Simple Procedures for Ethynylmagnesium Bromide, Ethynyltrialkylsilanes and Ethynyltrialkylstannanes

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Abstract: 1 Molar solutions of ethynylmagnesium bromide in tetrahydrofuran can be successfully prepared by introducing acetylene into a cooled solution of ethylmagnesium bromide. Subsequent reaction with trialkylsilyl or trialkylstannyl chloride gives the expected ethynyl derivatives in excellent yields.

Key words: alkynes, disproportionation, ethynyl di-magnesium halides, Grignard reactions, magnesium, silicon, tin, organometallic reagents

Ethynylmagnesium halides are extremely versatile intermediates for the preparation of monosubstituted acetylenes. Traditionally, solutions of ethynylmagnesium halides are prepared by a procedure of inverse addition, i.e. slow addition of a solution of alkylmagnesium halide in THF to a saturated solution of acetylene in this solvent.[1–4]

The inverse addition seems to be essential, since the mono-Grignard derivative is thought to be capable of reacting with alkylmagnesium halide to form the di-Grignard derivative. A serious drawback of this procedure is that its correct performance requires considerable experimental skill and continuous alertness throughout the introduction of acetylene over three hours. During this period the temperature is kept below 30 °C in order to avoid formation of the di-Grignard derivative by a disproportionation reaction, while the rate of addition of the solution of alkylmagnesium halide has to be continuously readjusted due to the formation of solid material in the lower part of the dropping funnel. In a recent Organic Syntheses procedure[2] a hot (60 °C) solution of butylmagnesium chloride is added from the dropping funnel, but the advantage of easier addition is relatively small when it is realized that butylmagnesium chloride is much less smoothly prepared than ethylmagnesium bromide. As a consequence, the synthesis of mono-substituted acetylenes via ethynylmagnesium halide is not highly attractive, especially when the acetylenes are only needed incidentally.

In this communication we present a procedure for ethynylmagnesium bromide that should be preferred to the traditional ones. Its success is demonstrated by the preparation of the useful synthetic intermediates, ethynyltrialkylsilanes and -stannanes, in excellent yields. In our procedure acetylene is simply introduced into a 1 M solution of ethylmagnesium bromide in THF at temperatures around 10 °C (Scheme 1).

$$\mathrm{C_2H_5MgBr} \quad + \quad \mathrm{HC{\equiv}CH} \xrightarrow[\text{5-15 °C}]{\text{THF}} \mathrm{HC{\equiv}CMgBr} \quad + \quad \mathrm{C_2H_6}$$

Scheme 1

Although formation of the di-Grignard derivative BrMgC≡CMgBr is in principle possible, we strongly suspect that the formation of the mono-Grignard reagent will occur to a significant extent if the acetylene is introduced quickly and the concentration of the solution of ethylmagnesium bromide is not higher than 1 mol/L. Reactions of the thus obtained suspension with chlorotrimethylsilane, chlorotrimethylstannane and chlorotributylstannane gave the expected ethynyl derivatives in 70% or higher yields (Scheme 2).

$$\mathrm{HC{\equiv}CMgBr} \xrightarrow{\mathrm{R_3XCl}} \mathrm{HC{\equiv}C{-}XR_3}$$

X = Si, R = CH_3 : 75-80%
X = Sn, CH_3 : 70%
X = Sn, C_4H_9 : 85%

Scheme 2

It is essential to add the chloro compounds quickly with efficient stirring. Slow addition may favour the formation of disubstituted acetylenes, according to us by a process of proton abstraction and subsequent substitution (compare Ref. 2, note 7) (Scheme 3).

$$\mathrm{R_3X{-}C{\equiv}CH} \xrightarrow{\mathrm{HC{\equiv}CMgBr}} \mathrm{R_3X{-}C{\equiv}C{-}MgBr} \xrightarrow{\mathrm{R_3XCl}} \mathrm{R_3X{-}C{\equiv}C{-}XR_3}$$

Scheme 3

Also higher concentrations of ethylmagnesium bromide have to be avoided as the reaction mixtures become difficult to stir. As a result, the distribution of the chloro compounds through the suspension becomes less efficient and disubstituted acetylenes may form by the process mentioned above.

From our results one may conclude that the reluctance to apply the normal addition procedure for ethynylmagnesium halides is not fully justified. It has not been proved that the formation of significant amounts of disubstituted acetylenes is due to conversion of $HC\equiv CMgX$ into $XMgC\equiv CMgX$ by a disproportionation reaction at temperatures below 30 °C. Our earlier[3] described synthesis of $Me_3SiC\equiv CSiMe_3$ with an excellent yield by introducing acetylene at ~50 °C into a solution of C_2H_5MgBr and subsequent silylation suggests that this disproportionation actually can occur at temperatures above 40 °C.

