Preparation of Some Bis(fluorodimethylsilyl)alkanes

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Sommer and his co-workers[1] observed that certain organosilicon structures undergo the selective cleavage of one methyl group from each trimethylsilyl grouping, Me_3Si, as methane, when treated with concentrated sulfuric acid. It has also been well established that the demethylation reaction takes place smoothly, even in heterogeneous systems. For example, Sommer and Ansul[2] found that 1,4-bis(trimethylsilyl)butane can be converted into 2,7-dimethyl-2,7-difluoro-2,7-disilaoctane by sulfuric acid cleavage, followed by hydrolysis and then by treatment with boron trifluoride etherate.

$$n\mathrm{Me_3Si(CH_2)_4SiMe_3} \xrightarrow[2)\ H_2O]{1)\ H_2SO_4} -\left[\begin{array}{cc} Me & Me \\ | & | \\ -Si(CH_2)_4Si-O- & \\ | & | \\ Me & Me \end{array}\right]_n - + 2n\mathrm{CH_4}$$

$$\mathrm{FMe_2Si(CH_2)_4SiMe_2F} \xleftarrow{BF_3\cdot Et_2O}$$

Kumada and his co-workers[3] observed that hexamethyldisilane behaves towards concentrated sulfuric acid in a manner similar to that of the above silahydrocarbon except that the demethylation reaction in this case proceeds in two distinct steps. Thus, chloro(or fluoro)-pentamethyldisilane or 1,2-dichloro(or 1,2-difluoro)tetramethyldisilane can be obtained selectively if the reaction mixture is treated with ammonium chloride (or fluoride) when, respectively, one or two equivalents of methane have been evolved.

$$\mathrm{Me_3SiSiMe_3} \xrightarrow[2)\ NH_4X]{1)\ H_2SO_4} \begin{cases} \mathrm{Me_3SiSiMe_2X} + \mathrm{CH_4} \\ \mathrm{XMe_2SiSiMe_2X} + 2\mathrm{CH_4} \end{cases}$$

In the present study we have established that the demethylation by sulfuric acid, followed by fluorination by the same method as above, can successfully be used for the method generally applicable to the preparation of bis(fluorodimethylsilyl)alkanes (Eq. 1), important intermediates for the preparation of hybrid paraffin-siloxanes.

$$\mathrm{Me_3SiRSiMe_3} \xrightarrow[2)\ NH_4F\cdot HF]{1)\ H_2SO_4} \mathrm{FMe_2SiRSiMe_2F} + 2\mathrm{CH_4} \qquad (1)$$

The starting compounds selected for the present study were eight bis(trimethylsilyl)-alkanes and one chlorine-substituted compound: bis(trimethylsilyl)methane (I), 1,1-bis(trimethylsilyl)ethane (II), 1,2-bis(trimethylsilyl)ethane (III), 1,3-bis(trimethylsilyl)propane (IV), 2,2-bis(trimethylsilyl)propane (V), 1,4-bis(trimethylsilyl)butane (VI), 1,5-bis(trimethylsilyl)pentane (VII), 1,6-bis(trimethylsilyl)hexane (VIII) and bis(trimethylsilyl)-chloromethane (IX). The respective normal products, bis(fluorodimethylsilyl)alkanes, are as follows: bis(fluorodimethylsilyl)methane (X), 1,1-bis(fluorodimethylsilyl)ethane (XI), 1,2-bis(fluorodimethylsilyl)ethane (XII), 1,3-bis(fluorodimethylsilyl)propane (XIII), 2,2-bis(fluorodimethylsilyl)propane (XIV), 1,4-bis(fluorodimethylsilyl)butane (XV), 1,5-bis(fluorodimethylsilyl)pentane (XVI), 1,6-bis(fluorodimethylsilyl)hexane (XVII) and bis(fluorodimethylsilyl)chloromethane (XVIII). The reaction conditions employed for the demethylation and the yields of fluorinated products are listed in Table I; the physical properties, together with analytical data for $FMe_2SiRSiMe_2F$, are shown in Table II.

1) a) L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett and R. P. Pioch, *J. Am. Chem. Soc.*, 73, 882 (1951); b) L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, ibid., 75, 2392 (1953).

2) L. H. Sommer and G. R. Ansul, ibid., 77, 2482 (1955).

3) M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima and K. Shiina, *J. Org. Chem.*, 21, 1264 (1956).

