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Effect of the Grignard Reagent on the X→C_{sp} Migration of the MR_3 Group in $HC{\equiv}CCH_2XMR_3$ Compounds*

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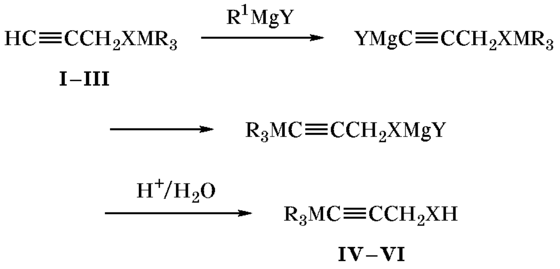
Abstract—The effect of the Grignard compounds (EtMgBr, PhMgBr, *t*-BuMgCl, *cyclo*-$C_6H_{11}MgBr$, and $PhC{\equiv}CMgBr$) on the isomerization of $HC{\equiv}CCH_2XMR_3$ into $R_3MC{\equiv}CCH_2XH$ (M = Si, Ge; X = O, S) was studied. The efficiency of the 1,4-(X→C_{sp})-migration of the R_3M group was shown to depend on the nucleophilicity of the Grignard compound and nature of the M–X bond.

We previously reported [1–4] on a new method for formation of an M–C_{sp} bond via isomerization of the terminal propynes $HC{\equiv}CC(R^1R^2)XMR_3$ into $R_3MC{\equiv}CC(R^1R^2)XH$ (X = O, S; M = Si, Ge) by the action of Grignard compounds. We studied the effect of the structure of heteroelement-containing propynes (the presence of substituents at the carbon atoms of trimethylsilyl alkynyl ethers and the nature of heteroelements X and M) on the ability of the MR_3 group to migrate from the X atom to C_{sp} [2–5]. An intermolecular mechanism of the process was proposed and substantiated [2]. The goal of the present work was to examine the effect of the Grignard compound on the isomerization. The following Grignard compounds were used: ethylmagnesium bromide, phenylmagnesium bromide, cyclohexylmagnesium bromide, phenylethynylmagnesium bromide, and *tert*-butylmagnesium chloride. The substrates were terminal propynes $HC{\equiv}CCH_2XMR_3$ (**I**–**III**), where X = O, S; M = Si, Ge. The isomerization process can be illustrated by Scheme 1.

Scheme 1.



$$HC{\equiv}CCH_2XMR_3 \xrightarrow{R^1MgY} YMgC{\equiv}CCH_2XMR_3 \longrightarrow R_3MC{\equiv}CCH_2XMgY \xrightarrow{H^+/H_2O} R_3MC{\equiv}CCH_2XH$$

I–III → **IV–VI**

I, **IV**, R_3M = Me_3Si, X = O; **II**, **V**, R_3M = Et_3Ge, X = O; **III**, **VI**, R_3M = Me_3Si, X = S; Y = Br, R^1 = Et, Ph, *cyclo*-C_6H_{11}, $PhC{\equiv}C$; Y = Cl, R^1 = *t*-Bu.

The data in table show that the efficiency of isomerization of compounds **I**–**III** strongly depends on the nature of the Grignard compound. With the use of ethylmagnesium bromide the yield of 3-trimethylsilyl-2-propyn-1-ol (**IV**) from 1-trimethylsiloxy-2-propyne (**I**) was 85% (tetrahydrofuran, 9 h under reflux) [2]. Under similar conditions, but in the presence of phenylmagnesium bromide, the yield of alcohol **IV** was 54% (83% on the reacted ether). These findings indicate that the isomerization slows down on replacement of EtMgBr by PhMgBr. The effect of RMgBr is seen most clearly in the isomerization of propynes **II** and **III** containing Ge–O and Si–S bonds. Under conditions optimal for the isomerization of ether **I**, the yield of 3-triethylgermyl-2-propyn-1-ol (**V**) from 1-triethylgermoxy-2-propyne (**II**) was as low as 12.5% [5]. On the other hand, in the presence of a softer nucleophile, phenylmagnesium bromide, the yield of 3-triethylgermyl-2-propyn-1-ol (**V**) increases almost fourfold (48%). The isomerization induced by PhMgBr successfully occurs at room temperature, the reaction time being prolonged by a factor of ~1.5. An analogous effect of the Grignard compound nature was observed in the isomerization of 1-trimethylsilylthio-2-propyne (**III**). Replacement of ethylmagnesium bromide [4] by phenylmagnesium bromide increases the yield of the

