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REACTION OF PROPARGYLTRIMETHYLSILANE MAGNESIUM BROMIDE WITH ALDIMINES: SYNTHESIS OF 1-(ALKYLAMINO)-2-(TRIMETHYLSILYL)BUT-3-YNE

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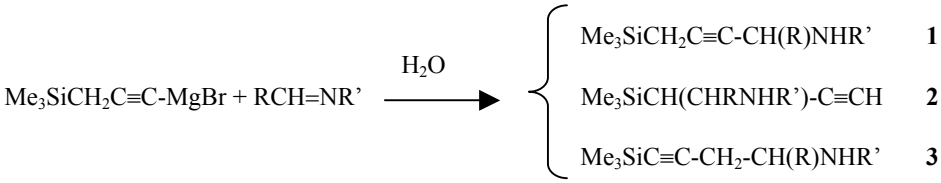
ABSTRACT. The reaction of propargylsilane magnesium bromide with aldimines provides in some cases, an isomeric mixture of 3 acetylenic amines **1**, **2**, **3** (**1**, **2**, as major products). The reaction has great potential and has been exploited for an efficient synthesis of the pure amine **2**.

KEY WORDS: Propargylsilane magnesium bromide, Aldimines, 1-(alkylamino)-2-(trimethylsilyl)but-3-yne, Acetylenic amines,

INTRODUCTION

Considerable attention has been given over the past few years to the use of propargyltrimethylsilane magnesium bromide as a synthetic reagent, such as: (a) in the study of the methylisosartotuate synthesis [1]; (b) in the reaction with carbonyl derivatives [2-4] for the preparation of 4-(trimethylsilyl)but-2-ynol, Me_3SiCH_2-C≡C-CRR'(OH); (c) in the treatment with epoxide [5] in order to obtain 5-(trimethylsilyl)pent-3-ynol, Me_3SiCH_2-C≡C-CH_2CH_2OH; and (d) in the reaction with trimethylchlorosilane [6] to give 1,3-(bistrimethylsilyl)prop-1-yne, Me_3SiCH_2-C≡C-$SiMe_3$.

In continuation of the work in this field, we wanted to obtain a convenient preparation of **1**. We obviously investigated the reaction of propargylsilane magnesium bromide with aldimines. The reaction is more complex as expected and gives a mixture of three products **1**, **2**, **3** after hydrolysis.



The amine **2** is the major product according to the experience. This paper describes the general method and the limitations for the preparation of this product.

RESULTS AND DISCUSSIONS

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Reaction of propargylsilane magnesium bromide with aldimines

Propargylsilane magnesium bromide was treated with two aliphatic aldimines and four benzaldimines. The results are summarised in Table 1. According to these results, in some cases an isomeric mixture of **1**, **2**, and **3** is obtained. Only traces of **3** were observed with the aldimine CH_2=NC$(CH_3)_3$, (R=H, R'=C$(CH_3)_3$).

Table 1. Reaction of $Me_3SiCH_2C{\equiv}C$-MgBr/Et_2O with RCH=NR'.

Aldimine RCH=NR'		Condition*	Amine	Yield (%)
R	R'			
H	Me_3C	(a)	**1a**	35
			2a	39
			3a	<2
H	Me_3C	(b)	**2a**	53
iPr	Me	(a)	**1b**	6
			2b	11
		(c)	**1b**	12
iPr	nBu	(a)	**2c**	10
C_6H_5	Me	(a)	**2d**	20
C_6H_5	Et	(a)	**2e**	75
C_6H_5	nPr	(a)	**2f**	70**
C_6H_5	nBu	(a)	**2g**	54**

*(a): mol propargyltrimethylsilane/mole ethylbromide magnesium/mol aldimine = 1/1.4/1.2. The reaction was carried out at room temperature for 16 hours. (b): mol propargyltrimethylsilane/mol ethylbromide magnesium/mol aldimine = 1/1.4/ 1.2. The reaction was carried out at room temperature for 16 hours. Then heated to reflux for 16 hours. (c): same as condition (a) but 1/ 1/ 1. ** Traces of **4** RCH(C_2H_5)NHR', yield < 3%.

