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Abstract

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Synthesis and Reactions of Trimethylsilylketene –Trimethylsiloxyacetylene

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It is known that alkoxyacetylenes possess high reactivity, especially in addition reactions ([1]). The bond of the acetylenic carbon to oxygen in alkoxyacetylenes is as strong as in other simple ethers. Thus, the action of water in the presence of dilute acids leads to the formation of acetates rather than acetic acid. Hydrolysis of the trialkylsilylalkoxyacetylenes first obtained by us also leads to the formation of the corresponding acetates ([3]).

At elevated temperatures (80–100°), alkoxyacetylenes undergo thermal decomposition as a result of homolytic cleavage of the O–Alk bond according to the scheme ([2]):

$$HC{\equiv}C{-}O{-}C{-}CH \rightarrow H_2C{=}C{=}O + C{=}C.$$

We have shown ([3]) that trimethylsilylalkoxyacetylenes also decompose at 120–130°, liberating the corresponding olefin and trimethylsilylketene $(CH_3)_3SiCH{=}C{=}O$ *. In the NMR spectrum of the product obtained, recorded with tetramethylsilane as the external standard **, however, it was not possible to detect a signal corresponding to the proton at the $C{=}C$ bond. In addition to a maximum at $\tau = 9.84$, corresponding to the $Si(CH_3)_3$ group, only one maximum was observed at $\tau = 8.27$, which can be assigned only to the proton of the C≡CH group. The IR spectrum contained, in the high-frequency region, intense bands at 3364 and 2112 cm^{-1}, which likewise indicated the presence of the C≡CH group. At the same time, in addition to the ν_{CH} bands of the $Si(CH_3)_3$ group at 2962 and 1900 cm^{-1}, the spectrum also contained a band at 3038 cm^{-1}, which evidently corresponds to a C–H bond at a $C{=}C$ group, i.e., to a ketene configuration. The "shoulder" of the 2112 cm^{-1} band at 2052 cm^{-1} may also be assigned to the $\nu_{O=C(=C)}$ vibration. The transition from the liquid spectrum to the gas spectrum (Fig. 1) changes the intensities of the 3364 and 3038 cm^{-1} bands (in comparison with the ν_{CH_3} bands): the first is strengthened, and the second weakened.

The foregoing can be explained only by assuming partial isomerization of the ketene formed, probably through an intermediate complex with pentavalent silicon, for example of the type

Fig. 1

Figure 1: Fig. 1

$$\begin{array}{c} \mathrm{H} \\ \mathrm{R_3Si\ \ C{=}C{=}O\ \cdots\ SiR_3}, \\ \mathrm{O{=}C{-}C} \\ \mathrm{H} \end{array}$$

* Storage of trimethylsilylalkoxyacetylenes at room temperature also leads to their decomposition.

** The authors express their gratitude to A. S. Khachaturov, who recorded the NMR spectra.

into the corresponding acetylene, i.e., of the tautomeric equilibrium

$$\underset{\text{(I)}}{\mathrm{R_3SiHC{=}C{=}O}} \rightleftarrows \underset{\text{(II)}}{\mathrm{HC{\equiv}C{-}OSiR_3}}.$$

In the spectra of both forms only one fundamental vibration can lie at 1100–1000 cm^{-1}: $\nu_{C-O(-Si)}$ in II and $\nu_{C=C(=O)}$ in I. The observed spectrum of the equilibrium mixture contains two lines, 1052 and 994 cm^{-1}; both frequencies are also present in the IR spectrum, and in the spectrum of the gas the relative intensity of the second of them decreases, confirming its assignment to form I. Within the liquid phase, lowering the temperature apparently somewhat increases the ketene content.

Fig. 1. IR spectrum of the equilibrium mixture $(CH_3)_3SiCH{=}C{=}O \rightleftarrows (CH_3)_3SiO{-}C{\equiv}CH$: *1* –liquid, layer thickness 0.011 mm; in the region 2000–2200 cm^{-1} –capillary layer; *2* –vapor, layer thickness 130 mm, pressure 30 mm Hg; in the region 2000–2200 cm^{-1}, pressure $\sim$ 5 mm.

