SYNTHESIS AND REACTIONS OF UNSATURATED ORGANOSILICON COMPOUNDS

COMMUNICATION 5. SYNTHESIS AND SOME REACTIONS OF 4-(TRIMETHYLSILYL)-AND 4-(TRIETHYLSILYL)-BUTYN-2-OLS

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The reactions of organosilicon acetylenic alcohols and their derivatives can have great possibilities in synthesis and are of considerable interest. In a previous paper [1] we described the synthesis and some reactions of secondary γ -silico acetylenic alcohols. We have now studied the reaction of the bromomagnesium derivative of 3butyn-2-ol with chlorotrimethyl- and chlorotriethyl-silanes:

 $\begin{array}{c} \mathrm{R}_{\$}\mathrm{SiCl} + \mathrm{BrMgC} \equiv \mathrm{C} - \mathrm{CHOMgBr} \rightarrow \mathrm{R}_{\$}\mathrm{SiC} \equiv \mathrm{C} - \mathrm{CH} \ (\mathrm{OH}) \ \mathrm{CH}_{\$} \\ & \downarrow \\ \mathrm{CH}_{\$} \\ \mathrm{R} = \mathrm{CH}_{\$}\mathrm{andC}_{2}\mathrm{H}_{\$} \end{array}$

The properties of the silico acetylenic alcohols obtained were investigated in relation to cyanoethylation, acetalization, hydrogenation, and reaction with thionyl chloride. The cyanoethylation of the γ -silico acetylenic alcohols was studied in presence of sodium methoxide and of 40% aqueous potassium hydroxide solution as catalysts:

$$\begin{array}{c} \mathrm{R}_{3}\mathrm{SiC} \equiv \mathrm{C} - \mathrm{CH}\;(\mathrm{OH})\;\mathrm{CH}_{3} + \mathrm{CH}_{2} = \mathrm{CH} - \mathrm{CN} \rightarrow \mathrm{R}_{3}\mathrm{SiC} \equiv \mathrm{C} - \mathrm{CHOCH}_{2}\mathrm{CH}_{2}\mathrm{CN}\\ & \downarrow\\ \mathrm{CH}_{3}\\ \mathrm{R} = \mathrm{CH}_{3}\mathrm{and}\mathrm{C}_{2}\mathrm{H}_{5} \end{array}$$

In the course of the investigation it was shown that secondary γ -silico acetylenic alcohols undergo cyanoethylation under milder conditions than tertiary γ -silico acetylenic alcohols. Whereas tertiary γ -silico acetylenic alcohols are cyanoethylated only under the influence of sodium methoxide [2], the alcohols investigated are cyanoethylated in presence of either catalyst. In fact, higher yields of 2-cyanoethyl ethers are obtained in presence of 40% aqueous potassium hydroxide solution. By the reaction of the 2-cyanoethyl ether of 4-(triethylsilyl)-3-butyn-2-ol with ethylmagnesium bromide we obtained the corresponding ketone:

$$(C_{2}H_{5})_{3} \operatorname{SiC} \equiv C - \operatorname{CHOCH}_{2}\operatorname{CH}_{2}\operatorname{CN} + C_{2}H_{5}Mg\operatorname{Br} \rightarrow (C_{2}H_{5})_{3} \operatorname{SiC} \equiv C - \operatorname{CHOCH}_{2}\operatorname{CH}_{2}\operatorname{COC}_{2}H_{5}$$

The reaction of the alcohols under investigation with vinyl ethers was studied for the case of reaction with butyl vinyl ether in presence of traces of concentrated hydrochloric acid:

$$R_{3}SiC \equiv C - CH (OH) CH_{3} + CH_{2} = CHOC_{4}H_{9} \rightarrow CH_{3} - CH$$

$$OC_{4}H_{9}$$

$$OC_{4}H_{9} \rightarrow CH_{3} - CH$$

$$OCH - C \equiv CSiR_{3}$$

$$CH_{3}$$

 $\mathrm{R}=\mathrm{C}\mathrm{H}_{3}\text{and}\mathrm{C}_{2}\mathrm{H}_{5}$

In absence of HCl no reaction was observed.

By the hydrogenation of 4-(trimethylsilyl)-3-butyn-2-ol over Raney nickel we obtained 4-(trimethylsilyl)-2butanol:

$$(CH_3)_3 \operatorname{SiC} \equiv C - CH (OH) CH_3 + H_2 \rightarrow (CH_3)_3 \operatorname{SiCH}_2 CH_2 CH (OH) CH_3$$

Reaction with thionyl chloride led to the corresponding γ -silico acetylenic chlorides of the propargyl type:

$$\begin{aligned} \mathrm{R}_3\mathrm{SiC} \equiv \mathrm{C} - \mathrm{CH} \ (\mathrm{OH}) \ \mathrm{CH}_3 + \mathrm{SOCl}_2 &\rightarrow \mathrm{R}_3\mathrm{SiC} \equiv \mathrm{C} - \mathrm{CHClCH}_3 + \mathrm{SO}_2 + \mathrm{HCl} \\ \mathrm{R} &= \mathrm{CH}_3\mathrm{and}\mathrm{C}_2\mathrm{H}_5 \end{aligned}$$

Here the cleavage of the Si-C bond conjugated with the multiple bond was not observed. The yield of secondary γ -silico acetylenic chlorides was 65-70%.

