

SHORT
COMMUNICATIONS

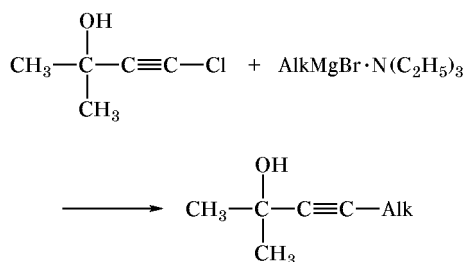
Effect of Complexing Agent on the Reactivity of Organomagnesium Compounds in Toluene

S. A. Shchelkunov, O. A. Sivolobova, and N. I. Yashnova

Institute of Organic Synthesis and Coal Chemistry, Ministry of Science and Higher Education of Kazakhstan, ul. 40 let Kazakhstana 1, Karaganda, 470061 Kazakhstan

Received December 6, 2001

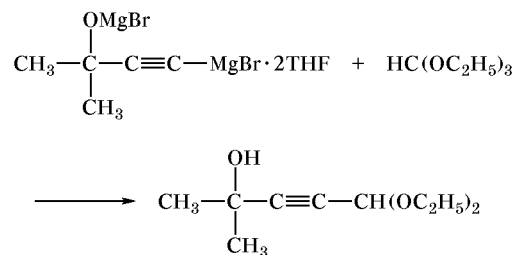
We previously showed [1] that the use of $\text{AlkMgX} \cdot \text{THF}$ complexes in aromatic hydrocarbons instead of Grignard compounds in diethyl ether ensures replacement of the chlorine atom in 4-chloro-2-methyl-3-butyn-2-ol and preparation of the corresponding alkyl-acetylenic alcohols in good yield; simultaneously, the fire risk of the process is considerably reduced. With the goal of further improving this procedure we have examined the possibility of replacing THF by cheaper and flame-proof triethylamine.



We have found that the reaction of Grignard compounds with 4-chloro-2-methyl-3-butyn-2-ol in toluene in the presence of triethylamine as complexing agent shows the same general relations as with the use of THF. Aliphatic Grignard compounds react much more readily than do arylmagnesium halides, and the yield of the target products attains 80%. Therefore, $\text{AlkMgX} \cdot \text{N}(\text{C}_2\text{H}_5)_3$ complexes are more appropriate than $\text{AlkMgX} \cdot \text{THF}$ for nucleophilic substitution of chlorine at the triple bond.

On the other hand, in reactions following the electrophilic elimination–addition pattern, where the crucial factor is the acidity of the cationic component of organomagnesium compound, the use of $\text{AlkMgX} \cdot \text{N}(\text{C}_2\text{H}_5)_3$ complexes gives no positive results. In particular, the reaction of Iotsich compound derived from 2-methyl-3-butyn-2-ol with triethyl orthoformate

gives only 23% of the target hydroxy acetal. In the presence of less donor THF the yield increases to 67%, which is comparable with the results obtained in diethyl ether [2].



2-Methyl-3-nonyn-2-ol (I). To the Grignard compound prepared from 4.0 g (0.17 mol) of metallic magnesium, 18.6 ml (22.65 g, 0.15 mol) of pentyl bromide, and 24.3 ml (17.51 g, 0.17 mol) of triethylamine in 50 ml of toluene [3] we added dropwise with stirring 5.5 ml (5.9 g, 0.05 mol) of 4-chloro-2-methyl-3-butyn-2-ol. The mixture was heated for 4 h at 60°C and decomposed with 3% hydrochloric acid on cooling, the organic phase was separated and dried over magnesium sulfate, and volatile fractions were distilled off. Vacuum distillation of the residue at 92–94°C (10 mm) gave 6.16 g (80%) of 2-methyl-3-nonyn-2-ol, $n_D^{20} = 1.4434$. Following a similar procedure, 72% of 2-methyl-3-decyn-2-ol (**II**) was obtained, $n_D^{20} = 1.4424$.

4-Hydroxy-4-methyl-2-pentynal diethyl acetal (III). Butyl bromide, 2.2 ml (2.74 g, 0.02 mol), was added to a mixture of 5.3 g (0.22 mol) of metallic magnesium, 50 ml of toluene, and 1.6 ml (1.44 g, 0.02 mol) of THF. The mixture was heated to 40°C. When the reaction started, 9.8 ml (8.4 g, 0.10 mol) of 2-methyl-3-butyn-2-ol, 19.4 ml (24.66 g, 0.18 mol) of butyl bromide, and 14.7 ml (12.96 g, 0.18 mol) of

THF in 50 ml of toluene were simultaneously added dropwise with stirring at 40°C. The mixture was heated for 0.5 h, 16.4 ml (14.8 g, 0.10 mol) of ethyl orthoformate was added, and the mixture was heated for 4 h at 60°C and decomposed with a saturated solution of NH₄Cl on cooling with water. The organic phase was separated and dried over magnesium sulfate, and volatile fractions were distilled off. Vacuum distillation of the residue at 91–92°C (3 mm) gave 12.46 g (67%) of 4-hydroxy-4-methyl-2-pentynal diethyl acetal, n_D^{20} 1.4400.

The IR spectra of compounds **I–III** contained absorption bands typical of C≡C bond (2220–2230 cm⁻¹) and OH group (3350–3400 cm⁻¹). Compound **III** also showed in the IR spectrum a band at 1250 cm⁻¹, which is typical of stretching vibrations of ether moiety.

The physical properties of products **I–III** were consistent with published data [1, 2]. The IR spectra were recorded on a UR-20 spectrometer.

REFERENCES

1. Shchelkunov, S.A., Sivolobova, O.A., Mataeva, S.O., Minbaev, D.B., and Muldakhmetov, Z.M., *Russ. J. Org. Chem.*, 2001, vol. 37, no. 1, pp. 5–8.
2. Shchelkunov, A.V., Vasil'eva, R.L., and Krichevskii, L.A., *Sintezy i vzaimnye prevrashcheniya monozameshchennykh atsetilenov* (Syntheses and Mutual Transformations of Monosubstituted Acetylenes), Alma-Ata: Nauka, 1976, pp. 142–143.
3. Fieser, L.F. and Fieser, M., *Reagents for Organic Synthesis*, New York: Wiley, 1968, vol. 1. Translated under the title *Reagenty dlya organicheskogo sinteza*, Moscow: Mir, 1970, vol. 1, p. 231.