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Abstract

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THE INFLUENCE OF THE SIZE OF ALKYL RADICALS R ON THE STABILITY OF THE Si –R BOND TOWARD THE ACTION OF CONCENTRATED SULFURIC ACID

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In 1951, Sommer and co-workers ([1]) found that, when concentrated sulfuric acid acts on organosilicon compounds containing the grouping $(CH_3)_3Si$, one methyl group is split off, and after hydrolysis with water compounds containing a siloxane bond are formed. The intermediate product is an organosilicon sulfate ([2]), which decomposes under the action of water with formation of the bond ≡ Si—O—Si ≡. This reaction, new in the chemistry of organosilicon compounds, was carried out with a series of compounds containing various functional groups (X) in the side chain: −COOH, $-NH_2$, and $-CO-CH_3$.

$$2(CH_3)_3Si(CH_2)_nX \xrightarrow[H2O]{H_2SO_4} [X(CH_2)_nSi(CH_3)_2]_2O + 2CH_4.$$

Later A. F. Platé, N. A. Belikova, and Yu. P. Egorov ([3,4]) established that an analogous reaction takes place under the action of H_2SO_4 also on silicon hydrocarbons containing six- and five-membered rings; in the first case, along with splitting off of a methyl group, cleavage of the six-membered ring occurred, whereas in the second case only the five-membered ring underwent cleavage. Compounds containing four-membered rings behaved similarly. Under the action of H_2SO_4 on dimethyltrimethylsilylmethylsilane ([5]), only the ring was cleaved. In contrast to these compounds, tetraethylsilane proved to be very resistant to the action of concentrated H_2SO_4. Shaking this compound with H_2SO_4 even for 9.5 hours caused cleavage of the Si—C_2H_5 bond by only 4-5% ([3]).

The chemical stability of the Si—C_2H_5 bond was recently confirmed by us as well ([6]), using the example of the action of concentrated H_2SO_4 on methyldiethylsilylpropionic acid. It was established that only the Si—CH_3 bond underwent cleavage.

From these data one may conclude that the stability of the ≡ Si—C ≡ bond toward the action of concentrated H_2SO_4 must depend on the size and structure of

the hydrocarbon radicals attached to this carbon atom. To test this supposition, we synthesized three new monobasic γ-organosilicon acids (VII, VIII, and IX) of the general formula $CH_3(R)_2SiCH_2CH_2COOH$ (where R = *n*-C_3H_7, *n*-C_4H_9, and *u*-C_5H_{11}) and studied their behavior toward the action of concentrated H_2SO_4 under standard conditions. As a result of the investigations carried out, three dibasic organosilicon acids were obtained: 4,4,6,6-tetra-*n*-propyl-4,6-disila-5-oxanonanedicarboxylic acid (X), 4,6-dimethyl-4,6-di-*n*-butyl-4,6-disila-5-oxanonanedicarboxylic acid (XI), and 4,6-dimethyl-4,6-diisoamyl-4,6-disila-5-oxanonanedicarboxylic acid (XII).

The structure of the acids obtained indicates that cleavage of the Si–C bond in the starting acids VII, VIII, and IX occurred at different radicals. In acid VII, which contained the grouping $CH_3(n\text{-}C_3H_7)_2Si$—, cleavage occurred at the ≡ Si—CH_3 bond; in the other two acids (VIII and IX), the ≡ Si—C_4H_9 and ≡ Si—C_5H_{11} bonds underwent cleavage.

$$CH_3(R)_2SiCH_2CH_2COOH \xrightarrow[H_2O]{H_2SO_4} \begin{cases} [HOOCCH_2CH_2SiR_2]_2O + 2CH_4, & R = n\text{-}C_3H_7 \text{ (X)}, \\ [HOOCCH_2CH_2Si(CH_3)R]_2O + 2RH, & R = n\text{-}C_4H_9 \text{ (XI) and } n\text{-}C_5H_{11} \end{cases}$$

The data obtained by us confirmed the supposition that in γ-organosilicon acids containing the grouping $(CH_3)R_2Si$—, the order of cleavage of the Si—CH_3 and Si—R bonds under the action of concentrated H_2SO_4 is determined by the size of the hydrocarbon radical R. When R = C_2H_5 and *n*-C_3H_7, cleavage occurs at the Si—CH_3 bond; when R = *n*-C_4H_9 and *n*-C_5H_{11}, cleavage occurs at the Si—R bond.

