Synthesis and Reactions of Acetylenic Silicon Hydrocarbons

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Abstract

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Synthesis and Reactions of Acetylenic Silicon Hydrocarbons

It was previously established by us ([1]) that, in tetrahydrofuran, the reaction

$$HC \equiv CMgBr + BrSi(C_2H_5)_3 \rightarrow (C_2H_5)_3SiC \equiv CH + MgBr_2$$

proceeds with a high yield (85%) of triethylsilylacetylene, which readily formed an organomagnesium compound capable of reacting with carbonyl compounds.

$$(C_2H_5)_3SiC \equiv CMgBr \rightarrow \begin{cases} (C_2H_5)_3SiC \equiv CCH(OH)CH{=}CH_2 \\ \qquad\qquad\qquad\quad CH_3 \\ (C_2H_5)_3SiC \equiv C{-}C(OH){-}CH_2Cl \end{cases}$$

$CH_2{=}CH{-}C(=O)H$

CH_3COCH_2Cl

$$(C_2H_5)_3SiC \equiv C{-}C(OH){-}CH_2Cl \rightarrow (C_2H_5)_3SiC \equiv C{-}C(CH_3)\begin{pmatrix} O \end{pmatrix}CH_2$$

Continuing this investigation, in the present work we synthesized various acetylenic silicon hydrocarbons and obtained some of their derivatives according to the following scheme:

$$R_3SiC \equiv CMgBr \xrightarrow{Br_2} R_3SiC \equiv C{-}Br$$

$$\xrightarrow{CO_2} R_3SiC \equiv C{-}C(=O)OH$$

$$\xrightarrow{(CH_3)_3SiCl} R_3SiC \equiv CSi(CH_3)_3$$

$$\xrightarrow{CH_2=CH-CH_2Br} R_3SiC \equiv C{-}CH_2{-}CH{=}CH_2$$

$$R = (C_2H_5)_3Si{-},\ (C_3H_7)_3Si,\ (CH_3HC_6H_5)Si{-},\ (C_6H_5)_4Si{-}$$

In the vibrational spectra of monosubstituted silylacetylenes containing a triple bond in the α-position to the silicon atom, attention is drawn to the lowered value of the frequency of the C ≡ C vibration (about 2030 cm^{-1}), which may be compared with the analogous lowering of the frequency of C ≡ C vibrations in vinylsilanes ([2]). In the spectra of disubstituted silylacetylenes this effect is expressed much less sharply ([3]).

In the IR spectrum of $(C_2H_5)_3SiC \equiv C{-}COOH$, the stretching vibrations of the hydroxyl correspond to broad bands near 2630 and 2508 cm^{-1}; the position of these bands, characterizing the strength of the hydrogen bonds, makes it possible to consider this acid somewhat stronger than saturated aliphatic acids (but weaker than dibasic acids). Comparison of the dissociation constants of triethylsilylethynylcarboxylic acid and acetic acid confirms this conclusion.

Table 1

No.	Compound	B.p., °C	P, mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.*	Yield, %
1	$(n\text{-}C_3H_7)_3SiC{\equiv}CH$	97	20	1.4376	0.7980	59.95	60.59	77
2	$CH_3(H)C_6H_5SiC{\equiv}CH$	97.5	12	1.5159	0.9169	48.17	48.59	59
3	$C_2H_5(H)C_6H_5SiC{\equiv}CH$	98	7	1.5161	0.9161	52.76	52.87	58.5
4	$(C_2H_5)_2Si(C{\equiv}CH)_2$	78–79	84	1.4393	0.8147	44.03	44.52	34
5	$(n\text{-}C_3H_7)_2Si(C{\equiv}CH)_2$	77.5–78.5	15	1.4429	0.8094	58.71	53.82	–
6	$(C_2H_5)_3SiC{\equiv}C{-}COOH$	132.2–132.8	3	1.4682	0.9439	54.29	53.30	50
7	$(n\text{-}C_3H_7)_3SiC{\equiv}C{-}Br$	115–116	11	1.4740	1.0688	68.73	68.68	80**
8	$CH_3(H)C_6H_5SiC{\equiv}C{-}CH_2{-}OH$	120.5–120.7	1.5	1.5280	0.9958	61.97	62.17	64.5**
9	$CH_3(H)C_6H_5SiC{\equiv}C{-}Si(CH_3)_3$	129–129.5	25	1.5039	0.8968	72.12	72.27	58
10	$(CH_3(H)C_6H_5Si)_2C{=}C$	166	6	1.5579	0.9840	87.30	87.22	–
11	$(C_2H_5(H)C_6H_5Si)_2C{=}C$	172–174	2	1.5508	0.9732	96.53	96.88	–
12	$(C_6H_5)_3SiC{\equiv}CH$ ***	48.5–49	1.5	–	–	–	–	–