We have previously [3] studied the condensation of primary and tertiary γ -silico acetylenic chlorides with sodioacetoacetic and sodiomalonic esters. In connection with this it was of interest to investigate the behavior of secondary γ -silico acetylenic chlorides in this reaction. We studied the reaction of the chloro compounds under investigation with sodioacetoacetic ester:

$$\begin{array}{c} R_{3}SiC \equiv C - CHClCH_{3} + Na + CH_{3}COCH_{2}COOC_{2}H_{5} \rightarrow \\ \rightarrow R_{3}SiC \equiv C - CH - CH - COOC_{2}H_{5} + NaCl \\ & | \\ CH_{3} \quad COCH_{3} \end{array}$$

$$R = CH_3$$
 and C_2H_5

The stability of an Si⁻C bond conjugated with a multiple bond was observed also in this reaction. However, in this case the yield of silico acetylenic keto esters was lower than in the condensation of primary γ -silico acetylenic chlorides. On the other hand our earlier attempts to condense tertiary γ -silico acetylenic chlorides with sodio-acetoacetic esters [3] were unsuccessful.

It presented considerable interest to study the behavior of the keto esters under investigation in the ketone-cleavage reaction occurring in presence of concentrated hydrochloric acid. We obtained only the corresponding silico acetylenic acid:

We did not succeed in isolating the silico acetylenic ketone that was to be expected in ketone cleavage.

EXPERIMENTAL

<u>4-(Trimethylsilyl)-3-butyn-2-ol (I)</u>. With stirring and cooling (from -5° to -10°) 70 g of 3-butyn-2-ol was added dropwise to a Grignard reagent prepared from 48.6 g of magnesium and 218 g of ethyl bromide. The mixture was stirred further for two hours with cooling and then left overnight. On the next day the reaction mixture was added dropwise. The contents of the flask were stirred for three hours at room temperature, and then, under cooling (-5°), 108 g of chlorotrimethylsilane was added dropwise. The contents of the flask were stirred for three hours at room temperature and for 5-6 hours with heating in a water bath. Then, with cooling of the reaction mixture (0-5°) 10% hydrochloric acid was added dropwise until the precipitate dissolved completely. The ether layer was separated, and the aqueous layer was neutralized with bicarbonate and extracted with ether. The ether layer and ether extracts were dried over calcined potassium carbonate; ether was distilled off, and the residue was vacuum-distilled. In the distillation we obtained 85.2 g (60%) of a substance having b.p. 76° (15 mm); n_D^{20} 1.4442; d_4^{20} 0.8614. Found: Si 19.94%; MR 43.93. C₇H₁₄SiO. Calculated Si 19.73%, MR 44.11. In an analogous way we prepared 4-(triethylsilyl)-3-butyn-2-ol, whose physical and chemical constants are given in the table.

<u>4-(Trimethylsilyl)-2-butanol (II).</u> About 0.7 g of Raney nickel in 20 ml of ethanol was placed in a hydrogenation flask. The catalyst was saturated with hydrogen, and 7.11 g of 4-(trimethylsilyl)-3-butyn-2-ol was introduced and hydrogenated until the absorption of hydrogen stopped (2257 ml of hydrogen was absorbed; theory requires 2240