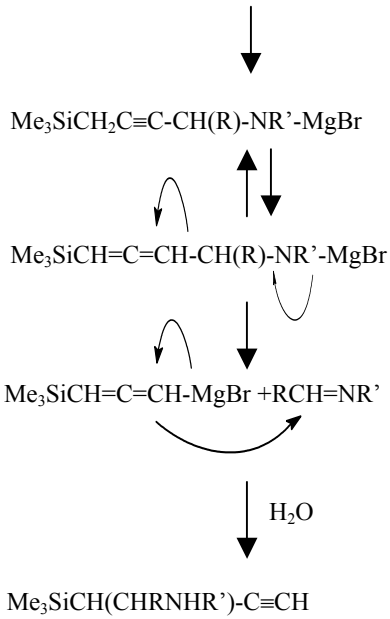
For the aliphatic aldimines the yields are relatively weak probably because of enamine formation [7]. The benzaldimines give pure **2** in good yields without heating. An excess of EtMgBr is usually necessary for better results (conditions (a) and (b)). The presence of the excess of EtMgBr seems to be important for the obtention of pure **2**. Heating may accelerate the reaction (condition (b)). Formation of **2** can be explained by the isomerisation of the expected amine **1** into **2** under the influence of the excess of EtMgBr. This involves deprotonation of **1** with EtMgBr, then conversion of the metallated acetylenic amine into its allenic isomer. The metallated allenic amine rearrangement liberates the aldimine and an allenic magnesium. The reaction of the obtained allenic magnesium and the aldimine affords **2** (Scheme 1).

The aldimine also reacts with an excess of EtMgBr to give after hydrolysis small amounts of the amine R(C_2H_5)CHNHR' 4 which have been isolated for heavy R' susbtituents (Scheme 2).

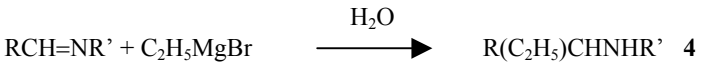
In order to confirm the proposed mechanism, we have prepared allenic amine $Me_3SiCH{=}C{=}CH\text{-}CH_2NHC(CH_3)_3$ **5** from reaction of **2a** with polyoxymethylene in acetonitrile in the presence of trifluoroacetic acid according to [8]. The treatment of **5** with excess of EtMgBr lead to pure **2a** (yield 24%).

In conclusion, we developed an efficient route for the preparation of pure propargylsilanes **2** with amine function; these compounds may be useful intermediates for the synthesis of new unsaturated amines via reduction reaction [9] and amino methylation [10-12].

$$Me_3SiCH_2C{\equiv}C\text{-MgBr} + RCH{=}NR'$$



Scheme 1



Scheme 2

EXPERIMENTAL

IR spectra were recorded on an IR 4220 Beckman, the frequencies are given in cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX 90 MHz spectrometer at 90 MHz and 22.5 MHz, respectively, in $CDCl_3$, unless otherwise stated, chemical shifts are given in δ units. Some of ^{1}H NMR spectra were obtained on a Perkin Elmer R 24A spectrometer at 60 MHz in CCl_4. Mass spectra were obtained on a GC 8000-MS FISONS TRIO 1000 at 70 eV.