Thus, the radicals studied may be arranged according to their resistance to the action of concentrated H_2SO_4 in the following series:

$$C_2H_5, \quad n\text{-}C_3H_7 > CH_3 > n\text{-}C_4H_9, \quad n\text{-}C_5H_{11}.$$

The starting monobasic γ-organosilicon acids were obtained by the method described by Sommer et al. (7). $CH_3SiCl_2(CH_2Cl)$ was obtained by photochemical chlorination of $(CH_3)_2SiCl_2$ (8) and was converted into $CH_3(R)_2SiCH_2Cl$ by the action of RMgX.

The constants of the compounds obtained are presented in Table 1.

Table 1

Compound no.	Formula	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D calc.***	MR_D found
I*	$CH_3(n\text{-}C_3H_7)_2SiCH_2Cl$	91.5–192.5/758	1.4432	0.8882	53.64	53.37
II**	$CH_3(n\text{-}C_4H_9)_2SiCH_2Cl$	98.5–102/12	1.4475	0.8845	62.90	62.54
III	$CH_3(n\text{-}C_5H_{11})_2SiCH_2Cl$	110–175/5	1.4474	0.8731	72.16	71.93
IV	$CH_3(n\text{-}C_3H_7)_2SiCH_2CH(OC_2H_5)_2$	87–88/5	1.4402	0.9520	84.75	83.93
V	$CH_3(n\text{-}C_4H_9)_2SiCH_2CH(OC_2H_5)_2$	108–110/5	1.4445	0.9436	94.01	93.13
VI	$CH_3(n\text{-}C_5H_{11})_2SiCH_2CH(OC_2H_5)_2$	134–175/5	1.4460	0.9317	103.27	102.81
VII	$CH_3(n\text{-}C_3H_7)_2SiCH_2CH_2COOH$	147.5/5	1.4508	0.9156	59.61	59.48
VIII	$CH_3(n\text{-}C_4H_9)_2SiCH_2CH_2COOH$	180.5/11	1.4510	0.9082	68.87	68.31
IX	$CH_3(n\text{-}C_5H_{11})_2SiCH_2CH_2COOH$	174.5/6	1.4536	0.8949	78.13	78.05
X	$[HOOCCH_2CH_2Si(n\text{-}C_3H_7)_2]_2O$	148–140.5/11	1.4560	0.9998	107.58	106.30
XI	$[HOOCCH_2CH_2Si(n\text{-}C_4H_9)(CH_3)]_2O$	154/8	1.4670	1.0025	98.32	99.35
XII	$[HOOCCH_2CH_2Si(n\text{-}C_5H_{11})(CH_3)]_2O$	155/7	1.4675	1.0064	107.58	106.90

* Literature data: b.p. 192°; n_D^{20} 1.4450; d_4^{20} 0.8902 (9).

** Literature data: b.p. 227.5/767; n_D^{20} 1.4480; d_4^{20} 0.8827 (10).

*** MR_D was calculated according to Warrick (11).

Experimental Part

Methyldi-*n*-propylchloromethylsilane (I). Obtained by the reaction of magnesium *n*-propyl bromide (prepared from 112 g (4.6 g-at.) of magnesium and 738 g (6 mol.) of *n*-propyl bromide) with 226 g (1.38 mol.) of methyldichloromethylsilane. Fractionation gave 105 g (0.58 mol.) of I. Yield 42%.