TABLE I. CLEAVAGE OF SOME SILAHYDROCARBONS $Me_3SiRSiMe_3$ BY SULFURIC ACID, FOLLOWED BY FLUORINATION

Compound			H_2SO_4	Temp.	Gas evolved[a]	$NH_4F \cdot HF$	Yield of product, g. (%)		
No.	R	g. (mol.)	g.	°C	%	g.	Me_3SiF	$FMe_2SiRSiMe_2F$	$HRSiMe_2F$
I	CH_2	30 (0.19)	130	30	65	17	5.5(32)	14.5(46)	5.5(32)[b]
II	CHMe	21.5(0.12)	89	30	75	12	5 (44)	10 (45)	6 (46)[c]
III	$(CH_2)_2$	18 (0.10)	80	30	80	11	2.5(26)	10.5(58)	2.6(25)[d]
IV	$(CH_2)_3$	19 (0.10)	70	43	80	11	1 (11)	13 (67)	1 (10)[e]
V	CMe_2	21 (0.11)	80	30	100	10	0	20 (92)	0
VI	$(CH_2)_4$	40 (0.19)	180	40～45	94	30	2 (8)	28 (72.5)	3 (12)[f]
VII	$(CH_2)_5$	24 (0.11)	80	60～63	95	11	0.8(8)	19 (77)	1.5(9)[g]
VIII	$(CH_2)_6$	30 (0.10)	80	62～65	95	10	0.8(9)	19 (79)	2 (12)[h]
IX	CHCl	18 (0.09)	80	38	95	12	Trace	16 (86)	Trace

a) Not analyzed.
b) In addition, 1.5 g. of a liquid, b. p. 26°C was caught in a trap cooled at −78°C. It is believed to be tetramethylsilane, b. p. 26～27°C [A. Bygden, *Z. physik. Chem.*, **90**, 243 (1915)].
c) B. p. 51°C, n_D^{20} 1.3543, d_4^{20} 0.7972 (Found: F, 17.73. Calcd. for $C_4H_{11}FSi$: F, 17.89%). B. p. 51°C, n_D^{15} 1.3570 are reported by C. Eaborn, *J. Chem. Soc.*, **1949**, 2755; **1952**, 2846.
d) B. p. 51°C, n_D^{20} 1.3540, d_4^{20} 0.7958 (Found: F, 17.73. Calcd. for $C_4H_{11}FSi$: F, 17.89%).
e) B. p. 77～78°C, n_D^{20} 1.3660.
f) B. p. 103°C, n_D^{20} 1.3810, d_4^{20} 0.8119 (Found: F, 14.20. Calcd. for $C_6H_{15}FSi$: F, 14.15).
g) B. p. 36°C/26 mmHg, n_D^{20} 1.3900, d_4^{20} 0.8212 (Found: F, 12.75. Calcd. for $C_7H_{17}FSi$: F, 12.81 %).
h) B. p. 44°C/14 mmHg, n_D^{20} 1.3980, d_4^{20} 0.8222 (Found: F, 11.76. Calcd. for $C_8H_{19}FSi$: F, 11.71%).

TABLE II. PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR $FMe_2SiRSiMe_2F$

Compound		B. p.	n_D^{20}	d_4^{20}	F, %	
No.	R	°C/mmHg			Calcd.	Found
X[a]	CH_2	115	1.3810	0.9203	22.57	22.50
XI	CHMe	114.5	1.3934	0.9377	20.84	20.68
XII	$(CH_2)_2$	136～137	1.3870	0.9193	20.84	20.58
XIII[b]	$(CH_2)_3$	156	1.3926	0.9137	19.38	19.0
XIV	CMe_2	149	1.4055	0.9410	19.38	19.13
XV[c]	$(CH_2)_4$	176	1.7990	0.9664	18.06	18.2
XVI	$(CH_2)_5$	93/26	1.4050	0.9113	16.93	16.89
XVII	$(CH_2)_6$	95/14	1.4087	0.9037	15.93	15.90
XVIII	CHCl	53/21	1.4105	1.0700	18.74	18.55

a) B. p. 114～116°C, n_D^{20} 1.3780, d_4^{20} 0.920 are reported by B. A. Bluestein, *J. Am. Chem. Soc.*, **70**, 3068 (1948).
b) Reported values:[6] b. p. 160.5°C, n_D^{20} 1.3945, d_4^{20} 0.9124.
c) Reported value:[1] b. p. 176°C.