Reaction of propargyltrimethylsilanemagnesium bromide with aldimines

Propargylsilane was prepared according to [13]. The aldimines were prepared according to [14]. In a three necked flask equipped with mechanical stirrer, propagyltrimethylsilane 0.048 mole (5 g) in 10 mL of anhydrous ethylether was added to 0.007 mole of ethylmagnesiumbromide. The reaction mixture was heated at 35 °C under nitrogen for 3 hours. A solution of 0.05 mole of aldimine in 10 mL of anhydrous ethylether was added dropwise at room temperature and the mixture was stirred at this temperature for 16 hours. The reaction mixture was treated cold 200 mL of saturated NH_4Cl solution. After separation of the layers, the aqueous phase was extracted with ethylether (3 x 25 mL). The resulting organic phase was treated with HCl 2 M (2 x 25 mL) and extracted with ethylether (3 x 25 mL). The organic phase was washed with water (3 x 25 mL). The resulting cooled aqueous layers were made basic by addition of NaOH 2 M

(75 mL) and extracted with ethylether (3 x 25 mL). The combined organic layers were washed with water, dried over potassium carbonate and concentrated. The residue is distilled to give the amine **2**. For mixtures of products the concentrated organic phases was distilled bulb-to-bulb into a liquid nitrogen cooled receiver and separation is made by preparative GLC (30% SE 30 on chromosorb W columns)

*$Me_3SiCH_2C{\equiv}C\text{-}CH(R)NHR'$ **1***

***1a**:(R = H, R' = $C(CH_3)_3$) 4-(Tertbutylamino)-1-(trimethylsilyl)but-2-yne*. n_D^{20} = 1.4545, b.p. 64 °C/0.1 torr. IR (cm^{-1}): 3310 w (NH); 2220 w (C≡C); 1410 w (CN); 1360 m ($C(CH_3)_3$); 1250 s 840 s, 755 m ($SiMe_3$). ^{1}H NMR ($CDCl_3$) δ: 0.10 (s, 9H, $SiMe_3$); 0.85 (s, 1H, NH); 1.05 (s, 9H, CH_3); 1.40(t, J = 2.4Hz, 2H, CH_2); 3.25 (t, J = 2.4Hz, 2H,CH_2N). ^{13}C NMR ($CDCl_3$) δ: –2.05 ($SiMe_3$); 6.75 ($SiCH_2$); 28.89 (CH_3); 50.25 (C); 51.95 (CH_2-N); 72.23 ($SiCH_2C{\equiv}$); 82.79 (≡CCH(R)). HRMS (EI): calculated for $C_{11}H_{23}NSi$: 197.16009, found: 197.1607.

***1b**: (R = iPr, R'= CH_3) 1-(Methylamino)-1-(ipropyl)-4-(trimethylsilyl)but-2-yne*. n_D^{20} = 1.4549. IR (cm^{-1}): 3320 w (NH); 2195 w (C≡C); 1410 w (CN); 1250 s, 840 s, 755 m ($SiMe_3$). ^{1}H NMR ($CDCl_3$) δ: 0.10 (s, 9H, $SiMe_3$); 0.90 (d, J = 6.4 Hz, 6H, CH_3); 1.05 (s, 1H, NH); 1.40 (d, J = 2.3 Hz, 2H, CH_2); 1.45-1.90 (m, 1H, CH); 2.30 (s, 3H, NCH_3); 2.85 (dt, J = 5.2 Hz, J = 2.3 Hz, 1H, ≡C-CH). ^{13}C NMR ($CDCl_3$) δ: –2.10 ($SiMe_3$); 6.70 ($SiCH_2$); 21.89 (CH_3); 22.01 (CH_3); 32.15 (CH); 37.01 (NCH_3); 70.10 (CHN); 72.55 ($SiCH_2C{\equiv}$); 82.75 (≡CCH(R)). HRMS (EI): calculated for $C_{11}H_{23}NSi$: 197.16009, found: 197.1609.

