnesium in the presence of catalytic amounts of tantalum (V) chloride in a toluene solution after hydrolysis gives tetraalkyl-substituted (*E*,*E*)-buta-1,3-dienes in high yield. A plausible mechanism of the reaction was proposed.

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

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Conflicts of Interest: The authors declare no conflict of interest.

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