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Effect of the Grignard compound on the isomerization

$$\mathrm{HC{\equiv}CCH_2XMR_3} \xrightarrow{(1)\ \mathrm{R^1MgY};\ (2)\ \mathrm{H^+/H_2O}} \mathrm{R_3MC{\equiv}CCH_2XH}$$

R_3M	X	R^1MgBr	Solvent	Temperature, °C	Time, h	Yield, %	Reference
Me_3Si	O	EtMgBr	Ether	35–36	9	24.5	[2]
Me_3Si	O	EtMgBr	THF	64–65	9	85	[2]
Me_3Si	O	PhMgBr	Ether	25	15	22	
Me_3Si	O	PhMgBr	THF	64–65	9	54 (83^a)	
Me_3Si	O	*t*-BuMgCl	THF	64–65	9	3.5	
Me_3Si	O	*cyclo*-C_6H_{11}	THF	64–65	9	12.5	
Me_3Si	O	PhC≡CMgBr	THF	64–65	9	23^b	
Et_3Ge	O	EtMgBr	THF	64–65	9	12.5	[5]
Et_3Ge	O	PhMgBr	THF	64–65	9	48	[5]
Et_3Ge	O	PhMgBr	THF	25	9	43	[5]
Et_3Ge	O	PhC≡CMgBr	THF	25	15	12	
Me_3Si	S	EtMgBr	THF	25	5	31^c $(17)^d$	[4]
Me_3Si	S	PhMgBr	THF	25	6	48^d	

[a] Calculated on the reacted ether.

[b] 1-Phenyl-2-trimethylsilylacetylene was also isolated in 20% yield.

[c] Isolated as $Me_3SiC{\equiv}CCH_2SMe$.

[d] Isolated as $Me_3SiC{\equiv}CCH_2SEt$.

isomerization product almost threefold (the product was isolated as the corresponding *S*-ethyl derivative, $Me_3SiC{\equiv}CCH_2SEt$). These data indicate a greater efficiency of using phenylmagnesium bromide in the isomerization of propynes **II** and **III**; the Ge–O and Si–S bonds in the latter are more sensitive to organomagnesium compounds than the Si–O bond in **I**. Unlike phenylmagnesium bromide, ethylmagnesium bromide as a stronger nucleophile readily cleaves the Ge–O and Si–S bonds in compounds **II** and **III**, thus reducing the yield of isomerization products **V** and **VI**.

tert-Butylmagnesium chloride and cyclohexylmagnesium bromide showed a weak activity in the isomerization under study. In the presence of these Grignard compounds the yield of alcohol **IV** from ether **I** was 3.5 and 12.5%, respectively. A possible reason for the low yields of the isomerization product is heterolytic cleavage of the Si–O bond by the action of *t*-BuMgCl and *cyclo*-$C_6H_{11}MgBr$ which are stronger bases than EtMgBr.

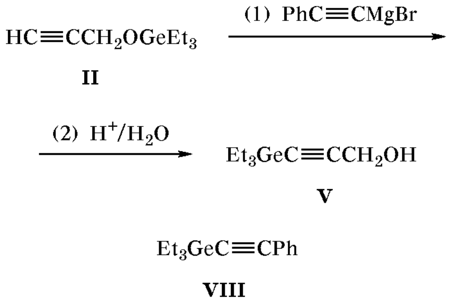
Phenylethynylmagnesium bromide as nucleophile gave rise to different results of the rearrangements of trimethylsilyl and triethylgermyl 2-propynyl ethers **I** and **II**. The reaction of ether **I** with PhC≡CMgBr in THF gave 23% of expected alcohol **IV** and 20% of phenyltrimethylsilylacetylene **VII** (Scheme 2). The formation of product **VII** is explained by participation of the trimethylsilyl group of initial ether **I** in the C_{sp}-silylation of phenylacetylene. The reaction mixture also contained phenylacetylene, 2-propynyl alcohol, and hexamethyldisiloxane (GLC).

