[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

The Analogy between Aromatic Bromination and the Cleavage of Trialkylarylsilanes by Bromine

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Five trimethylarylsilanes were cleaved with bromine. The following sequence, representing decreasing ease of cleavage was observed: 2-bromo-5-trimethylsilylthiophene > phenyltrimethylsilane > *m*-nitrophenyltrimethylsilane > *p*-nitrophenyltrimethylsilane > *o*-nitrophenyltrimethylsilane. The reaction of phenyltrimethylsilane with bromine was found to exhibit over-all third-order kinetics (second order in bromine). The above data suggest a strong similarity between these silane cleavage reactions and aromatic bromination. By employing this analogy the stability of alkylarylsilanes toward halogen or any electrophilic reagent can be predicted by the application of aromatic orientation rules.

It is well known that halogens can be used to effect the cleavage of aromatic carbon–silicon bonds.

$$\text{(alkyl)}_3\text{Si-aryl} \xrightarrow{X_2} \text{aryl-X} + \text{(alkyl)}_3\text{SiX} \qquad (1)$$

This unusually clean-cut reaction has been utilized in organosilicon chemistry as a preparative method[1] as well as to establish the structure of unknown silanes.[2] The latter is possible since one atom of the halogen becomes attached to the aromatic nucleus at the position originally occupied by the silicon, thus yielding a fragment which can be identified readily.

In the present investigation the cleavage of phenyltrimethylsilane by bromine in carbon tetrachloride was studied in some detail. This reaction proceeds smoothly and in good yield forming trimethylbromosilane and bromobenzene.[1]

$$\text{Me}_3\text{SiC}_6\text{H}_5 \xrightarrow[\text{CCl}_4]{\text{Br}_2} \text{Me}_3\text{SiBr} + \text{C}_6\text{H}_5\text{Br} \qquad (2)$$

The course of the reaction was followed by testing a sample of the mixture for unreacted bromine. Over a restricted concentration and temperature range it exhibited over-all third-order kinetics (second order in bromine, first order in silane).

The bromine cleavages of 2-bromothienyltrimethylsilane and the isomeric mononitrophenyltrimethylsilanes were also studied on a semi-quantitative basis. The results clearly indicated that the thienylsilane was cleaved twenty to thirty times as rapidly as the unsubstituted phenyl under comparable conditions. On the other hand, the rates of cleavage of the mononitrophenyltrimethylsilanes in carbon tetrachloride were so slow as to be negligible. When the solvent was changed to nitrobenzene in these cases, the following order of decreasing ease of cleavage was determined: *m*-nitrophenyl > *p*-nitrophenyl > *o*-nitrophenyl. Significantly the rate of cleavage of phenyltrimethylsilane in nitrobenzene was so rapid it could not be measured conveniently.

Experimental

Phenyltrimethylsilane.—Prepared from phenyllithium and trimethylchlorosilane, b.p. 169–169.5°, $n^{20}\text{D}$ 1.4909.

2-Bromo-5-trimethylsilylthiophene.—One hundred and thirty-seven grams (0.569 mole) of 2,5-dibromothiophene[3] was dissolved in 300.0 ml. of anhydrous ethyl ether and placed in a dry, 500 ml., three-necked flask, fitted with a reflux condenser, mechanical stirrer and dropping funnel, the whole apparatus being flushed with dry nitrogen. The stirrer was started and 13.8 g. (0.569 g. atom) of magnesium turnings was added in small portions at such a rate as to keep the ether solvent refluxing gently. After all the magnesium had reacted there was added 62.0 g. (0.569 mole) of trimethylchlorosilane. The reaction mixture was refluxed on a steam-bath until it no longer gave a positive Color Test I. It was then hydrolyzed by pouring into cold, dilute, hydrochloric acid solution. The ether layer was separated, shaken with two portions of saturated sodium carbonate solution, then shaken with two portions of distilled water and finally dried with Drierite. The solvent was removed by distilling at atmospheric pressure and the residue was distilled through a modified Claisen flask at reduced pressure. There was collected 66.5 g. (50%) of a clear liquid, b.p. 92–96° at 10 mm., 72–75° at 4 mm. This was fractionated through a thirty-inch, glass helix-packed column at atmospheric pressure to give 30.0 g. of 2-bromo-5-trimethylsilylthiophene, b.p. 218–218.5°, $n^{20}\text{D}$ 1.5315, d^{20}_{20} 1.298.