* MR_D calc. was calculated according to Fogel.

** The yield was calculated on the silicon hydrocarbon introduced into the reaction.

*** In contrast to trialkylsilylacetylenes, this silicon hydrocarbon is readily hydrolyzed by water, even in the cold, with formation of $(C_6H_5)_3SiOH$ with m.p. 152–164°.

In all syntheses of monosubstituted silicon acetylenes, small amounts of the corresponding disubstituted acetylenes were obtained.

Table 1 gives the properties of the synthesized alkyl- and alkylarylsilyl-monoacetylenic hydrocarbons of the type

$$-Si-C\equiv CH,$$

of some derivatives of the type

$$-Si-C\equiv C-\Phi$$

(where $\Phi = Br$, $COOH$, etc.), of disubstituted monoacetylenic hydrocarbons of the type

$$-Si-C\equiv C-Si-,$$

and also of bialkyldiethynylsilanes of the type $R_2Si-(C\equiv CH)_2$.

Experimental Part

Synthesis of tripropylsilylacetylene $(n\text{-}C_3H_7)_3SiC\equiv CH$ (1). Ethynylmagnesium bromide was prepared by Jones' s method ([4]) from 10.0 g of magnesium, 50.0 g of ethyl bromide, and acetylene in 310 ml of dry tetrahydrofuran; then 60.5 g of tripropylbromosilane was added. The contents of the flask were stirred for 10 h and decomposed with a saturated solution of NH_4Cl.

Found, %: C 71.62; H 12.49; Si 15.65
$C_{11}H_{22}Si$. Calculated, %: C 72.50; H 12.10; Si 15.40

Analogously, $(n\text{-}C_3H_7)_2Si(C\equiv CH)_2$ (5), $C_2H_5(H)C_6H_5SiC\equiv CH$ (3) were prepared:

Found, %: C 75.22; H 7.64; Si 17.20
$C_{10}H_{12}Si$. Calculated, %: C 75.00; H 7.50; Si 17.50

$CH_3(H)C_6H_5SiC\equiv CH$ (2):

Found, %: Si 18.7
$C_9H_{10}Si$. Calculated, %: Si 19.1

$(C_2H_5)_2Si(C\equiv CH)_2$ (4):

Found, %: C 70.40; H 8.96; Si 20.32
$C_8H_{12}Si$. Calculated, %: C 70.40; H 8.88; Si 20.16

$(C_6H_5)_3SiC\equiv CH$ (12):

Found, %: Si 10.0
$C_{20}H_{16}Si$. Calculated, %: Si 9.9

Synthesis of $(C_3H_7)_3SiC \equiv CBr$. To tripropylsilylethynylmagnesium bromide (from 2.4 g of magnesium, 12.0 g of bromoethyl, and 18.5 g of (1)) in absolute ether, 8.0 g of dry bromine was slowly added dropwise with stirring and cooling by CO_2. As bromine was added, a precipitate of $MgBr_2$ formed. The contents of the flask were then hydrolyzed with dilute HCl, washed with saturated Na_2CO_3 solution and with water, and dried. The ether was distilled off and the residue was distilled in vacuo. Compound (7) was isolated.