*$Me_3SiCH(CHRNHR')\text{-}C{\equiv}CH$ **2***

***2a**: (R = H, R' = $C(CH_3)_3$) 1-(Tertbutylamino)-2-(trimethylsilyl)but-3-yne*. n_D^{20} = 1.4549, b.p. 80 °C/12 torr. IR (cm^{-1}): 3310 s, 2100 s (C≡CH); 1405 w (CN); 1360 s ($C(CH_3)_3$); 1245 s, 835 s, 750 m ($SiMe_3$). ^{1}H NMR ($CDCl_3$) δ: 0.04 (s, 9H, $SiMe_3$); 0.94 (s, 1H, NH); 1.03 (s, 9H, CH_3); 1.68-1.87 (m, 1H, CH); 1.94 (d, J = 2.8 Hz, 1H, ≡CH); 2.54-2.61 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ: –3.08 ($SiMe_3$); 21.75 (CH); 28.94 (CH_3); 42.12 (CH_2); 50.13 (C); 69.27 (≡CH); 85.35 (C≡). HRMS (EI): calculated for $C_{11}H_{23}NSi$: 197.16009, found: 197.1611.

***2b**: (R = iPr, R' = CH_3) 1-(Methylamino)-1-(isopropyl)-2-(trimethylsilyl)but-3-yne*. IR (cm^{-1}): 3320 s, 2100 s (C≡CH); 1405 w (CN); 1250 s, 840 s, 750 m ($SiMe_3$). ^{1}H NMR (CCl_4) δ: 0.10 (s, 9H, $SiMe_3$); 0.85 (d, J = 6.2 Hz, 3H); 0.87 (d, J = 6.3 Hz, 3H, CH_3); 1.35 (s, 1H, NH); 1.40-1.95 (m, 2H, CH); 1.95-2.45 (m, 5H, $CHNCH_3$, ≡CH). ^{13}C NMR ($CDCl_3$) δ: –2.30 ($SiMe_3$); 18.12 and 19.38 (CH_3); 22.54 (Si-CH); 32.15 (CH); 37.15 (NCH_3); 61.05 (CHN); 70.75 (≡CH); 84.05 (C≡). HRMS (EI): calculated for $C_{11}H_{23}NSi$: 197.16009, found: 197.1604.

***2c**: (R = iPr, R' = nBu) 1-(Butylamino)-1-(isopropyl)-2-(trimethylsilyl)but-3-yne*. IR (cm^{-1}): 3315 s; 2095 s (C≡CH); 1405 w (CN); 1250 s, 840 s, 750 m ($SiMe_3$). ^{1}H NMR ($CDCl_3$) δ: 0.10 (s, 9H, $SiMe_3$); 0.80-1.05 (m, 9H, CH_3); 1.20-1.50 (m, 6H, NH, $CHCH_3$, CH_2); 1.80-2.05 (m, 2H, CH, ≡CH); 2.25-2.65 (m, 3H, $CHNCH_2$). ^{13}C NMR ($CDCl_3$) δ: –2.33 ($SiMe_3$); 14.02, 19.48 (CH_3); 20.52 ($\underline{C}H_2CH_3$); 22.64 (CH); 32.25 ($\underline{C}HCH_3$); 32.99 (CH_2); 48.06 (CH_2N); 61.10 (CHN); 70.50 (≡CH); 84.70 (C≡). HRMS (EI): calculated for $C_{14}H_{29}NSi$: 239.20707, found: 239.2076.

***2d**: (R = C_6H_5, R' = CH_3) 1-(Methylamino)-2-(phenyl)-2-(trimethylsilyl)but-3-yne*. b.p. 105 °C/0.1 torr. IR (cm^{-1}): 3320 s, 2105 s (C≡CH); 3035 m, 1605 m, 1495 s (C_6H_5); 1410 w

(CN); 1250 s, 850 s, 750 m ($SiMe_3$). ^{1}H NMR (CCl_4) δ: 0.10 (s, 9H, $SiMe_3$); 1.85 (s, 1H, NH); 2.00-2.20 (m, 2H, CH, ≡CH); 2.25 (s, 3H, CH_3); 3.60 (d, J = 7.3 Hz, 1H, CHN); 7.25 (s, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ: –2.40 ($SiMe_3$); 29.79 (Si-CH); 61.04 (CH_3); 62.28 (CH); 71.20 (≡CH); 84.21 (C≡); 127.29, 127.51, 128.12, 143.15 (C_6H_5). HRMS (EI): calculated for $C_{14}H_{21}NSi$: 231.1444, found: 231.1451.