Anal. Calcd. for $C_7H_{11}SSiBr$: Si, 11.9. Found: Si, 12.2, 12.1.

When the Grignard reagent of this compound was carbonated, 5-trimethylsilylthiophenecarboxylic acid was obtained, m.p. 134.5–135°. This compound did not depress the melting point of an authentic sample of the acid.[4]

Bromine.—The bromine (Mallinckrodt, reagent grade) was purified by first distilling from solid potassium bromide, then shaking with an equal volume of concentrated sulfuric acid and again distilling. The purified bromine was stored in dry, glass stoppered bottles.

Carbon Tetrachloride.—This solvent was purified by first shaking with a dilute potassium dichromate–sulfuric acid solution, then with dilute sodium hydroxide and finally with distilled water. After a preliminary drying with anhydrous sodium sulfate it was distilled from phosphorus pentoxide into a dry jug, and stored over phosphorus pentoxide.

Action of Bromine on Phenyltrimethylsilane.—In order to establish that the phenyltrimethylsilane was cleaved under our reaction conditions as shown in equation 2, 20 g. (0.127 mole) of the silicon compound was dissolved in 100 ml. of dry carbon tetrachloride and 20.8 g. (0.13 mole) of bromine was added slowly to the solution. The mixture was allowed to stand for four hours and then distilled. There was collected 13.5 g. (68%) of bromobenzene, b.p. 154–155°.

Procedure I.—Exactly 250 ml. of bromine solution in carbon tetrachloride was made up at bath temperature and standardized by withdrawing five or ten-ml. portions, running them into a solution consisting of 25 ml. of potassium iodide solution (40 g. potassium iodide per liter), 50 ml. of disodium phosphate solution (60 g. of disodium phosphate per liter) and excess standard arsenious oxide solution. The excess arsenious oxide was back-titrated with standard iodine solution, using starch indicator.

A sample of the silicon compound was weighed out on an analytical balance and then made up to exactly 50 ml. at bath temperature with dry carbon tetrachloride.

The reaction was started by mixing the two solutions in a 500-ml. black-painted volumetric flask. At suitable time intervals five or ten-ml. samples were withdrawn and the unreacted bromine determined by the same procedure described above for the standardization of the bromine.

Procedure II.—This procedure differed from I only in that the solutions were standardized at room temperature and

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[1] F. C. Whitmore, *et al.*, THIS JOURNAL, **70**, 433 (1948).

[2] R. A. Benkeser and P. E. Brumfield, *ibid.*, **73**, 4770 (1951).

[3] W. Steinkoff and H. Kohler, *Ann.*, **532**, 250 (1937).

[4] R. A. Benkeser and R. B. Currie, THIS JOURNAL, **70**, 1780 (1948).

the reaction carried out in sealed vials each holding 10 ml. of the reaction mixture at room temperature. The vials were placed in a beaker, wrapped with aluminum foil to exclude light, and placed in the constant temperature bath. After allowing them to reach the bath temperature, vials were removed at suitable intervals and broken in a flask containing 25.0 ml. of potassium iodide solution (20.0 g. of potassium iodide per liter), 50 ml. of disodium phosphate solution (60.0 g. of disodium phosphate per liter) and an excess of standard arsenious oxide solution.

Table I summarized the kinetic data for phenyltrimethylsilane.

TABLE I

RATES OF CLEAVAGE OF PHENYLTRIMETHYLSILANE WITH BROMINE IN CARBON TETRACHLORIDE AT 35° AND 40°

Concn., moles/l.		Reacn. time, min.	Reaction, %		Temp., °C. ± 0.02	k_2[a]	k_3[b]
Br_2	$Me_3SiC_6H_5$		Br_2	$Me_3SiC_6H_5$			
0.141	0.126	1497	60	66	35	0.047	0.100
.101	.112	1410	50	46	35	.078	.102
.089	.108	1803	54	42	35	.067	.101
.103	.064	784	30	49	40	.057	.126
.047	.409	531	55	6	40	.0057	.128

[a] k_2 units are liters/mole minute. [b] k_3 units are liters²/mole² minute.

