

**Acknowledgment.**—The assistance of Dr. David T. Mowry and Dr. W. Frederick Huber in carrying out the dehydrations and some of the reductions is gratefully acknowledged.

### Summary

*p*-Fluorostyrene and 2-fluoro-4'-vinylbiphenyl have been synthesized from the corresponding

methyl aryl ketones by reduction to the secondary carbinol and dehydration of the latter to the vinyl derivative.

*m*-Trifluoromethylstyrene has been prepared by dehydration of the secondary carbinol which was obtained through the Grignard reaction from *m*-bromobenzotrifluoride.

DAYTON, OHIO

RECEIVED MARCH 6, 1946

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT AND THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

## Methylbromosilanes

BY W. F. GILLIAM, R. N. MEALS<sup>1</sup> AND ROBERT O. SAUER

Mixtures of the methylbromosilanes were first prepared by Rochow<sup>1a</sup> by the vapor phase reaction of methyl bromide with copper-silicon masses. This alkyl halide reacts smoothly at about 300° to give a dense liquid condensate from which we have isolated methyltribromosilane, dimethyldibromosilane, and trimethylbromosilane. In addition, indications of small amounts of tribromosilane and silicon tetrabromide have been found in the crude product. It is interesting to note that the apparent anomaly in the boiling points of the methylchlorosilanes<sup>2</sup> is not repeated with the methylbromosilanes; the boiling points of the latter all lie within the range fixed by the boiling points of silicon tetramethyl (27°) and silicon tetrabromide (151°).

Trimethylbromosilane has also been synthesized in good yield by the action of phosphorus tribromide on hexamethyldisiloxane. This reaction is analogous to the cleavage of alkoxy silanes by phosphorus trichloride, as reported by Friedel and Ladenburg.<sup>3</sup>

As further evidence of the identity of the di- and tribromo compounds we have also prepared the 2-bromoethyl ethers by the action of ethylene oxide.<sup>4</sup> In the case of trimethylbromosilane hydrolysis yielded the known hexamethyldisiloxane. The properties of the new compounds prepared are given in Table I.

TABLE I

THE NEW METHYLBROMOSILANES AND METHYL-2-BROMOETHOXY SILANES

Formula	B. p., °C.	Press., mm.	<i>d</i> <sub>4</sub> <sup>20</sup> (vac.)	<i>n</i> <sub>D</sub> <sup>20</sup>
(CH <sub>3</sub> ) <sub>3</sub> SiBr	79.9	754	1.189	....
(CH <sub>3</sub> ) <sub>2</sub> SiBr <sub>2</sub>	112.3	760	1.727	....
CH <sub>3</sub> SiBr <sub>3</sub>	133.5	764	2.253	....
(CH <sub>3</sub> ) <sub>2</sub> Si(OCH <sub>2</sub> CH <sub>2</sub> Br) <sub>2</sub>	95	3	1.5425	1.4780
CH <sub>3</sub> Si(OCH <sub>2</sub> CH <sub>2</sub> Br) <sub>3</sub>	130-131	1	1.7635	1.5001

(1) Present address: Buckman Laboratories, Memphis, Tenn.

(1a) Rochow, *THIS JOURNAL*, **67**, 963 (1945).

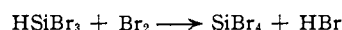
(2) Gilliam, Liebafsky and Winslow, *ibid.*, **63**, 801 (1941).

(3) Friedel and Ladenburg, *Ann.*, **145**, 179 (1868).

(4) Sauer and Patnode, *THIS JOURNAL*, **67**, 1548 (1945).

Our experiments indicate that occasionally some of our samples of dimethyldibromosilane were contaminated by an impurity which was presumed to be tribromosilane because of the proximity of its boiling point (111.8°) to that of dimethyldibromosilane (112.3°) and the fact that trichlorosilane is a product of the reaction<sup>1a</sup> of methyl chloride with copper-silicon. We found that this impurity could be eliminated by treatment of the sample with bromine, removal of the excess bromine with mercury, and subsequent distillation to obtain the pure dimethyldibromosilane.

