

# Transformation of Dialkyl-Substituted Alkynes under the Action of the TaCl<sub>5</sub>-Mg and NbCl<sub>5</sub>-Mg Reagent System <sup>†</sup>

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**Abstract:** A regioselective method for the preparation of *p*-tolyl-substituted alkanes is presented based on the reaction of dialkyl-substituted alkynes with four equivalents of TaCl<sub>5</sub> or NbCl<sub>5</sub> in the presence of stoichiometric amounts of metallic magnesium in toluene solution. It was found that the reaction of 5-decyne with the TaCl<sub>5</sub>-M reagent system (where M = Mg, Zn, Fe, Sm, Al, and Mn) in a toluene solution is accompanied by the selective formation of 1-(decan-5-yl)-4-methylbenzene in high yields (79–90%). The effect of solvents on the selectivity of the conversion of 5-decyne under the action of the TaCl<sub>5</sub>-Mg reagent system has been studied.

**Keywords:** alkynes; tantalum (V) chloride; niobium (V) chloride; metallic magnesium; toluene



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## 1. Introduction

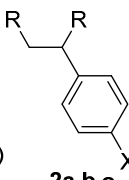
The reduction of non-functionalized alkynes using tantalum (V) and niobium (V) chloride in the presence of Mg and Zn in a solution of benzene-1,2-dimethoxyethane is a classic effective approach for the preparation of alkenes [1]. It is known from the literature [1] that the key intermediates of this method for the reduction of alkynes are low-valence complexes of tantalum and niobium—tantalum (III) and niobium (III) chlorides, generated as a result of the reduction of tantalum and niobium halides in a two-component solvent system—benzene-DME under the action of magnesium and zinc. Currently, we have demonstrated for the first time that the NbCl<sub>5</sub>-Mg reagent system is an effective tool for the reduction of such functionally substituted alkynes, such as 2-alkynyl amines and 3-alkynylols [2]. This study also proposes an efficient method for the chlorothiolation of 2-alkynyl amines using methanesulfonyl chloride in the presence of the NbCl<sub>5</sub>-Mg reagent system in a toluene solution, which allows the regio- and stereoselective preparation of *E*-β-chlorovinyl sulfides. One of the important conclusions of the proposed approach is the possibility of generating low-valent paramagnetic niobium complexes, initiating the radical addition of methanesulfonyl chloride to the triple bond of propargylamines. In connection with the obtained results, it was interesting for us to study the reaction of alkynes with low-valence complexes of tantalum and niobium generated as a result of the reduction of TaCl<sub>5</sub> and NbCl<sub>5</sub> using metallic Mg in a toluene solution. This work presents the first studies of the interaction of the triple bond of alkynes with low-valent complexes of tantalum and niobium, which are formed in aromatic solvents in the presence of metals of different nature.

## 2. Results and Discussion

We have found for the first time that the reaction of dialkyl-substituted alkynes 1a,b,c (5-decyne, 4-octyne, 3-hexyne) with four equivalents of TaCl<sub>5</sub> and three equivalents of magnesium in a solution of toluene (Table 1) after 3 h leads to the regioselective formation