The IR spectrum of an equimolecular mixture of the compound under study with absolute CH_3OH coincided with the spectrum of $(CH_3)_3SiCH_2COOCH_3$ and contained no bands attributable to form II. In the spectra of mixtures with the ratio $(CH_3)_3SiCHCO : CH_3OH > 1 : 1$ (2:1; 3:1; 5:1), simultaneous weakening of the bands of forms I and II was observed. This (as well as the high yield obtained in the reaction with methyl alcohol) indicates conversion of II into I during the reaction.

An energetic estimate from sums of average bond energies gives a result unexpected at first sight: the ketene form proves to be much more favorable than

Fig. 2

Figure 2: Fig. 2

the acetylene form. If the bond energy of the $Si(CH_3)_3$ group is unchanged and the bond energies for Si—O and Si—C are 108 and 76 kcal/mole (for methylpolysiloxanes ([4])), then, using the values of the energies of other bonds from ([5]), we obtain a difference in the energies of I and II of 4 kcal/mole, if for the C=O bond one adopts a value characteristic of ketones. In reality, the energy of the C=O bond in ketenes is considerably greater, and if for it one adopts the bond energy in the CO_2 molecule*, the difference in the energies of I and II increases to 34 kcal/mole**. Therefore the existence of an equilibrium mixture of I and II with a high concentration of the latter is possible only with a substantial increase, relative to average values, of the bond energies in the group Si—O—C≡CH. This is naturally attributed to conjugation of the $(p \to d)\pi$ bond Si—O with the $(p-p)\pi$ bond C≡C. (An analogous phenomenon in the group Si—CH=C=O cannot be of substantial significance because of the absence of unshared electron pairs on the C atom.) The situation arising is shown schematically in Fig. 2, from which it follows–

Fig. 2. Conjugation of the Si—O and C≡C bonds (schematically)

* This follows, for example, from the recently calculated dynamic coefficients of the $H_2C{=}C{=}O$ molecule ([6]).

** The use for the groups Si—CH=C=O and Si—O—C≡CH of bond-energy data from other sources gives, on average, differences in the energies of I and II of about 15–20 kcal/mole.

Table 1

No.	Compound	b.p., °C	P, mm*	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Found, % C	Found, % H	Found, % Si	Found, % Br	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % Br	Yield, %
1	$(CH_3)_3SiCH=C=O$	82	755	1,4101**	0,8176	34,67	34,51	52,72	8,94	24,49	–	52,58	8,82	24,59	–	90
2	$(CH_3)_3SiCH_2COOCH_3$	141–142	761	1,4128	0,8859	41,15	41,24	48,42	9,54	–	–	49,27	9,64	–	–	81
3	$(CH_3)_3SiCH_2COOC_2H_5$	156	759	1,4150	0,8764***	45,79	45,89	–	–	–	–	–	–	–	–	77,5
4	$(CH_3)_3SiCH_2COOC_4H_9$-n	86,5	17	1,4235	0,8723	55,03	55,18	57,89	10,87	14,80	–	57,39	10,70	14,91	–	85
5	$(CH_3)_3SiCHBrCOBr$	76,2	6,5	1,5015	1,6205	50,99	50,24	–	–	–	58,49	–	–	–	58,33	84
6	$(CH_3)_3SiCH_2COOSi(C_2H_5)_3$	72,5–74	3	1,4355	0,8821	72,45****	73,06	53,3	10,65	22,33	–	53,59	10,63	22,79	–	77

No.	Compound	b.p., °C	P, mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Found, % C	Found, % H	Found, % Si	Found, % Br	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % Br	Yield, %
7	$(CH_3)_3SiCH_2CONHC_6H_5$	115 – 116°	–			–		64,48	8,52	13,86	–	63,72	8,27	13,55	–	