Since we were unable to find a literature reference to the reaction



we treated tribromosilane<sup>5</sup> with bromine to provide assurance that bromination did occur. We found, as expected,<sup>5a</sup> that tribromosilane slowly decolorized bromine at room temperature, and that the reaction was decidedly photosensitive.

### Experimental

**Dimethyldibromosilane and Methyltribromosilane.**—**Run 1.**—A mixture of crude products<sup>1a,6</sup> prepared by passing methyl bromide over a pressed sintered mass of copper-silicon (20:80) at 275° was fractionally distilled in a 0.8 × 65 cm. column<sup>6a</sup> of approximately 50 theoretical plates packed with 1/16-in., single turn helices made from platinum-iridium wire. From a definite plateau in the boiling point curve a middle fraction, b. p. 112.3° at 760 mm., was separated. Analysis showed this substance to be dimethyldibromosilane.

*Anal.* Calcd. for C<sub>2</sub>H<sub>8</sub>SiBr<sub>2</sub>: Br, 73.33. Found: Br, 73.4, 73.0.

A middle fraction, b. p. 133.5° at 764 mm., from a second plateau was identified as methyltribromosilane.

(5) The authors desire to thank Prof. Walter Schumb of the Massachusetts Institute of Technology who kindly supplied the sample of pure tribromosilane used in this experiment.

(5a) Ladenburg [*Ann.*, **164**, 329 (1872)] and Kraus and Nelson [*THIS JOURNAL*, **56**, 195 (1934)] brominated triethylsilane to give triethylbromosilane, and Friedel and Ladenburg [*Ann.*, **145**, 187 (1867)] isolated trichlorobromosilane as a bromination product of trichlorosilane.

(6) The authors wish to thank Dr. E. C. Rochow of the Research Laboratory who prepared and kindly provided this material.

(6a) Whitmore, *et al.*, *THIS JOURNAL*, **62**, 797 (1940).

*Anal.* Calcd. for  $\text{CH}_3\text{SiBr}_3$ : Br, 84.76. Found: Br, 84.8, 84.4.

In the above analyses for bromine hydrolysis of a weighed sample was carried out as described under Run 2; the liberated hydrogen bromide was determined volumetrically by the standard Volhard method.

**Run 2.**—By passing methyl bromide through a 0.75-in. glass tube packed to a length of 18 in. with sintered copper-silicon (10:90) powder and maintained at 295–325° by means of an electric furnace, 774 g. of crude methylbromosilanes was prepared over a period of one hundred eighty hours. This product was charged to a 1.0 × 44 cm. column packed with  $\frac{3}{32}$ -in., single turn, stainless steel helices and having roughly 15 theoretical plates. Appreciable methyl bromide was evolved. The distillation (at 760 ± 1 mm.) and analytical data are summarized in the table.

Fraction	B. p., °C., cor.	Wt., g.	% Br	$d_{40}^{20}$ (vac.)
A	71–110	48.3		
B	109.9–112.4	8.8	73.72	
C	112.4–112.8	62.6	73.67	1.738
D	112.8–112.9	61.2	73.77	1.736
E	112.9–113.8	19.6	73.74	
F	113.8–132.1	59.7		
G	132.6–133.5	32.3	84.54	
H	133.5	79.2	84.83	2.254
I	133.5–133.7	90.4	84.85	2.252
J	133.4–135.2	23.6		
K	135.2–156.3	24.6		
Residue		99.5		

Fraction H is pure methyltribromosilane; the density of this substance was measured in a 25-ml. dilatometer. However, the bromine analyses on the dimethyldibromosilane fractions (B, C, D, E) are appreciably higher than the calculated value for the pure substance (73.33% Br). We interpret this to indicate the presence of tribromosilane, b. p. 111.8°,  $d_{40}^{20}$  ca. 2.7, 89.19% Br.