of corresponding *p*-tolyl-substituted alkanes 2a,b,c with a yield of 81–90%. We believe that the observed complete reduction of the triple bond of disubstituted alkynes 1 with the addition of the *p*-tolyl fragment from the solvent molecule (toluene) is initiated under the action of low-valent tantalum complexes. It is known from the literature [1,3] that the reduction of non-functionalized alkynes to the corresponding olefins was carried out under the action of TaCl<sub>5</sub>-Zn, TaCl<sub>5</sub>-Mg and NbCl<sub>5</sub>-Zn reagent systems in DME-benzene or DME-toluene reagent system. In this work, we found that the reaction of disubstituted alkynes with stoichiometric amounts of TaCl<sub>5</sub> and Mg in a toluene solution, in the absence of DME, produces only *p*-tolyl-substituted alkane. The study of the mechanism of the transformation is the subject of our subsequent research. The reaction of 1-octyne (terminal alkyne) with the TaCl<sub>5</sub>-Mg reagent system in a toluene solution leads to the exceptional formation of the cyclotrimerization product 1,3,5-trihexylbenzene. It was found that the conversion of 5-decyne to 1-(decan-5-yl)-4-methylbenzene proceeds equally selectively in the case of using such metals as Zn, Fe, Sm, Al, and Mn (Table 1, Entry 2–6, respectively). When using anisole instead of toluene, the reaction proceeds in a similar manner and was accompanied by complete reduction of the triple bond with the addition of *n*-methoxybenzene moiety (Table 1, Entry 7). However, along with the target product (1-(decan-5-yl)-4-methoxybenzene, 40% yield), a mixture of high-molecular compounds was formed (according to analysis by gas chromatography and chromatomass spectrometry). When ethylbenzene is used instead of toluene, the conversion of 5-decyne is 70%, and along with the target product (1-(decan-5-yl)-4-ethylbenzene, 30%), a difficult-to-analyze mixture of compounds, was formed (Table 1, Entry 9). The transformation of 5-decyne in a benzene solution with the formation of decan-5-ylbenzene with a yield of 35% also proceeds nonselectively (Table 1, Entry 8). It should be noted that the reaction of 5-decyne with four equivalents of NbCl<sub>5</sub> and three equivalents of magnesium in toluene solution (Table 1, Entry 10) after 3 h leads to the regioselective formation of 1-(decan-5-yl)-4-methylbenzene 2c in 87% yields.

**Table 1.** Reaction of disubstituted alkynes with the reagent system TaCl<sub>5</sub>-M<sup>5</sup> and NbCl<sub>5</sub>-Mg.

$\text{R}-\text{C}\equiv\text{C}-\text{R}$ <p><b>1a,b,c</b></p>		<p>1. TaCl<sub>5</sub> (4 equiv.) M (3 equiv.)</p> <p>toluene, r.t., 3 h</p> <p>2. NaOH solution (15%)</p>	 <p><b>2a,b,c</b></p>
<p><b>2a:</b> R = Et, 81%, X = Me. <b>2b:</b> R = Pr, X = Me, 87%. <b>2c:</b> R = Bu, X = Me, 90%  <b>3c:</b> R = Bu, X = OMe, 40%. <b>4c:</b> R = Bu, X = H, 35%. <b>5c:</b> R = Bu, X = Et, 30%</p>			
Entry	Metal	Time	Yield of 2c, 3c, 4c, 5c (%)
1	Mg	3 h	90
2	Zn	3 h	84
3	Fe	3 h	80
4	Sm	3 h	79
5	Al	3 h	81
6	Mn	3 h	89
7	Mg	3 h	40 <sup>1</sup>
8	Mg	3 h	35 <sup>2</sup>
9	Mg	3 h	30 <sup>3</sup>
10	Mg	3 h	92 <sup>4</sup>

<sup>1</sup> Anisole was used instead of toluene. <sup>2</sup> Benzene was used instead of toluene. <sup>3</sup> Ethylbenzene was used instead of toluene. <sup>4</sup> NbCl<sub>5</sub> was used instead of TaCl<sub>5</sub>. <sup>5</sup> M = Mg, Zn, Fe, Sm, Al, Mn.

### 3. Conclusions

A new regioselective transformation of dialkyl-substituted alkynes into *p*-tolyl-substituted alkanes under the action of TaCl<sub>5</sub> or NbCl<sub>5</sub> and metals such as Mg, Zn, Fe, Sm, Al, or Mn in a toluene solution has been discovered. It was found that toluene is the most effective solvent for the selective formation of aryl-substituted alkanes from di-alkyl-substituted alkynes in a series of aromatic solvents such as anisole, ethylbenzene, benzene, and toluene.

### 4. Experimental Part

Commercially available reagents were used (5-decyne, 4-octyne, 3-hexyne, TaCl<sub>5</sub>, NbCl<sub>5</sub>, Mg, Zn, Fe, Sm, Al, and Mn). The reactions were carried out in a dry argon atmosphere. Toluene was refluxed with sodium and benzophenone. 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.

