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Communication

Two routes of tantalum-catalyzed alkene carbomagnesiation with ethyl Grignard reagents

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ABSTRACT

Carbomagnesiation of 1-alkenes with EtMgX (X = Cl, Et) has been implemented in the presence of $TaCl_5$ as a catalyst to give a mixture of 2-(R-substituted)- and 3-(R-substituted)-*n*-butylmagnesiums (5:4 ratio) ina total yield of 98%. The probable mechanism of their formation through tantalacyclopentanes as key intermediates is discussed.

1. Introduction

As we have earlier shown, the Zr-catalyzed regioselective carbomagnesiation of monosubstituted unactivated alkenes with EtMgX (X = Et, Cl, Br) is a convenient and efficient route to different organomagnesiums (OMCs) (Scheme 1) [1].

Later, this reaction became a research subject in a few research groups of chemists, who have developed its powerful synthetic potential [2] and have proposed its reaction mechanism (Scheme 2) [3].

Zirconium cyclopentadienyl derivatives were found to be the most active and effective catalysts for this reaction.

Niobium and tantalum complexes are known to be active catalysts for alkene dimerization and codimerization [4], metathesis [5], ethylene polymerization [6], etc. However, there are no published data on the catalytic behavior of transition metal (V, Nb, Ta) salts and complexes in the reactions with unsaturated hydrocarbons involving organic derivatives of nontransition metals (eg. Mg, Al, Zn).

In this paper, we report the first use of $TaCl_5$ as a catalyst for carbomagnesiation of 1-alkenes with ethyl Grignard reagents.

2. Results and discussions

Our experiments showed that tantalum pentachloride $TaCl_5$ has high catalytic activity in the reaction of 1-alkenes with ethylmagnesiums. The reaction products, in this case, surprisingly differ from those produced in this reaction involving Cp_2ZrCl_2.

Thus, the model reaction between 1-octene and EtMgCl (1:2 ratio) in the presence of the $TaCl_5$ catalyst (octene:[Ta] = 100:5) in THF (20 °C, 3 h) affords a mixture of two OMCs **1b** and **2b** in a total yield of 90% towards initial 1-octene (Scheme 3).

The only product 3-methylnonane **3b** [1a] has been obtained after hydrolysis of **1b** and **2b** with dilute (8%) hydrochloric acid, while deuterolysis of the reaction mixture led to two monodeuterated hydrocarbons **4b** and **5b** (5:4 ratio). The yield and the molar ratio of the resultant regioisomers were found by calculating their g.l.c. peak area ratios.

The ^{13}C NMR spectrum of the predominant regioisomer **4b** exhibits the signal at $\delta(C^{10})$ 18.85 ppm (see Section Experimental) with characteristic spin–spin coupling constant (SSCC) $^{1}J_{C-D}$ = 19.0 Hz and a diagnostic signal at $\delta(C^{1})$ 11.34 Hz. The deuterium isotope effect on the ^{1}H chemical shift of the C^{10}-methyl group causes its shielding as compared to that of compound **5b**. This shielding effect results in the chemical shift of 0.31 ppm. The ^{13}C NMR spectrum of regioisomer **5b** also contains the characteristic triplet signal at $\delta(C^{1})$ 11.04 ppm ($^{1}J_{C-D}$ = 19.0 Hz).

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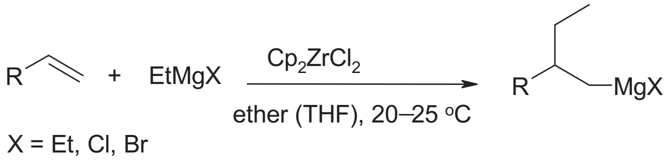


Scheme 1.

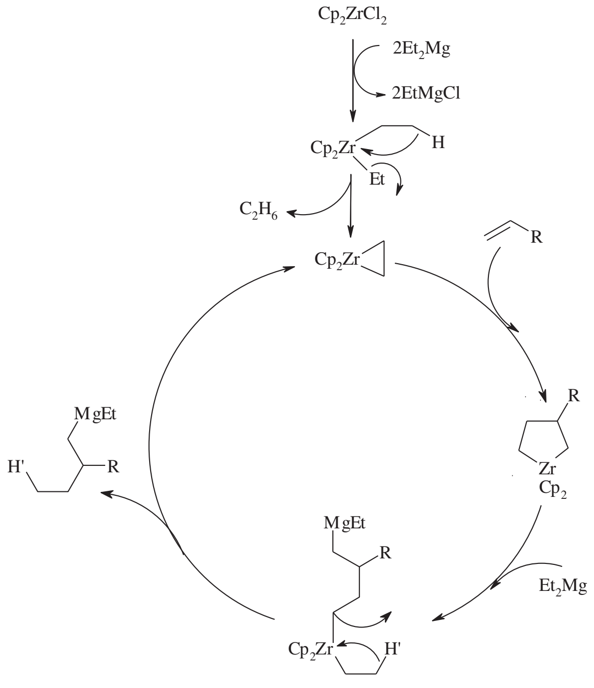
In an analogous fashion, the deuterium isotope effect in compound **5b** causes the shielding of the C^1-methyl group. The shielding effect, in this case, resulted in the chemical shift of 0.30 ppm.