In order to remove the small amount of tribromosilane (ca. 2%) which contaminated our dimethyldibromosilane fractions, we combined the portions of fractions B, C, D and E remaining after analysis (141.9 g.) and added about 6 g. of liquid bromine (1.8 g. required to brominate the estimated 3 g. of tribromosilane). After standing at room temperature for sixty-five hours the reaction mixture was shaken for four hours with excess mercury to remove the unreacted bromine. The mercury bromides were removed by filtration and the precipitate extracted three times with fresh 100-ml. portions of chlorobenzene.

The dimethyldibromosilane filtrate and the chlorobenzene extracts were combined and charged to the same distilling column used previously. The distillation and analytical data are summarized in the table.

Fraction	B. p., °C., cor.	Mm.	Wt., g.	% Br <sup>a</sup>
L	110.3–111.5	746	9.6	71.68
M	111.5–111.8	746	21.0	73.12
N	111.8–112.0	746	50.5	73.30
O	111.9–112.0	762	8.5	73.16
P	112.0–112.7	762	7.0	72.98
Q	112.7–113.5	762	12.5	73.04

<sup>a</sup> Calcd. for  $(\text{CH}_3)_2\text{SiBr}_2$ , 73.33.

Fraction N (average % Br, 73.38) was used for the density determination (25-ml. dilatometer);  $d_{40}^{20}$  (vac.) 1.727.

The bromine analyses reported above and for trimethylbromosilane (see below) were performed as follows: A 1–2 g. sample of the bromosilane was weighed in a 2-ml. corked vial and hydrolyzed after weighing by opening the vial

and dropping vial and cork into a mixture of ether, water and ice contained in a glass-stoppered Erlenmeyer flask. After shaking vigorously the bromine was analyzed by the Volhard technique; an excess of a 0.5 N solution of silver nitrate (made up by weight) was added from a weight buret, and the excess back-titrated with 0.1 N ammonium thiocyanate added from a volume buret.

**Dimethyldi-2-bromoethoxysilane.**—An attempt was made to treat dimethyldibromosilane (39 g., 0.18 mole) with ethylene oxide under pressure as described for the chlorosilanes<sup>4</sup> but the reaction was so vigorous that considerable precaution was necessary to prevent overheating. The ethylene oxide pressure was reduced to 5 lb. and no shaking was employed until the reaction became more moderate. During the later stages it was possible to admit the ethylene oxide intermittently at 12 lb. with a brief shaking period, cool the flask in an ice-bath, and then repeat the addition. Fractional distillation of the product at reduced pressure gave 48.9 g. (89%) of dimethyldi-2-bromoethoxysilane, b. p. 95.5° at 3 mm.,  $n_D^{20}$  1.4780,  $d_{40}^{20}$  (vac.) 1.5425.

*Anal.* Calcd. for  $\text{C}_2\text{H}_{14}\text{SiO}_2\text{Br}_2$ : C, 23.54; H, 4.61; Si, 9.17; Br, 52.22. Found: C, 23.3; H, 4.4; Si, 9.2; Br, 52.4, 51.9.

**Methyltri-2-bromoethoxysilane.**—The procedure described for dimethyldi-2-bromoethoxysilane was employed; 74.5 g. (0.263 mole) of methyltribromosilane with excess ethylene oxide gave 94.6 g. (87%) of the desired ether, b. p. 130–131° at 1 mm.,  $n_D^{20}$  1.5001,  $d_{40}^{20}$  (vac.) 1.7635.

*Anal.* Calcd. for  $\text{C}_7\text{H}_{15}\text{SiO}_3\text{Br}_3$ : C, 20.26; H, 3.64; Br, 57.77. Found: C, 20.1; H, 3.4; Br, 57.1, 57.2.