* The IR spectra, in addition to the bands characteristic of the $Si(CH_3)_3$ group, contain: 2 –very strong bands of COOR at 1730 and 1265 cm^{-1}, as well as 1145 and 1108 cm^{-1}; 5–1815 cm^{-1} (increased at the expense of Hα and the C=O frequency), and also 1207 cm^{-1}; 6 –COOR bands at 1700–1686 and 1286 cm^{-1}, as well as 1137 cm^{-1} (a second absorption band of about 1100 cm^{-1}, present in spectrum 2, is superimposed on the 995 cm^{-1} band of the C_2H_5 group attached to Si). The formula of compound 5, given in the preliminary communication[4], proved to be erroneous.

** Molecular weight found 112,7, 118,7; calculated 114,2.

*** Literature data[8]: b.p. 157° (730 mm), n_D^{20} 1,4149; d_4^{20} 0,8762.

**** Ester number (determined by direct titration with 0,1 N NaOH) found 161,4, calculated 162,4; molecular weight found 247,5, calculated 246,5. In the IR spectrum of the reaction product before distillation, in addition to those indicated above, a fairly intense νOH absorption band was observed, similar to the corresponding band of $(CH_3)_3SiCH_2COOH$. After distillation this band disappeared.

It follows, in particular, that the effect of such conjugation increases as the angle ∠SiOC approaches 180° (*sp*-configuration of the O atom). The large conjugation energy resulting from the estimates given permits one to expect a strong straightening of ∠SiOC. The results of a spectroscopic study, consistent with these considerations, will be published separately.

In all the addition reactions investigated, the product reacted in the ketene form according to the scheme:

$$(CH_3)_3SiCH{=}C{=}O \begin{cases} \xrightarrow{H_2O} & (CH_3)_3SiCH_2COOH \\ \xrightarrow{ROH} & (CH_3)_3SiCH_2COOR \\ \xrightarrow{Br_2} & (CH_3)_3SiCHBrCOBr \\ \xrightarrow{R_3SiOH} & (CH_3)_3SiCH_2COOSiR_3 \\ \xrightarrow{PhNH_2} & (CH_3)_3SiCH_2CONHPh \end{cases}$$

Trimethylsilylacetic acid* was identified by its melting point, which coincided with the literature data ([7]). According to the results of potentiometric titration with 0.1 N NaOH, the neutralization equivalent of the acid is 140.

Experimental Part

Thermal decomposition of $(CH_3)_3SiC{\equiv}C{-}OC_2H_5$**.** Into a distillation flask were placed 50 g of trimethylsilylethoxyacetylene (b.p. 63°/45 mm; n_D^{20} 1.4240; d_4^{20} 0.8276), and the flask was heated on a silicone bath to 120-130°. The evolved gas was bubbled through a Tishchenko bottle with bromine water. Redistillation of the distillate on a column gave 21.7 g (90% of theoretical) of a product with a sharp odor (see Table 1). The contents of the Tishchenko bottle were extracted with ether, the ethereal extracts were dried over $CaCl_2$, and the ether was distilled off. Distillation of the residue yielded 28 g (70% of theoretical) of dibromomethane with b.p. 127-130°, n_D^{20} 1.5355.

Addition reaction of H_2O**, ROH,** Br_2**,** $C_6H_5NH_2$**,** R_3SiOH **to** $(CH_3)_3SiCH{=}C{=}O$**.** Into a flask equipped with a stirrer, reflux condenser, and dropping funnel was placed the reagent to be added, and, with cooling to −10 to −15°, ketene was added dropwise. The corresponding product was isolated by fractionation (the acid was not distilled).

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* The IR spectrum contains bands of the COOH group at 3200-3500 cm^{-1} (maximum intensity at 3050 cm^{-1} and weaker bands at $\sim$ 2800, 2650, 2560 cm^{-1}), 951 and 926 cm^{-1} (γOH), 1710 and 1297 cm^{-1} (very strong), as well as 1133 and 1105 cm^{-1}.

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