Physical and Chemical Constants of the Compounds Obtained

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	B.p., °	υ	20	.20	MR	o de la constante de la constan	Si,	%	Y íeld,
Formula or compound	(p, m <u>a</u>	(gHt	Ūu.	d_4	found	calc.	found	calc.	°р
$(CH_3)_5SiC \equiv C - CH(OH)CH_3$	16	(15)	1,4442	0,8614	43,93	44,11	19,97	19,73	60,0
	6464,5	(8)					-		
$(C_2H_5)_3SIC \equiv C - CH(OH)CH_3$	120	(25)	1,4605	0,8697	58,13	58,00	15, 49	15, 23	56,5
(CH ₃) ₃ SiCH ₂ CH ₂ CH(OH)CH ₃	72	(15)	1;4440	0,8583	45,03	45,72	19,06	19,29	81,0
$(CH_3)_3SiC \equiv C - CHCICH_3$	4546	(10)	1,4512	0,9084	47,92	47,40	17,40	17,65	68,3
	37,5-38	(9)							
$(C_{a}H_{s})_{s}SIC \equiv C - CHClCH_{s}$	6465	(2)	1,4642	0,9043	62,05	61,39	13,69	13,87	64,6
$(CH_3)_S SiC \equiv C - CH(CH_3)OCH(CH_3)OC_4H_5$	98	(5)	1,4320	0,8540	73,02	73,88	11,17	11,59	51,5
(CH ₃) ₃ SiCH ₂ CH ₂ CH(CH ₃)OCH(CH ₃)OC ₄ H ₉	8283	(3)	1,4298	0,8450	75,30	75,49	11,26	11,37	57,6
$(C_2H_5)_3SIC \equiv C - CH(CH_3)OCH(CH_3)OC_4H_9$	110111	(2)	1,4462	0,8715	88,31	87,77	9,53	9,71	48,3
$(CH_3)_3SiC \equiv C - CH(CH_3)OCH_2CH_2CN$	60	(8)	1,4385	0,8689	59,06	58,10	14,03	14,39	44,0
$(C_2H_5)_3SIC \equiv C - CH(CH_3)OCH_2CH_2CN$	124	(1)	1,4590	0,9062	71,58	71,99	11,52	11,83	69,1
$(C_{3}H_{5})_{3}SIC \equiv C - CH(CH_{3})OCH_{2}CH_{2}COC_{2}H_{5}$	96	(9)	1,4600	0,8946	32,17	31,37	10,32	10,44	38,8
$(CH_3)_3SIC \equiv C - CH(CH_3)CH(COCH_3)COOC_2H_5$	5253	(15)	1,4368	0,9204	72,37	72,11	11,26	11,04	34,6
$(C_{3}H_{5})_{3}SIC \equiv C - CH(CH_{3})CH(COCH_{3})COOC_{2}H_{5}$	60	(1)	1,4600	0,9222	88,03	86,00	9,29	9,47	32,1
$(C_2H_5)_3SIC \equiv C - CH(CH_3)CH(COCH_3)COOH$	6869	(2)	1,4648	0,9587	77,31	76,52	10,69	10,46	50,5

ml). At the end of the hydrogenation the reaction mixture was separated from catalyst, washed with water, dried over potassium carbonate, and vacuum-distilled. We obtained 5.8 g (81%) of a substance of b.p. 72° (15 mm); n_D^{20} 1.4440; d_A^{20} 0.8583. Found: Si 19.06%; MR 45.03. C₇H₁₈SiO. Calculated: Si 19.29%; MR 45.72.

Acetaldehyde Butyl 1-Methyl-3-(trimethylsilyl)-2-propynyl Acetal (III). With stirring 1-2 drops of concentrated hydrochloric acid were added to a mixture of 3 g of 4-(trimethylsilyl)-3-butyn-2-ol and 2.1 g of butyl vinyl ether. The temperature of the mixture rose to 58°. The contents of the flask were then stirred for 90 minutes at 80° and left overnight. On the next day the reaction mixture was neutralized with calcined potassium carbonate and vacuum-distilled. We obtained 2.8 g (51.5%) of a substance of b.p. 98° (5 mm); n_D^{20} 1.4320; d_4^{20} 0.8540. Found: Si 11.17%, MR 73.02. $C_{13}H_{26}SiO_2$. Calculated: Si 11.59% MR 73.88.

In an analogous way we prepared the butyl 1-methyl-3-(triethylsilyl)-2-propynyl and the butyl 1-methyl-3-(trimethylsilyl)propyl acetals of acetaldehyde; the constants of these are given in the table.

2-Cyanoethyl Ether of 4-(Trimethylsilyl)-3-butyn-2-ol (IV). a) A 100-ml three-necked round-bottomed flask fitted with reflux condenser, mechanical stirrer, dropping funnel, and thermometer was charged with 10 g of 4-(trimethylsilyl)-3-butyn-2-ol and 0.42 g of potassium hydroxide as a 40% aqueous solution. Over a period of one hour with stirring 3.75 g of acrylonitrile was then added. The temperature of the reaction mixture was kept at not above 35°. The mixture was stirred further for six hours, neutralized with 15% hydrochloric acid, filtered, separated from water, dried, and distilled. We obtained 6.2 g (44%) of a substance of b.p. 90° (8 mm); n_D^{20} 1.4385; d_4^{20} 0.8689. Found: Si 14.03% MR 59.06. C₁₀H₁₇SiON. Calculated: Si 14.39% MR 58.10.

b) A mixture of 14.25 g of 4-(trimethylsilyl)-3-butyn-2-ol, 15 ml of benzene, and 1.5 ml of sodium methoxide was placed in the apparatus described, and with stirring 10.6 g of acrylonitrile was added dropwise. Every ten minutes a further 1 ml of sodium methoxide was added to the reaction mixture. The temperature of the mixture rose to 56°. The mixture was then stirred for four hours, neutralized with dilute (1:1) hydrochloric acid, and filtered; benzene was distilled off, and the residue was vacuum-distilled. We obtained 5.1 g (26.5%) of a substance of b.p. 68° (3 mm); n_D^{20} 1.4380; d_4^{20} 0.8685.