Scheme 2.

$$\underset{\textbf{I}}{\mathrm{HC{\equiv}CCH_2OSiMe_3}} \xrightarrow{(1)\ \mathrm{PhC{\equiv}CMgBr}} \xrightarrow{(2)\ \mathrm{H^+/H_2O}} \underset{\textbf{IV}}{\mathrm{Me_3SiC{\equiv}CCH_2OH}} + \underset{\textbf{VII}}{\mathrm{Me_3SiC{\equiv}CPh}}$$

The reaction of germanium analog **II** with phenylethynylmagnesium bromide under the conditions favoring the isomerization (THF, room temperature, 15 h) gave 3-triethylgermyl-2-propyn-1-ol (**V**) in 12% yield (Scheme 3). According to the GLC data, the reaction mixture also contained phenylacetylene, 2-propynyl alcohol, and hexaethyldigermoxane, while no phenyltriethylgermylacetylene (**VIII**) was detected. It could be expected that heterolytic cleavage of the Ge–O bond in ether **II** by the action of PhC≡CMgBr with formation of compound **VIII** would occur more readily than in the case of silyl analog **I**. The obtained

Scheme 3.



$$HC{\equiv}CCH_2OGeEt_3 \xrightarrow{(1)\ PhC{\equiv}CMgBr} \xrightarrow{(2)\ H^+/H_2O} Et_3GeC{\equiv}CCH_2OH + Et_3GeC{\equiv}CPh$$

II, V, VIII

results may be explained as follows. In both cases phenylethynylmagnesium bromide acts as a weak metalating agent which converts ethers **I** and **II** into the corresponding Iotsitch compounds. Taking into account that the isomerization of propyne **I** is a relatively slow process (see table), concurrent heterolysis of the Si–O bond by the action of phenylethynylmagnesium bromide leads to formation of compound **VII**. The rearrangement of germanium-containing analog **II** is faster, so that its bromomagnesium derivative is removed from the reaction, favoring metalation of the triple bond of the substrate. Presumably, just the higher rate of isomerization, i.e., of heterolytic cleavage of the Ge–O bond by the Iotsitch reagent derived from ether **II** rather than by phenylethynylmagnesium bromide (to give phenyltriethylgermylacetylene **VIII**), is responsible for the observed reaction pattern.

We can conclude that efficient 1,4-migration of a heteroelement-containing group R_3M from heteroatom X to the terminal C_{sp} atom requires proper choice of Grignard compound. The main requirement is the stability of the X–M bond in terminal alkyne **I**–**III** toward organomagnesium halide. The use of phenylmagnesium bromide as a less basic nucleophile than ethylmagnesium bromide is preferable in the isomerization of propynes in which the X–M bond readily undergoes heterolytic cleavage. More nucleophilic Grignard compounds, such as *tert*-butylmagnesium chloride and cyclohexylmagnesium bromide, give rise to cleavage of even stronger Si–O bond in the ethers under study by those reagents rather than by the corresponding Iotsitch compounds. Phenylethynylmagnesium bromide is a weak metalating agent in the formation of Iotsitch compounds from 1-trimethylsiloxy- and 1-triethylgermoxy-2-propynes, which is responsible for unsatisfactory yields of the rearrangement products. Trimethylsilyl 2-propynyl ether undergoes concurrent heterolysis of the Si–O bond by the action of PhC≡CMgBr, leading to formation of phenyltrimethylsilylacetylene.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer. GLC analysis was performed on an LKhM-80 chromatograph equipped with a thermal conductivity detector; carrier gas helium; column 1500 × 3.0 mm; stationary phase 10% of polymethylsiloxane on Chromaton.

Isomerization of 1-trimethylsiloxy-2-propyne (I). *A. By the action of PhMgBr. a.* 1-Trimethylsiloxy-2-propyne, 5.13 g (0.04 mol), was added to the Grignard compound prepared from 1.94 g (0.08 mol) of magnesium and 6.28 g (0.04 mol) of freshly distilled phenyl bromide in 50 ml of THF (the solution was filtered from excess magnesium), and the mixture was refluxed for 9 h. The solvent was distilled off, and the residue was treated with 5% hydrochloric acid and extracted with ether. The extract was dried over anhydrous $MgSO_4$ and evaporated to obtain 4.9 g of the residue which was analyzed by GLC using an authentic sample of 3-trimethylsilyl-2-propyn-1-ol. The yield of alcohol **IV** was 54% (83% on the reacted ether **I**).

b. Ether **I**, 2.1 g (0.016 mol), was quickly added to the Grignard compound prepared from 0.48 g (0.02 mol) of magnesium and 3.14 g (0.02 mol) of phenyl bromide in 20 ml of THF. The mixture was stirred for 15 h at 20°C and was then treated as described above. The residue, 1.9 g, contained 22% of alcohol **IV** (GLC).