Methyldi-*n*-butylchloromethylsilane (II). Obtained by the reaction of magnesium *n*-butyl bromide (prepared from 150 g (6 g-at.)

magnesium and 822 g (6 mol) of *n*-butyl bromide) with 410 g (2.5 mol) of methyldichlorochloromethylsilane. 270 g (1.3 mol) of II was obtained. Yield 52%.

Methyldiisoamylchloromethylsilane (III). Obtained by the interaction of isoamylmagnesium bromide (prepared from 109 g (4.5 g-at.) of magnesium and 722 g (4.7 mol) of isoamyl bromide) with 256 g (1.6 mol) of methyldichlorochloromethylsilane. Fractionation gave 202 g (0.86 mol) of III. Yield 54%.

$C_{12}H_{27}ClSi$.	Found %:	Si 11.54
	Calculated %:	Si 11.95

The methyldialkylsilylmethyl malonates described below were obtained by reacting sodium malonic ester with methyldialkylchlorosilanes according to the method described in the literature (7).

Methyldi-*n*-propylsilylmethyl malonate (IV). Obtained by the interaction of sodium malonic ester (prepared from 11.5 g (0.5 g-at.) of metallic Na, 800 ml of absolute ethanol, and 83.5 g (0.52 mol) of malonic ester) with 90 g (0.5 mol) of I. Fractionation gave 96 g (0.31 mol) of IV. Yield 62%.

$C_{15}H_{30}O_4Si$.	Found %:	Si 9.36.	Ester no.* 374
	Calculated %:	Si 9.28.	Ester no. 370

Methyldi-*n*-butylsilylmethyl malonate (V). Obtained by the interaction of sodium malonic ester (prepared from 25.5 g (1.11 g-at.) of metallic Na, 800 ml of absolute ethanol, and 186.5 g (1.16 mol) of malonic ester) with 240 g (1.11 mol) of II. Fractionation gave 150 g (0.49 mol) of V. Yield 45%.

$C_{17}H_{34}O_4Si$	Found %:	Si 8.48.	Ester no. 335
	Calculated %:	Si 8.50.	Ester no. 338

Methyldiisoamylsilylmethyl malonate (VI). Obtained from 19 g (0.81 g-at.) of metallic Na, 800 ml of absolute ethanol, 132 g (0.82 mol) of malonic ester, and 190 g (0.81 mol) of III. Fractionation gave 160 g (0.45 mol) of VI. Yield 56%.

$C_{19}H_{48}O_4Si$	Found %:	Si 7.86.	Ester no. 309
	Calculated %:	Si 7.83.	Ester no. 312

The methyldialkylsilylmethyl malonates IV, V, and VI obtained were converted into monobasic acids by saponification with strong KOH (1 : 1) according to the method described in the literature (7).

γ-Methyldi-*n*-propylsilylpropionic acid (VII). 90 g (0.3 mol) of IV was saponified with strong alkali. 51.5 g (0.26 mol) of VII was isolated. Yield 85%.

$C_{10}H_{22}O_2Si$.	Found %:	Si 14.0.	Acid no.** 269
	Calculated %:	Si 13.87.	Acid no. 276

γ-Methyldi-*n*-butylsilylpropionic acid (VIII). 145 g (0.44 mol) of V was saponified with strong alkali. 93 g (0.4 mol) of VIII was isolated. Yield 91%.

$C_{12}H_{26}O_2Si$.	Found %:	Si 12.32.	Acid no. 239
	Calculated %:	Si 12.20.	Acid no. 243

γ-Methyldiisoamylsilylpropionic acid. 150 g (0.42 mol) of VI was saponified with strong alkali. 85 g (0.33 mol) of IX was isolated. Yield 80%.

$C_{14}H_{30}O_2Si$.	Found %:	Si 10.84.	Acid no. 215
	Calculated %:	Si 10.86.	Acid no. 217

Interaction of γ-methyldialkylsilylpropionic acids with concentrated sulfuric acid.