In an analogous way we obtained the 2-cyanoethyl ether of 4-(triethylsilyl)-3-butyn-2-ol, whose constants are presented in the table.

<u>1-[1-Methyl-3-(triethylsilyl)-2-propynyl]-3-pentanone (V)</u>. With stirring 8 g of the cyanoethyl ether of 4-(triethylsilyl)-3-butyn-2-ol was added dropwise at room temperature to a Grignard reagent prepared from 1.5 g of magnesium and 6.6 g of ethyl bromide. The reaction mixture was then stirred for three hours and decomposed with dilute (1:20) hydrochloric acid. The ether layer was separated, ether was distilled off, and the residue was vacuum distilled. We obtained 3.5 g (38.8%) of a substance of b.p. 96° (6 mm); nD²⁰ 1.4600; d₄²⁰ 0.8946. Found: Si 10.32%; MR 32.17. C₁₀H₂₇SiO₂. Calculated: Si 10.44%; MR 31.37.

<u>3-Chloro-1-(trimethylsilyl)-1-butyne (VI).</u> A mixture of 21 g of 4-(trimethylsilyl)-3-butyn-2-ol and 3 ml of pyridine was prepared in a 75-ml three-necked round-bottomed flask fitted with mechanical stirrer, dropping funnel, reflux condenser, and thermometer. With stirring and cooling, 26.55 g of thionyl chloride was then added. The mixture was stirred for two hours and left overnight. On the next day the mixture was stirred for three hours, sulfur dioxide was removed by passage of nitrogen, and 20 ml of water was added. The organic layer was separated, dried with calcium chloride, and vacuum-distilled. We obtained 16.21 g (68.3%) of a substance of b.p. 45-46° (10 mm); n_D²⁰ 1.4512; d₄²⁰ 9084. Found: Si 17.4%; MR 47.92. C₇H₁₃SiCl. Calculated: Si 17.65%; MR 47.40. In an analogous way we prepared 3-chloro-1-(triethylsilyl)-1-butyne (see table).

Ethyl 1-Acetyl-3-methyl-5-(trimethylsilyl)-4-pentynoate (VII). A mixture of alcoholic sodium ethoxide, prepared from 1.15 g of sodium and 20 ml of ethanol, and 6.5 g of freshly distilled acetoacetic ester was stirred and heated (50-60°) while 8 g of 3-chloro-1-(trimethylsilyl)-1-butyne was added dropwise. The mixture was stirred at 50-60° for eight hours and then decomposed with 50 ml of water. The organic layer was separated, washed with water, dried over sodium sulfate, and distilled. We obtained 4.5 g (34.6%) of a substance of b.p. 52-53° (15 mm); n_D^{20} 1.4368; d_4^{20} 0.9204. Found: Si 11.26%, MR 72.37. C₁₃H₂₂SiO₃. Calculated: Si 11.04%, MR 72.11.

In an analogous way we prepared ethyl 2-acetyl-3-methyl-5-(triethylsilyl)-4-pentynoate (see table).

2-Acetyl-3-methyl-5-(triethylsilyl)-4-pentynoic Acid(VIII). A mixture of 4 g of ethyl 2-acetyl-3-methyl-5-(triethylsilyl)-4-pentynoate, 20 ml of concentrated hydrochloric acid, and 20 ml of ethanol was prepared in a 25ml three-necked flask. The mixture was heated for 10-15 minutes at 90°. The organic layer was separated, dried, and distilled. We obtained 1.8 g (50.5%) of a substance of b.p. 68-69° (2 mm); n_D^{20} 1.4648; d_4^{20} 0.9587. Found: Si 10.69%; MR 77.31. C₁₄H₂₄SiO₃. Calculated: Si 10.46%; MR 76.52.

SUMMARY

1. The reaction of bis(halomagnesium) derivatives of 3-butyn-2-ol with chlorotrimethyl- and chlorotriethylsilanes was investigated.

2. A study was made of the cyanoethylation, hydrogenation, and acetalization of 4-(trialkylsilyl)-3-butyn-2-ols and their reaction with thionyl chloride.

3. The condensation of secondary silico acetylenic chlorides of the formation of the corresponding silico acetylenic keto esters. The ketone cleavage of the latter was carried out.

LITERATURE CITED

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