**Trimethylbromosilane.**—Although the two runs described above for the reaction of methyl bromide with copper-silicon powder indicated negligible amounts of trimethylbromosilane, some runs (see the following section) have given appreciable yields of this compound. A sample (52.4% Br) obtained in this way distilled at 80° and yielded hexamethyldisiloxane,<sup>8</sup>  $n_D^{20}$  1.3771, on hydrolysis. We have since prepared<sup>9</sup> the pure substance in larger amounts by cleavage of hexamethyldisiloxane with phosphorus tribromide.

Into a bottle capped with a pressure-tight gasket was weighed 163 g. (1.0 mole) of hexamethyldisiloxane, 459 g. (1.69 moles) of phosphorus tribromide and 1.0 g. of iron (III) chloride hexahydrate and the contents mixed thoroughly by shaking. After standing for twenty hours at room temperature the reaction mixture was charged to the previously described column of approximately fifteen theoretical plates. The distillation and analytical data are summarized in the table.

Fraction	B. p., °C., cor.	Mm.	Wt., g.	% Br <sup>a</sup>
A	65–79.3	751	15.3	53.7 <sup>b</sup>
B	79.4–79.6	751	41.0	53.0
C	79.7–79.8	754	35.0	52.59
D	79.8–79.9	754	47.6	52.15
E	79.9	754	36.0	52.19
F	79.9–80.0	755	35.6	52.13
G	80.0–80.1	755	15.0	...

<sup>a</sup> Calcd. for  $(\text{CH}_3)_3\text{SiBr}$ : 52.21% Br, <sup>b</sup> By acid-base titration with 0.5 N sodium hydroxide solution.

Densities ( $d_{40}^{20}$ ) were determined on the following fractions in a 25-ml. dilatometer: D, 1.190; E, 1.188; F, 1.189. The yield of trimethylbromosilane based on hexamethyldisiloxane was 73%.

**Yield and Composition Data for the Methyl Bromide-Copper-Silicon Reaction.**—In each experiment of the following series 400 g. of sintered copper-silicon (10:09) powder was charged to an iron pipe reactor (1 in. diam.) immersed in an oil-bath at 300°. The red-brown, crude methylbromosilanes were charged to the previously de-

(8) Sauer, *ibid.*, **66**, 1707 (1944).

(9) See also Hurd, *ibid.*, **67**, 1546 (1945).

(7) Schumb and Young, *This Journal*, **52**, 1464 (1930).

scribed column of about fifteen theoretical plates. Analysis by distillation indicated that, in addition to the compounds reported above, appreciable amounts of silicon tetrabromide were present in the crude products. The following table lists the results of five successive runs (the values of  $n$  refer to the formula  $(\text{CH}_3)_n\text{SiBr}_{4-n}$ ).

CH <sub>3</sub> Br, g.	Time, hr.	Product,		Composition (vol. %)		
		g.	ml.	$n = 3$	$n = 2$	$n = 1$
1180	118	847	492	18	60	20
1390	119	1021	530	7	35	32
1250	118	962	493	7	38	35
1170	96	586	249	3	11	33
1710	114	976	488	4	37	33

**Acknowledgment.**—The authors are grateful to Dr. Earl W. Balis of the Research Laboratory for the carbon and hydrogen analyses reported in this paper.

### Summary

Methyltribromosilane, dimethyldibromosilane and trimethylbromosilane, isolated as products of the reaction of methyl bromide with sintered copper-silicon powder at 300°, have been purified and characterized.

SCHENECTADY, N. Y.