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* Ester no. —ester number.
** Acid no. —acid number.

All experiments were carried out under the following standard conditions. Into a round-bottom flask equipped with a reflux condenser, a dropping funnel, and a mechanical stirrer with a mercury seal was introduced conc. H_2SO_4, sp. gr. 1.83, calculated as 200 ml per 1 mole of organosilicon dibasic acid. Then, from the dropping funnel, with stirring over the course of 1 hour, the organosilicon acid was added. During this, the reaction mixture became heated and gaseous or low-boiling products were evolved. Stirring was continued for another 2 hours, after which the mixture was poured onto ice. The dicarboxylic acid, which separated in the form of a viscous oil, was extracted with ether; the ethereal solution was washed with water, dried over anhydrous $CuSO_4$, the ether was distilled off, and the dicarboxylic acid was isolated by fractional distillation in vacuum.

Interaction of methyldi-*n*-propylsilylpropionic acid with H_2SO_4. To 44 ml of H_2SO_4 was added 45 g (0.22 mole) of VII. Fractional distillation gave 32 g (0.08 mole) of 4,4,6,6-tetra-*n*-propyl-4,6-disila-5-oxanonanedicarboxylic acid (X). Yield 73%.

Found, %: Si 14.40. N. E. 286
$C_{18}H_{38}O_5Si_2$. Calculated, %: Si 14.37. N. E. 287

Interaction of methyldi-*n*-butylsilylpropionic acid with H_2SO_4. To 76 ml of H_2SO_4 was added 88 g (0.38 mole) of VIII. Fractional distillation gave 62 g (0.17 mole) of 4,6-dimethyl-4,6-di-*n*-butyl-4,6-disila-5-oxanonanedicarboxylic acid (XI). Yield 90%.

Found, %: Si 15.50. N. E. 299
$C_{16}H_{34}O_5Si_2$. Calculated, %: Si 15.48. N. E. 300

Interaction of methyldiisoamylsilylpropionic acid with H_2SO_4. To 62 g of H_2SO_4 was added 80 g (0.31 mole) of IX. The reaction was accompanied by evolution of a volatile product boiling at 27–29° (isopentane). Frac-

tional distillation gave 47 g (0.12 mole) of 4,6-dimethyl-4,6-diisoamyl-4,6-disila-5-oxanonanedicarboxylic acid XII. Yield 77%.

Found, %: Si 14.32. N. E. 287
$C_{18}H_{38}O_5Si_2$. Calculated, %: Si 14.37. N. E. 287

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REFERENCES

1. L. H. Sommer, N. S. Marans et al., *J. Am. Chem. Soc.*, **73**, 882 (1951).
2. L. H. Sommer, W. P. Barie, J. Gould, *J. Am. Chem. Soc.*, **75**, 3765 (1953).
3. A. F. Platé, N. A. Belikova, Yu. P. Egorov, *DAN*, **102**, No. 6, 1131 (1955).
4. A. F. Platé, N. A. Belikova, Yu. P. Egorov, *Izv. AN SSSR, OKhN*, 1956, 1085.
5. L. H. Sommer, G. A. Baum, *J. Am. Chem. Soc.*, **76**, 5002 (1954).
6. N. D. Dolgov, E. V. Kukharskaya, D. N. Andreev, *Izv. AN SSSR, OKhN*, 1957, 968.
7. L. H. Sommer, J. R. Gold, G. M. Goldberg, N. S. Marans, *J. Am. Chem. Soc.*, **71**, 1509 (1949).
8. V. A. Ponomarenko, V. F. Mironov, *DAN*, **94**, No. 3, 485 (1954).
9. V. F. Mironov, N. A. Pogonkina, *Izv. AN SSSR, OKhN*, 1955, 182.
10. V. F. Mironov, *DAN*, **108**, No. 2, 266 (1956).
11. E. L. Warrik, *J. Am. Chem. Soc.*, **68**, 2456 (1946).

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