1-(decan-5-yl)-4-methylbenzene; Typical Procedure.

In a 50 mL reaction flask, magnesium powder (144 mg, 6 mmol) was placed under an argon atmosphere. Toluene (24 mL) was added to the magnesium powder at room temperature. 5-Decyne (361 mg, 2 mmol) and TaCl<sub>5</sub> (2866 mg, 8 mmol) were added by stirring and the resulting mixture was stirred at room temperature for 3 h. After 3 h at room temperature, the reaction mixture was diluted with Et<sub>2</sub>O (20 mL), and 25 wt% KOH solution (15 mL) was added dropwise while the reaction flask was cooled in an ice bath. The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over anhydrous MgSO<sub>4</sub>. The reaction mixture was filtered through a filter paper and concentrated in vacuo to produce a crude product such as yellow oil. The residue was distilled through a micro column at 2.4 mmHg to give **2c** (418 mg, 90%) as a colourless oil. B.p. 128–130 °C (2.4 mmHg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 0.85–0.88 (m, 6H), 1.14–1.29 (m, 9H), 1.51–1.67 (m, 5H), 2.36 (s, 3H), 2.44–2.49 (m, 1H), 7.07 (d, *J* = 7 Hz, 2H), 7.13 (d, *J* = 7 Hz, 2H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ = 14.05, 14.12, 21.04, 22.59, 22.85, 29.90, 32.05, 36.77, 37.03, 45.61, 127.53 (2C), 128.86 (2C), 134.99, 143.39. MS (EI): *m/z*, % = 232 (11) [M<sup>+</sup>], 175 (12), 161 (13), 105 (100). Anal. Calcd for C<sub>17</sub>H<sub>28</sub>, (%): C, 87.86; H, 12.14; Found, %: C, 87.93; H, 11.99. 1-Methyl-4-(octan-4-yl)benzene (**2b**). Using the procedure described above, 220 mg of oct-4-yne (2 mmol) produced a crude product that was distilled through a micro column at 3.1 mmHg to afford **2b** (351 mg, 87%) as a colourless oil. b.p. 106–108 °C (3.1 mmHg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 0.85–0.89 (m, 6H), 1.14–1.32 (m, 6H), 1.55–1.63 (m, 4H), 2.36 (s, 3H), 2.46–2.52 (m, 1H), 7.06 (d, *J* = 7 Hz, 2H), 7.13 (d, *J* = 7 Hz, 2H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ = 14.05, 14.19, 20.75, 21.04, 22.84, 29.89, 36.74, 39.33, 45.33, 127.54 (2C), 128.86 (2C), 134.99, 143.33. MS (EI): *m/z*, % = 204 (15) [M<sup>+</sup>], 161 (11), 147 (13), 117 (18), 105 (100). Anal. calcd for C<sub>15</sub>H<sub>24</sub>, (%): C, 88.16; H, 11.84; Found, %: C, 88.25; H, 11.91. 1,3,5-Trihexylbenzene. Using the procedure described above, 220 mg of oct-1-yne (2 mmol) produced a crude product that was distilled through a micro column at 1.5 mmHg to afford 1,3,5-trihexylbenzene (530 mg, 80%) as a colourless oil. b.p. 190–192 °C (1.5 mmHg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 0.97–0.99 (t, *J* = 6 Hz, 9H), 1.41 (s, 12H), 1.66–1.72 (m, 12H), 2.63–2.65 (t, *J* = 7 Hz, 6H), 6.90 (s, 3H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ = 14.07 (3C), 22.71 (3C), 29.23 (3C), 31.67 (3C), 31.85 (3C), 36.08 (3C), 125.89 (3C), 142.74 (3C). Anal. calcd for C<sub>24</sub>H<sub>42</sub>, (%): C, 87.19; H, 12.81; Found, %: C, 87.24; H, 11.90.

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