RECEIVED JANUARY 28, 1946

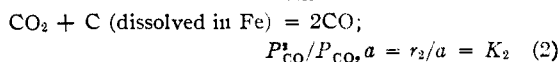
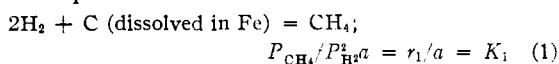
[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION]

## Equilibrium of Iron-Carbon Alloys with Mixtures of CO-CO<sub>2</sub> and CH<sub>4</sub>-H<sub>2</sub>

BY RODNEY P. SMITH

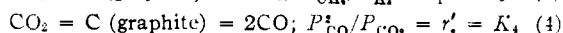
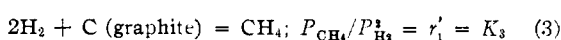
As the consistency and range of the available data on the equilibrium between carbon dissolved in iron and definite mixtures of either carbon monoxide with carbon dioxide, or methane with hydrogen, leaves something to be desired, and as accurate information on this matter has considerable practical significance, it was decided to re-investigate these systems. Accordingly measurements were made of the concentration of carbon, induced in iron at a number of temperatures ranging from 750 to 1200°, by contact with each of a series of ratios of one or other of these pairs of gases.

The equilibria involved may be represented by the equations



where  $P$  is measured in atmospheres and  $a$  is the activity of dissolved carbon. For either system in equilibrium at constant temperature and pressure, a given value of the partial pressure ratio  $r$  determines the composition of the solid phase, or *vice versa*, so long as only one solid phase is present. In the temperature range considered the solid phase may be ferrite, a solid solution of carbon in  $\alpha$ -iron (body-centered cubic), or austenite, a solid solution of carbon in  $\gamma$ -iron (face-centered cubic), the transition temperature depending upon the carbon content; accordingly interpretation of the results to be presented is facilitated by reference to the pertinent portion of the iron-carbon equilibrium diagram represented in Fig. 1, in which, for clarity, the scale of abscissa for the line  $GP$  is ten times as large as for the other lines. If we consider the isothermal line  $A, B, C, D$  it is evident that for a gas mixture of low carburizing power the solid phase is ferrite, and as carburizing power increases each gas ratio produces a solid phase of definite composition in the range  $A$  to

$B$ .<sup>1</sup> The gas mixture in equilibrium with ferrite of composition  $B$  is also in equilibrium with austenite of composition  $C$ , and the gross composition of the solid phase may have any value from  $B$  to  $C$  depending on the relative amount of the two solid phases. A further increase in carburizing power of the gas causes the ferrite phase to transform completely to austenite, and the gas ratio fixes its composition in the range  $C$  to  $D$ . The line  $S'E'$  represents the equilibrium of austenite with graphite; thus the gas ratio,  $r$ , in equilibrium with austenite of composition  $D$  is also in equilibrium with graphite, and its value ( $r'$ ) at this point gives the equilibrium constant  $K_3$  or  $K_4$  for the reactions



The case is similar for all temperatures between 738 and 910° except that, as temperature increases, the range of stability of ferrite decreases and that of austenite increases. For the temperatures 1000 and 1200° and the carbon range 0 to 1.5%, the only solid phases encountered are austenite and graphite.<sup>1</sup>

If graphite is chosen as the standard state for carbon, the constants  $K_1, K_2$  of equations (1) and (2) become identical with the constants  $K_3, K_4$  of equations (3) and (4). Equation (1) and (2) may then be written

$$a_c = P_{\text{CH}_4}/P_{\text{H}_2}^2 K_3 = r_1/K_3 \quad (1a)$$

$$a_c = P_{\text{CO}}^2/P_{\text{CO}_2} K_4 = r_2/K_4 \quad (2a)$$

where  $a_c$  is the activity of carbon in iron relative to graphite, and  $r_1$  or  $r_2$  is the ratio at equilibrium with carbon dissolved in iron at a concentration corresponding to the activity  $a_c$ . Thus measurements of these ratios and the corresponding carbon

(1) In the case of CO-CO<sub>2</sub> mixtures low in carbon monoxide, the system is complicated by the presence of an iron oxide phase. The above statements apply only to gas mixtures which will not oxidize iron at these temperatures.