B. By the action of t-BuMgCl. 1-Trimethylsiloxy-2-propyne, 2.83 g (0.022 mol), was added to the Grignard compound prepared from 0.97 g (0.04 mol) of magnesium and 3.7 g (0.04 mol) of *tert*-butyl chloride in 40 ml of THF (activation with iodine; yield 55%, according to the data of titration with 0.1 N hydrochloric acid [6]), and the mixture was refluxed for 9 h. The solvent was distilled off, and the residue was hydrolyzed with 5% hydrochloric acid. After appropriate treatment, 2.3 g of a residue was obtained. According to the GLC data, it was a mixture of 2-propynyl alcohol, hexamethyldisiloxane, and 3-trimethylsilyl-2-propyn-1-ol (**IV**); the yield of the latter was 4%.

C. By the action of cyclo-C_6H_{11}MgBr. A solution of 5 g (0.04 mol) of 1-trimethylsiloxy-2-propyne (**I**) in 5 ml of THF was added to the Grignard compound prepared from 1.94 g (0.08 mol) of magnesium and 6.52 g (0.04 mol) of cyclohexyl bromide in 40 ml of THF (the solution was filtered from excess magnesium under nitrogen). The mixture was treated as described above to isolate 4.2 g of a residue. According to the GLC data, the residue was a mixture of

2-propynyl alcohol, hexamethyldisiloxane, and 3-trimethylsilyl-2-propyn-1-ol (**IV**) (13%).

D. By the action of PhC≡CMgBr. Phenylacetylene, 8.17 g (0.08 mol), was added over a period of 5 min to the Grignard compound prepared from 2 g (0.08 mol) of magnesium and 9 g (0.08 mol) of ethyl bromide in 80 ml of THF, and the mixture was stirred for 0.5 h at room temperature. A solution of 10.26 g (0.08 mol) of 1-trimethylsiloxy-2-propyne (**I**) in 10 ml of THF was added, and the reaction mixture was refluxed for 9 h. By appropriate treatment we obtained 17 g of a residue which, according to the GLC data, contained 23% of 3-trimethylsilyl-2-propyn-1-ol (**IV**), 20% of 1-phenyl-2-trimethylsilylacetylene (**VII**), phenylacetylene, 2-propynyl alcohol, and hexamethyldisiloxane, which were identified by comparing with authentic samples.

Isomerization of 1-triethylgermoxy-2-propyne (II) by the action of PhC≡CMgBr. A solution of 1 g (0.01 mol) of phenylacetylene in 3 ml of THF was added over a period of 5 min to the Grignard compound prepared from 0.21 g (9 mmol) of magnesium and 0.95 g (9 mmol) of ethyl bromide in 10 ml of THF. The mixture was stirred for 0.5 h, 1.9 g (9 mmol) of 1-triethylgermoxy-2-propyne (**II**) was added, and the mixture was stirred for 15 h at room temperature. The solvent was distilled off, and the residue was decomposed with a saturated solution of ammonium chloride and was then treated as described above. According to the GLC data, the residue, 2.5 g, contained 3-triethylgermyl-2-propyn-1-ol (12%), phenylacetylene, 2-propynyl alcohol, and hexaethyldigermoxane.

Isomerization of 1-trimethylsilylthio-2-propyne (III) by the action of PhMgBr. A solution of 1.61 g (0.011 mol) of 1-trimethylsilylthio-2-propyne in 3 ml of THF was added at 0–6°C to the Grignard compound prepared from 0.27 g (0.011 mol) of magnesium and 1.75 g (0.011 mol) of phenyl bromide in 7 ml of THF. The mixture was stirred for 1 h at 0–6°C, allowed to warm up to room temperature, and stirred for 6 h. Ethyl iodide, 2.6 g (0.016 mol), was added, and the mixture was left overnight. It was decomposed with a saturated solution of NH_4Cl, the product was extracted into ether, and the extract was dried over $MgSO_4$. The solvent was removed, and the residue, 3 g, was analyzed by GLC using an authentic sample of 3-ethylthio-1-trimethylsilylpropyne (**VI**) [4]. Yield 48%.

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