***2e**: (R = C_6H_5, R' = Et) 1-(Ethylamino)-1-(phenyl)-2-(trimethylsilyl)but-3-yne*. n_D^{20} = 1.5071, b.p. 90 °C/0.05 torr. IR (cm^{-1}): 3320 s, 2105 s (C≡CH); 3035 m, 1605 m, 1495 s (C_6H_5); 1410 w (CN); 1250 s, 850 s, 750 m ($SiMe_3$). ^{1}H NMR ($CDCl_3$) δ: -0.04 (s, 9H, $SiMe_3$); 1.05 (t, J = 7.1 Hz, 3H,CH_3); 1.96 (s, 1H, NH); 2.03-2.17 (m, 2H, CH, ≡CH); 2.40 (q, J = 7.1 Hz, 2H, CH_2); 3.73 (d, J = 7.7 Hz, 1H, CHN); 7.30 (s, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ: –2.45 ($SiMe_3$); 15.12 (CH_3); 29.86 (CH); 41.44 (CH_2); 62.38 (CHCN); 71.27 (≡CH); 84.31 (C≡); 127.27, 127.51, 128.17, 143.14 (C_6H_5). HRMS (EI): calculated for $C_{15}H_{23}NSi$: 245.16009, found: 245.1607.

***2f**: (R = C_6H_5, R' = Pr) 1-(Propylamino)-1-(phenyl)-2-(trimethylsilyl)but-3-yne*. n_D^{20} = 1.5060, b.p. 118 °C/1 torr. IR (cm^{-1}): 3310 s, 2100 s (C≡CH); 3025 m, 1600 m, 1490 s (C_6H_5); 1410 w (CN); 1250 s, 845 s, 760 m ($SiMe_3$). ^{1}H NMR ($CDCl_3$) δ: -0.02 (s, 9H, $SiMe_3$); 0.89 (t, J = 7.2 Hz, 3H, CH_3); 1.46 (m, 2H, CH_2); 2.00 (s, 1H, NH); 2.01-2.17 (m, 2H, CH, ≡CH); 2.35 (t, J = 6.9 Hz, 2H, CH_2N); 3.73 (d, J = 6.9 Hz, 1H, CHN); 7.31 (s, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ: –2.42 ($SiMe_3$); 11.78 (CH_3); 23.09 (CH_2); 30.01 (CH); 49.13 (CH_2N); 62.41 (CHCN); 71.30 (≡CH); 84.28 (C≡); 127.21, 127.51, 128.14, 143.29 (C_6H_5). HRMS (EI): calculated for $C_{16}H_{25}NSi$: 259.17575, found: 259.1765.

***2g**: (R = C_6H_5, R' = nBu) 1-(Butylamino)-1-(phenyl)-2-(trimethylsilyl)but-3-yne*. n_D^{20} = 1.5031, b.p. 108 °C/0.06 torr. IR (cm^{-1}): 3315 s, 2100 s (C≡CH); 3030 m, 1605 m, 1495 s (C_6H_5); 1410 w (CN); 1250 s, 850 s, 760 m ($SiMe_3$). ^{1}H NMR ($CDCl_3$) δ: -0.02 (s, 9H, $SiMe_3$); 0.88 (t, J = 6.4 Hz, 3H, CH_3); 1.15-1.55 (m, 4H, CH_2); 2.02 (s, 1H, NH); 2.03-2.16 (m, 2H, CH, ≡CH); 2.37 (t, J = 6.5 Hz, 2H, CH_2N); 3.72 (d, J 7.1 Hz, 1H,CHN); 7.31 (s, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ: – 2.42 ($SiMe_3$); 13.90 (CH_3); 20.40 ($\underline{C}H_2CH_3$); 30.01 (CH); 32.19 (CH_2); 49.93 (CH_2N); 62.53 (CHN); 71.33 (≡CH); 84.31 (C≡); 127.24, 127.51, 128.17, 143.32 (C_6H_5). HRMS (EI): calculated for $C_{17}H_{27}NSi$: 273.19141, found: 273.1919.