The mixture of a silahydrocarbon and sulfuric acid was stirred vigorously in a vessel connected to a gas-collecting apparatus. The reaction system was heterogeneous initially, but it became homogeneous as the reaction went on. In the $Me_3Si(CH_2)_xSiMe_3$ series of compounds, it was necessary to increase the reaction temperature along with an increase in the value of x in order to cause the demethylation to occur at a reasonable rate. At the temperatures indicated in Table I the reaction appeared to be completed within a few hours.

In agreement with the observation by Sommer and Ansul[2] of the cleavage of 1,4-bis(trimethylsilyl)butane (VI) by sulfuric acid, some percentage of the reaction gave a cleavage between silicon and the R grouping, while Si-Me cleavage was the main reaction in most cases. Less than a theoretical amount of methane (2 mol. of methane per mole of $Me_3SiRSiMe_3$) was evolved; accordingly, the fractional distillation of fluorinated products gave trimethylfluorosilane and alkyldimethylfluorosilanes, $HRMe_2SiF$, in some and nearly equal yields in most cases. With compound I, however, a small amount of a liquid believed to be tetramethylsilane was also detected.

Apart from the detailed reaction mechanism, undoubtedly these products were formed through the two different courses indicated by

Eqs. 2a-2b and 3a-3b:

$$Me_3SiRSiMe_3 \xrightarrow{H_2SO_4} Me_3Si(HSO_4) + HRSiMe_3 \quad (2a)$$

$$HRSiMe_3 \xrightarrow{H_2SO_4} HRSiMe_2(HSO_4) + CH_4 \quad (2b)$$

$$MeSiRSiMe_3 \xrightarrow{H_2SO_4} Me_3SiRSiMe_2(HSO_4) + CH_4 \quad (3a)$$

$$Me_3SiRSiMe_2(HSO_4) \xrightarrow{H_2SO_4} Me_3Si(HSO_4) + HRSiMe_2(HSO_4) \quad (3b)$$

Apparently tetramethylsilane is a product in reaction 2a; this volatile (b. p. 27°C) and paraffin-like compound leaves the reaction system without being attacked by concentrated sulfuric acid. Compounds of the $HRSiMe_2F$ type are probably produced through both courses, 2a-2b and 3a-3b.

Since the results in Table I are over-all ones from complicated reactions, heterogeneous and homogeneous, we cannot discuss the mechanism of silicon-carbon cleavage in detail. However, the following listing by relative ease of Si-R cleavage may be established on the basis of the yields of products:

$$CH_2,\ CHMe > (CH_2)_2 > (CH_2)_3 > (CH_2)_4,$$
$$(CH_2)_5,\ (CH_2)_6 > CHCl > CMe_2$$

These results seem to be fairly well explained in terms of electronic and steric effects of substituents on the methylene carbon to be attacked by the acid.

In order to learn more about the reaction path, further investigation into the homogeneous reaction using compounds such as $Me_3SiRSiMe_2OEt$ is being undertaken.

Experimental

Materials.—All the compounds used (I—IX) are known and prepared by known methods with the exception of compounds III and VIII, the preparation of which is described below. In the following list, the references given after the compounds are to the source or method of preparation: I,[4] b. p. 132~134°C, n_D^{20} 1.4172; II,[5] b. p. 160~161°C, n_D^{20} 1.4331; IV,[6] b. p. 170°C, n_D^{20} 1.4224; V,[7] b. p. 178°C, n_D^{20} 1.4459; VI,[2] b. p. 191°C, n_D^{20} 1.4272; VII,[6] b. p. 88°C/12 mmHg, n_D^{20} 1.4310; IX,[5] b. p. 71°C/21 mmHg, n_D^{20} 1.4491.

1, 2-Bis(trimethylsilyl)ethane (III).—To a Grignard solution prepared from 40 g. (0.33 mol.) of Me_3SiCH_2Cl and 7.8 g. (0.33 g. atom) of magnesium turnings in ether, 7 g. of anhydrous cobaltous chloride was added in several portions. To the resulting black solution 40 g. of Me_3SiCH_2Cl was added, and the reaction mixture was kept under reflux for 40 hr. After hydrolysis, an organic layer was separated, dried and fractionally distilled to give 21 g. of unchanged Me_3SiCH_2Cl and 14.3 g. (a 34% yield on the basis of the Me_3SiCH_2Cl unrecovered) of 1, 2-bis(trimethylsilyl)ethane; b. p. 149~150°C, n_D^{20} 1.4202, d_4^{20} 0.7506 (reported:[9] b. p. 152°C, n_D^{20} 1.4204, d_4^{20} 0.7536).

