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Proceeding Paper

Transformation of Dialkyl-Substituted Alkynes under the Action of the $TaCl_5$-Mg and $NbCl_5$-Mg Reagent System †

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Abstract: A regioselective method for the preparation of *p*-tolyl-substituted alkanes based on the reaction of dialkyl-substituted alkynes with 4 equiv. of $TaCl_5$ or $NbCl_5$ in the presence of stoichiometric amounts of metallic magnesium in toluene solution. It was found that the reaction of 5-decyne with the $TaCl_5$-M reagent system (where M = Mg, Zn, Fe, Sm, Al, Mn) in a toluene solution is accompanied by the selective formation of 1-(decan-5-yl)-4-methylbenzene in a high yield (79–90%). The effect of solvents on the selectivity of the conversion of 5-decyne under the action of the $TaCl_5$-Mg reagent system has been studied.

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

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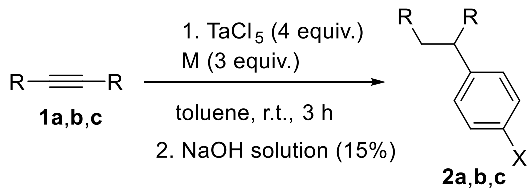
1. Introduction

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 $NbCl_5$-Mg reagent system is an effective tool for the reduction of such functionally substituted alkynes as 2-alkynyl amines and 3-alkynylols [2]. This work also proposes an efficient method for the chlorothiolation of 2-alkynyl amines using methanesulfonyl chloride in the presence of the $NbCl_5$-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 $TaCl_5$ and $NbCl_5$ 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 4 equiv. of $TaCl_5$ and 3 equiv. of magnesium in a solution of toluene (Table 1) after 3 h leads to regiosective 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 $TaCl_5$-Zn, $TaCl_5$-Mg and $NbCl_5$-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 $TaCl_5$ and Mg in a toluene solution, in the absence of DME, gives 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 $TaCl_5$-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 way and was accompanied by complete reduction of the triple bond with the addition of the *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 chromato-mass spec-trometry). 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 difficultly analyzed 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 4 equiv. of $NbCl_5$ and 3 equiv. 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% yield.

Table 1. Reaction of disubstituted alkynes with the reagent system $TaCl_5$-M[5] and $NbCl_5$-Mg.



2a: R = Et, 81%, X = Me. **2b**: R = Pr, X = Me, 87%. **2c**: R = Bu, X = Me, 90%
3c: R = Bu, X = OMe, 40%. **4c**: R = Bu, X = H, 35%. **5c**: R = Bu, X = Et, 30%

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 [1]
8	Mg	3 h	35 [2]
9	Mg	3 h	30 [3]
10	Mg	3 h	92 [4]

[1] Anisole was used instead of toluene. [2] Benzene was used instead of toluene. [3] Ethylbenzene was used instead of toluene. [4] $NbCl_5$ was used instead of $TaCl_5$. [5] 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 $TaCl_5$ or $NbCl_5$ 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, $TaCl_5$, $NbCl_5$, Mg, Zn, Fe, Sm, Al, Mn). The reactions were carried out in a dry argon atmosphere. Toluene were refluxed with sodium and benzophenone. Nuclear magnetic resonance spectroscopy was performed on a Brucker Avance 500. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C-{^{1}H} NMR spectra at 100 MHz in $CDCl_3$. 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 was placed magnesium powder (144 mg, 6 mmol) under an argon atmosphere. To the magnesium powder was added at room temperature toluene (24 mL). 5-Decyne (361 mg, 2 mmol) and $TaCl_5$ (2866 mg, 8 mmol) was added to the 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_2O (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), dried over anhydrous $MgSO_4$. 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 2,4 mmHg to give **2c** (418 mg, 90%) as a colourless oil. b.p. 128–130 °C (2,4 mmHg) ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{13}C NMR (500 MHz, $CDCl_3$): 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^+], 175 (12), 161 (13), 105 (100). Anal. calcd for $C_{17}H_{28}$, (%): 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) gave 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). ^{1}H NMR (500MHz, $CDCl_3$): 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* = 7Hz, 2H), 7. 13 (d, *J* = 7 Hz, 2H). ^{13}C NMR (500MHz, $CDCl_3$): 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^+], 161 (11), 147 (13), 117 (18), 105 (100). Anal. calcd for $C_{15}H_{24}$, (%): 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) gave 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). ^{1}H NMR (500MHz, $CDCl_3$): 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). ^{13}C NMR (500MHz, $CDCl_3$): 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 $C_{24}H_{42}$, (%): C, 87.19; H, 12.81; Found, %: C, 87.24; H, 11.90.

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