Me_3Si-C≡C-CH_2-CH(R)NHR' ***3***

***3a**: (R = H, R' = $C(CH_3)_3$) 4-(tert-Butylamino)-1-(trimethylsilyl)but-1-yne*. IR (cm^{-1}): 3310 w (NH); 2185 s (C≡C); 1405 w (CN); 1365 m ($C(CH_3)_3$); 1250 s, 840 s, 755 m ($SiMe_3$). ^{1}H NMR (CCl_4) δ: -0.03 (s, 9H, $SiMe_3$); 1.05 (s, 9H, CH_3); 1.10 (s, 1H, NH); 2.10-2.40 (m, 2H, CH_2); 2.50-2.80 (m, 2H, CH_2N). ^{13}C NMR ($CDCl_3$) δ: –0.03 ($SiMe_3$); 6.71 (CH_2); 29.01 (CH_3); 50.21 (C); 51.12 (CH_2-N); 83.22 (SiC≡); 92.48 (≡C). HRMS (EI): calculated for $C_{11}H_{23}NSi$: 197.16009, found: 197.1618.

$R(C_2H_5)$CHNH R' ***4***

***4f**:(R = C_6H_5, R' = Pr) N-(1-Phenylpropyl)propylamine*. IR (cm^{-1}): 3320 w (NH); 3030 m, 1605 m, 1495 s (C_6H_5); 1405 w (CN). ^{1}H NMR (CCl_4) δ: 0.60-1.05 (m, 7H, CH_3, NH)); 1.10-1.80 (m, 4H, CH_2); 2.30 (t, J = 6.3 Hz, 2H, CH_2N); 3.35 (t, J = 6.4 Hz, 1H, CH); 7.10 (s, 5H, C_6H_5).
***4g**: (R = C_6H_5, R' = nBu) N-(1-Phenylbutylpropyl)butylamine*. IR (cm^{-1}): 3325 w (NH); 3030 m, 1605 m, 1495 s (C_6H_5); 1405 w (CN). ^{1}H NMR (CCl_4) δ: 0.55-1.05 (m, 7H, CH_3, NH); 1.08-

1.82 (m, 6H, CH_2); 2.32 (t, J = 6.2 Hz, 2H, CH_2N); 3.38 (t, J = 6.2 Hz, 1H, CH); 7.10 (s, 5H, C_6H_5).

$Me_3SiCH=C=CH-CH_2-NHC(CH_3)_3$ ***5***. n_D^{20} = 1.5060. IR (cm^{-1}): 3310 w (NH); 1935 s, 845 s, (CH=C=CH); 1405 w (CN); 1360 m ($C(CH_3)_3$; 1245 s,835 s,755 m ($SiMe_3$). ^1H NMR (CCl_4) δ: 0.130 (s, 9H, $SiMe_3$); 0.85 (s, 1H, NH); 1.05 (s, 9H, CH_3); 2.95-3.20 (m, 2H, CH_2); 4.70-4.95 (m, 2H, CH=). ^{13}C NMR ($CDCl_3$) δ: –1.15 ($SiMe_3$); 15.25 (CH_3); 47.55 (CH_2); 50.51 (C); 82.62 (CH=); 83.43 (SiCH=); 209.45(=C=). HRMS (EI): calculated for $C_{11}H_{23}NSi$: 197.16009, found: 197.1615.

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