The results of a typical rate study are presented in Table II.

TABLE II

BROMINE CLEAVAGE OF PHENYLTRIMETHYLSILANE AT 40 ± 0.02°

t, min.	$a - x$[a]	$b - x$[a]	k_2[b]	k_3[c]
0	9.29	80.62	....	...
95	7.78	79.11	0.0082	0.120
237	5.96	77.49	.0062	.128
280	5.61	76.94	.0058	.130
349	5.11	76.44	.0053	.130
433	4.65	75.98	.0049	.128
463	4.48	75.81	.0047	.130
531	4.18	75.51	.0045	.130

[a] Units are ml. of 0.1004 N As_2O_3 solution where 9.29 ml. is equivalent to 0.047 mole of bromine and 80.62 ml. is equivalent to 0.409 mole of phenyltrimethylsilane. [b] k_2 is in liters/mole minute. [c] k_3 is in liters²/mole² minute.

Table III lists some average k_3 values obtained for the cleavage of 2-bromo-5-trimethylsilylthiophene and the isomeric nitrophenyltrimethylsilanes. It must be emphasized that these values are to be employed in a *qualitative sense only*. Side reactions and slowness of reaction (in the case of the nitro compounds) made accurate determinations difficult. In addition no attempt was made to establish the kinetic order of the reaction in nitrobenzene.

TABLE III

Compound	Temp., °C.	Solvent	Av. k_3, l.^{2} mole^{-2} min.$^{-1}$
2-Bromo-5-trimethylsilylthiophene	35	CCl_4	2.7
o-Nitrophenyltrimethylsilane[a]	40	$C_6H_5NO_2$	0.01
m-Nitrophenyltrimethylsilane[a]	40	$C_6H_5NO_2$	.15
p-Nitrophenyltrimethylsilane[a]	40	$C_6H_5NO_2$	.06

[a] Kindly supplied by Dr. P. E. Brumfield (see THIS JOURNAL **73**, 4770 (1951)).

Discussion

A visual inspection of the k_2 and k_3 constants in Table I and II indicates that the cleavage of phenyltrimethylsilane by bromine at the temperatures and concentrations employed is almost exactly over-all third order (second order with respect to bromine and first order in silicon compound). This was further verified by employing the differential method of van't Hoff.[5]

It is noteworthy that Robertson[6] and co-workers in recent investigations on the mechanism of aromatic bromination have found it also to be second order or higher in bromine and have accordingly postulated an electrophilic attack by a positive bromonium ion in the rate-determining step.

The relative rates of cleavage of the trimethylsilyl group by bromine which were found, namely, 2-bromo-5-trimethylsilylthiophene > phenyltrimethylsilane > *m*-nitrophenyltrimethylsilane > *p*-nitrophenyltrimethylsilane > *o*-nitrophenyltrimethylsilane are exactly as would be predicted for electrophilic substitution. Thus, while the data herein presented are not sufficient to decide upon a mechanism, there does seem to be an over-all similarity between the removal of a trimethylsilyl group by bromine and the replacement of hydrogen in aromatic bromination. This view is valuable since it enables one to predict the stability of an aromatic carbon–silicon bond toward halogen or any electrophilic reagent by simply applying aromatic orientation rules.

Thus those silicon compounds containing meta-directing groups in the aromatic nucleus will undergo fission by electrophilic reagents with much greater difficulty than the unsubstituted phenyl or thiophene compounds. The silicon group in such compounds will be most vulnerable to electrophilic attack if situated meta to the meta-directing substituent. Likewise the silicon group will be exceedingly vulnerable to electrophilic cleavage if situated on an aromatic nucleus carrying ortho–para directing substituents, particularly if the silicon is situated ortho–para to such substituents.[7]

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(5) See S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 1047.

(6) See P. D. B. De LaMare, P. W. Robertson and W. T. G. Johnson, *J. Chem. Soc.*, 276 (1943); P. W. Robertson, J. E. Allen, K. N. Haldane and M. G. Simmers, *ibid.*, 933 (1949); P. W. Robertson and P. D. B. De LaMare, *ibid.*, 100 (1948).

(7) See R. A. Benkeser and H. R. Krysiak, THIS JOURNAL, **75**, 4528 (1953), for further evidence in this connection.