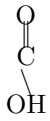
Found, %: Br 30.17

$C_{11}H_{21}SiBr$. Calculated, %: Br 30.56

Synthesis of $(C_2H_5)_3SiC \equiv C - COOH$ (6).* From 2.9 g of magnesium, 14.0 g of bromoethyl, and 17.0 g of $(C_2H_5)_3SiC \equiv CH$ in absolute ether, triethylsilylethynylmagnesium bromide was prepared, which was then poured onto 0.5 kg of crushed CO_2. After the usual work-up, 11.0 g of (6) was isolated by distillation. The neutralization equivalent, found by titration with 0.1 N NaOH, was 187.8; the neutralization equivalent equal to the molecular weight is 184.3.

IR spectrum ν (cm^{-1}): 735 (v. s. doublet), 797 (v. s.), 965, 968 (v. w.), 977 (m.), 1013 (s. doublet), 1070 (w.), 1157 (w.), 1246 (v. w.), 1265 (v. s.), 1355 (v. w.), 1378 (w.), 1390 (m.), 1412 (s.), 1468 (m.), 1695 (v. s.; unresolved maxima 1665 and 1695 cm^{-1} on the edges), 2180 (m.), 2508 (m.), 2630 (m.), 2765 (v. w.), 2820 (m.), 2898 (v. s.), 2920 (v. s.), 2975 (v. s.), 3100 (m., against the background of 2975).

The bands at 2630, 2508, 1695, and 1265 cm^{-1} are associated with vibrations of the group



the band at 2180 cm^{-1} corresponds to vibrations of the $C \equiv C$ bond; the very strong bands at 1246 and 797 cm^{-1} indicate the presence of the $Si(C_2H_5)_3$ group. The silver salt of the acid was obtained; in the dry state it explodes violently.

Found, %: C 58.66; H 9.25; Si 15.25

$C_9H_{16}SiO_2$. Calculated, %: C 58.66; H 8.75; Si 15.24

Synthesis of $CH_3(H)C_6H_5SiC \equiv C - CH_2 - CH = CH_2$ (8). To the organomagnesium compound prepared from 2.0 g of magnesium, 12.0 g of bromoethyl, and 11.02 g of (2), 11.0 g of allyl bromide was added. The contents of the flask were boiled for 5 h in ether; the ether was distilled off and the residue was heated for an hour on a water bath. Decomposition of the complex and subsequent work-up were carried out in the usual way.

IR spectrum ν (cm^{-1}): 731 (s.), 748 (s.), 837 (v. s.), 882 (v. s.), 916 (s.), 928 (m.), 991 (s.), 998 (s.), 1034 (s.), 1087 (w.), 1117 (v. s.), 1186 (w.), 1253 (m.), 1282 (w.), 1315 (w.), 1420 (m.), 1430 (m.), 1650 (m.), 2170 (s.), 2200 (s.), 2817 (w.), 2854 (v. w.), 2891 (w.), 2918 (w.), 2970 (m.), 3021 (m.), 3057 (m.), 3074 (m.), 3096 (w.). The bands at 2200 and 2170 cm^{-1} are evidently associated with the stretching vibrations of $C \equiv C$ and $Si - H$ (δ_{SiH}916 cm^{-1}). Absorptions at 3096 and 1650 cm^{-1} indicate the presence of the $C = CH_2$ group.

Analogously, $CH_3(H)C_6H_5SiC \equiv C - Si(CH_3)_3$ (9) was prepared.

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* When CO_2 was passed through triethylsilylethynylmagnesium bromide, we obtained crystals that decompose during distillation and during determination of the melting point. We tentatively assigned these crystals the formula of acid (1).

Note: Figure translations are in progress. See original paper for figures.