1, 6-Bis(trimethylsilyl)hexane (VIII).—This compound was prepared by the following sequence of reaction:

$$CH_2{=}CHCH_2CH_2CH{=}CH_2 + 2MeSiHCl_2 \rightarrow Cl_2MeSi(CH_2)_6SiMeCl_2$$
XIX
$$XIX + 2MeMgBr \rightarrow VIII$$

In a 100-ml. three-necked flask fitted with a thermometer, a dropping funnel and an efficient reflux condenser, there was placed 25 g. (0.35 mol.) of diallyl and 0.5 ml. of a 0.1 M $H_2PtCl_6 \cdot 6H_2O$ solution in isopropyl alcohol.[10] The exit of the apparatus was sealed with mercury so that the reaction might be carried out at temperatures higher than the boiling points of the starting materials. To the mixture 76 g. (0.66 mol.) of methyldichlorosilane was added drop by drop under reflux conditions. The reaction temperature gradually increased to 140~150°C over a period of 13 hr. Fractional distillation gave two products: 5-hexenylmethyldichlorosilane (b. p. 91°C/26 mmHg; 26 g., in a 41% yield based on the diallyl used (Found: Cl, 35.96. Calcd. for $C_7H_{14}Cl_2Si$: Cl, 36.20%)) and 1, 6-bis(dichloromethylsilyl)hexane (XIX) (b. p. 155~156°C/13 mmHg; 42 g., yield 44% (Found: Cl, 44.91. Calcd. for $C_8H_{18}Cl_4Si_2$: Cl, 45.46%)).

To a Grignard solution containing about 1 mol. of methylmagnesium bromide 68 g. (0.22 mol.) of compound XIX was added over a 2/3-hr. period. The reaction mixture was allowed to stand-overnight, refluxed for 1 hr. and then hydrolyzed with dilute hydrochloric acid. After a work-up in the usual way, the product was fractionally distilled to give 33 g. (66% yield) of 1, 6-bis(trimethylsilyl)hexane; b. p. 101°C/7 mmHg, n_D^{25} 1.4322, d_4^{25} 0.773 (reported:[8] b. p. 109.5°C/16 mmHg, n_D^{25} 1.4298, d_4^{25} 0.772).

The Demethylation, Followed by Fluorination, of Silahydrocarbons.—The technique followed in detail that used in the demethylation, followed by the fluorination, of hexamethyldisilane.[3] The organic products were fractionally distilled through a small Stedman column rated at about 20 theoretical plates to give, in most cases, trimethylfluorosilane (b. p. 16°C), alkyldimethylfluorosilanes and bis(fluorodimethylsilyl)alkanes (see Tables I and II).

Summary

It has been established that the demethylation of bis(trimethylsilyl)alkanes of the

4) M. Kumada and M. Yamaguchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **57**, 175 (1954).
5) M. Kumada and M. Ishikawa, *J. Organometallic Chem.*, **1**, 411 (1964).
6) M. Kumada and A. Habuchi, *J. Inst. Polytech. Osaka City Univ., Ser. C*, **3**, 65 (1952).
7) M. Kumada, K. Naka and M. Ishikawa, *J. Organometallic Chem.*, in press.
8) R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 303 (1953).
9) D. C. Noller and H. W. Post, *J. Am. Chem. Soc.*, **74**, 1361 (1952).
10) J. L. Speier, J. A. Webster and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

general formula $Me_3SiRSiMe_3$ by concentrated sulfuric acid, followed by fluorination with ammonium hydrogenfluoride, can successfully be used for the method generally applicable to the preparation of bis(fluorodimethylsilyl)-alkanes, $FMe_2SiRSiMe_2F$. Although Si-Me cleavage was the main reaction in most cases, some part of the reaction gave a cleavage between silicon and the R grouping. The ease of the cleavage of R from silicon was found to decrease in the following order :

CH_2, $CHMe > (CH_2)_2 > (CH_2)_3 > (CH_2)_4$, $(CH_2)_5$, $(CH_2)_6 > CHCl > CMe_2$

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