We should also note the presence of β-isotope effects in both compounds **5b** ($\Delta\delta_{\beta\text{-isotop}}$ C^2 = 0.07 ppm) and **4b** ($\Delta\delta_{\beta\text{-isotop}}$ $C^3 = 0.06$ ppm).

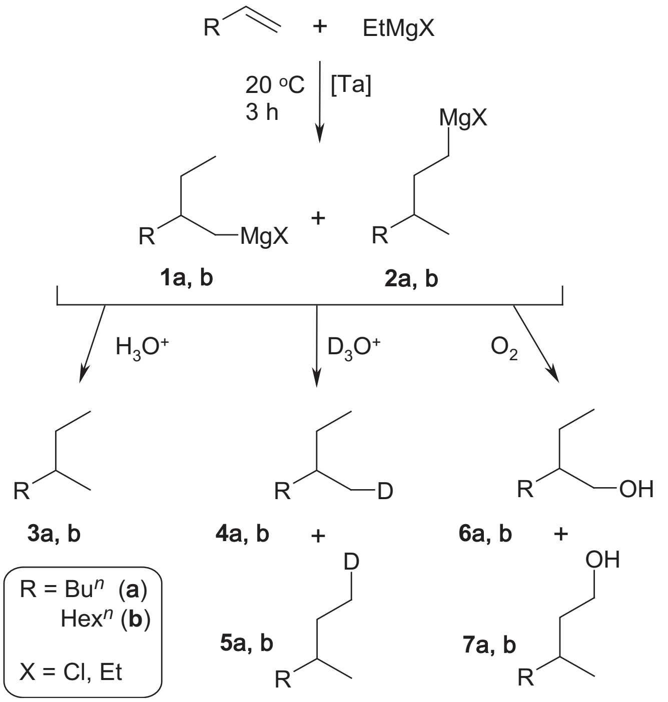
Oxidation of the reaction mixture with dry oxygen affords regioisomeric alcohols **6b** and **7b**, in which the hydroxyl groups are attached to different carbon atoms (see Section Experimental). Thus, in the ^{13}C NMR spectrum of regioisomer **7b**, the carbinol signal appeared at higher field (δC^1 61.07 ppm) as compared to the corresponding signal in the spectrum of regioisomer **6b** (δC^{10} 65.18 ppm). Moreover, one can observe the significant difference between positions of the low field methyl carbon resonance (δC^{10} 19.65 ppm) and the shielded methyl carbon signal (δC^1 11.08 ppm) in the spectra of compounds **7b** and **6b** respectively. The 5:4 ratio of regioisomers **6b** and **7b** has been calculated through ^1H NMR experiments, from integration of unambiguously different proton signals belonging to the hydroxymethylene groups ($\delta C^1\underline{H}_2$ 3.51 and $\delta C^1\underline{H}_2$ 3.64 ppm for compounds **6b** and **7b** resp.).

For a study of tantalum-catalyzed alkene carbomagnesiation in more detail, we compared the reactivity of EtMgCl and Et_2Mg in the reaction with 1-octene (Table 1).

As seen in Table 1, carbomagnesiation of 1-octene with Et_2Mg (1:1.1 M ratio) in THF for 3 h afforded organomagnesiums **1b** and **2b** in almost quantitative yield (Table 1, entry 4), whereas the higher OMC:olefin ratios (2:1) are required to achieve the same results with EtMgCl (Table 1, entries 2 and 5).



Scheme 2.



Scheme 3.

It should be noted that we could not obtain the desired result while using the diethyl ether as a solvent. The above reaction can proceed satisfactorily only in the presence of tetrahydrofuran (Et_2O:THF = 1:1), but a total yield of **1b** and **2b**, in this case, was much smaller than in pure THF (Table 1, entry 8).

Carbomagnesiation of other 1-alkenes, e.g. 1-hexene, in the presence of $TaCl_5$ occurs in a similar manner. The yields of the target products and their molar ratios remain the same.

Further, we intend to study this reaction involving various tantalum complexes, other unsaturated hydrocarbons and alkylmagnesiums as well. The stoichiometric variants of the reaction discovered will be also explored. Special efforts will be focused on developing selective synthesis of the unusual products **2a**,**b**.

The detailed mechanism of the interaction between 1-alkene and EtMgCl (or Et_2Mg) requires additional research. Nevertheless, our experimental findings as well as the literature data [4,7] allow us to suggest possible ways for the simultaneous formation of the OMCs **1** and **2** (Scheme 4).

We suppose that carbomagnesiation of 1-alkene with an excess of EtMgCl (or Et_2Mg) in the presence of $TaCl_5$ proceeds along two parallel reaction pathways. The first step of both routes involves the formation of the labile tantalacyclopentane intermediate **8**. The subsequent stepwise transmetallation of **8** through simultaneous formation of two bimetallic complexes **9** (route 1) and **10** (route 2) finally affords 2-(R-substituted)-*n*-butylmagnesium (product **1**) and 3-(R-substituted)-*n*-butylmagnesium (product **2**) compounds respectively as a result of β-hydride transfer.

3. Conclusions

Thus, we represent a new approach to the synthesis of mono-organomagnesiums from 1-alkenes mediated by ethyl Grignard reagents and $TaCl_5$ as a catalyst. In contrast to the known Zr-catalyzed carbomagnesiation, the new catalytic method makes it