Ethynyltrimethylsilane, Ethynyltimethylstannane and Ethynyltributylstannane; Typical Procedures

In a 2-L round-bottomed, three-necked flask equipped with a combination of a dropping funnel and a N_2 inlet, a mechanical stirrer and a combination of a thermometer and outlet were placed Mg turnings (33.6 g, 1.4 mol) and anhyd THF (150 mL). After activation of the Mg with 1,2-dibromoethane or I_2, the flask was filled with N_2 and THF (1.2 L) was added. EtBr (141.7 g, 1.3 mol) was added dropwise over 1 h, while keeping the temperature between 30 and 40 °C. After an additional hour (~35 °C) the solution was transferred into another 2-L three-necked flask (previously filled with N_2, Note 1), equipped with an inlet tube, a *very efficient* mechanical stirrer and a thermometer-outlet-combination. The excess of Mg was rinsed with THF (50 mL). The solution was cooled to about 5 °C (with temporary increase of the flow of N_2). Acetylene (freed from acetone by passing through two traps cooled at ~ –75 °C) was introduced with vigorous stirring (high turbulence!) at a rate of ~2 L/min during 10 min, while keeping the temperature of the suspension between 5 and 10 °C (during this period the heating effect, partly due to dissolution of acetylene in the THF is rather strong requiring efficient cooling). Subsequently the gas was introduced during 30 min at a rate of ~300 mL/min and the temperature of the suspension was maintained closely around 10 °C. The rate of stirring was then diminished and the suspension was stirred for an additional period of 1 h with slow (~100 mL/min) introduction of acetylene. External cooling was no longer carried out. After an half-hour interval (temperature of the suspension ~15 °C) the suspension was cooled to 5 °C and chlorotrimethylsilane (108.6 g, 1. 0 mol, distilled from ~10% of *N*,*N*-diethylaniline) was added in two to three portions during 2 min with vigorous stirring and keeping the temperatrure below 20 °C (the heating effect was moderate). The reaction mixture was stirred for 30 min at 15–20 °C, subsequently for 30 min at 35 °C.

A similar procedure was carried out with chlorotrimethylstannane (60.0g, 0.30 mol) and chlorotributylstannane (97.8 g, 0.30 mol) in a 1-L round-bottomed flask (volume of THF ~450 mL, amounts of Mg and EtBr 12 and 50 g, respectively).

For the workup the following operations were carried out. To the mixture from the reactions with Me_3SiCl and Me_3SnCl was added high boiling petroleum (bp ≥180 °C/760 Torr, 200 mL, Note 2) and pentane (200 mL) in the case of the reaction with Bu_3SnCl. The slurries were then poured with manual swirling into a cold (~5 °C) solution of NH_4Cl (150, 50 and 50 g, respectively) in H_2O (2, 1 and 1 L, respectively). After shaking (caution, some dissolved acetylene may escape!), the layers were separated. The upper layers were repeatedly (10 to 15 times) washed with H_2O (500 mL portions of ice water in the case of $Me_3SiC\equiv CH$ and $Me_3SnC\equiv CH$) in order to remove the THF as completely as possible. After drying ($MgSO_4$), the ethynyl derivatives were isolated.

Ethynyltrimethylsilane

Ethynyltrimethylsilane was distilled off at atmospheric pressure from the petroleum through a 25 cm Vigreux column. The fraction passing over between 50 and 110 °C still contained some THF. This was removed almost completely by washing with cold (0 °C) 3 M HCl (5 x 50 mL) in a small (200 mL) separating funnel. After drying over a small amount of $MgSO_4$, the ethynyltrimethylsilane was distilled at atmospheric pressure; bp ~52 °C; yield:75–80%.

Ethynyltrimethylstannane

The isolation of ethynyltrimethylstannane was carried out by subjecting the petroleum solution to a vacuum distillation (15 Torr), using a 40-cm Vigreux column and a receiver cooled at ~ –75 °C. The distillation was stopped when the petroleum began to reflux in the upper part of the column. Careful redistillation through a 30-cm spinning band column gave, after a first fraction mainly consisting of THF and ethynyltrimethylstannane; bp 98 °C/760 Torr; n_D^{20} 1.461 in 70% yield. The ^1H NMR spectrum (CCl_4) showed signals at $\delta = 2.0$ and 0.32.

Ethynyltributylstannane

Ethynyl tributylstannane; bp 92 °C/1 Torr; n_D^{20} 1.4758 (yield:85%) was obtained by removal of the solvents under reduced pressure followed by distillation through a 20 cm Vigreux column. The ^1H NMR spectrum shows inter alia the signal at $\delta = 2.0$ for the ethynyl proton. There was only about 4 g of higher boiling residue. The preparation of this ethynyl compound in only 31% yield from lithium acetylide-ethylene diamine complex and chlorotributylstannane is described in Organic Syntheses.[5] This modest yield may be due to metallation of $HC\equiv CSnBu_3$ by $LiC\equiv CH$ and subsequent conversion to $Bu_3SnC\equiv CSnBu_3$.

Notes

1. It is not absolutely necessary to separate the solution of EtMgBr from the excess of Mg.

2. In the Organic Syntheses procedure[2] for the preparation for ethynyltrimethylsilane, no solvent for the extraction of the product was used. This involves the risk of losing part of the volatile product during repeated washing with H_2O.

References

(1) Skattebøl, L.; Jones, E. R. H.; Whiting, M. C. *Org. Synth. Coll. Vol. 4* **1992**, 792.

(2) Holmes, A. B.; Sporikou, C. N.*Org. Synth., Coll. Vol. 8* **1993**, 606.

(3) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes, A Laboratory Manual*, Elsevier: Amsterdam, 1981.
L. Brandsma, *Preparative Acetylenic Chemistry,* 2nd ed., Elsevier, Amsterdam, 1988.

(4) Fieser; L. F.; Fieser, M. *Reagents for Organic Synthesis, Vol 1*, Wiley: New York, 1967.

(5) Renaldo, A. F.; Labadie, J. F.; Stille, J. K. *Org. Synth. Coll. Vol. 8* **1993**, 268.

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