(>99.9% pure) were stored over sodium mirrors in the vacuum line.

Catalysts.—The general technique of preparation of aluminum and gallium halides was described previously. The bulb in which the catalyst was to be prepared and the attached ampoule in which the eventual disproportionation reaction was to be conducted were thoroughly washed with water. The bulb and ampoule were dried under reduced pressure and then thoroughly dried and degassed at 10^{-6} mm. by heating with bunsen burner. Prior to the final degassing, a weighed amount of freshly polished C.P. aluminum wire (Fisher Scientific Co.) or purified gallium (Fisher Scientific Co.) was added to the bulb and, after degassing, a 100% excess of hydrogen chloride or bromide was added. The metal halide was produced by heating with a bunsen burner. The same catalytic efficiency was observed when Fisher C.P. aluminum wire, commercial aluminum foil (Reynolds Wrap) or a special sample of high purity aluminum (containing 0.006% silicon, 0.009% iron and 0.005% copper) furnished by the Aluminum Co. of America was used. Matheson Co. C.P. anhydrous hydrogen bromide and chloride were degassed in the vacuum line and a tensiometrically homogeneous middle fractions used for catalyst preparation. C.P. anhydrous hydrogen bromide and hydrogen bromide prepared from the bromination of tetralin gave identical results as judged from the catalyst efficiency. Aluminum iodide was prepared from the reaction of a weighed amount of C.P. iodine with an excess of aluminum foil. The boron fluoride and chloride were Matheson Co. C.P. grade. Tensiometrically homogeneous middle fractions were used. Resublimed C.P. ferric chloride was weighed and sealed under an inert atmosphere into an ampoule with a break-off tip which was then sealed to the final reaction ampoule which was in turn sealed to the vacuum line. After the vacuum line had been thoroughly dried, the break-off tip was opened and the ferric chloride sublimed into the reaction ampoule. Zirconium tetrachloride was handled in the same manner. Antimony pentachloride was measured by volume and distilled into the reaction ampoule. Most of the other catalysts summarized in Table III were weighed into dried ampoules in a nitrogen dry-box, the ampoule attached to a vacuum line by a greased joint and ethyltrimethylsilane added. This procedure, if used for aluminum bromide, would have resulted in a pronounced acceleration due to traces of moisture.

Co-catalysts.—The co-catalysts were measured by *PVT* relationship in a bulb of standard volume. The co-catalysts were always of C.P. grade or else were specially purified. Where necessary the co-catalysts were dried by sodium mirrors or by lithium aluminum hydride. Oxygen was generated in the vacuum line by heating silver oxide and the quantity added to the reaction ampoule estimated from the free space in the ampoule, the average temperature and the pressure.

Aluminum oxybromide was prepared by treating a sample of aluminum bromide, prepared as described previously, with a measured amount of water vapor. The ampoule was sealed and heated at 89° for 72 hr. The ampoule was reattached to the vacuum line by another break-off tip and the condensable gases removed and measured at 0°. From 1.87 mmoles of $AlBr_3$ and 0.29 mmole of water, there was obtained 0.49 mmole of hydrogen bromide (85%).

The products of the reaction of ethyl bromide, tetramethylsilane and aluminum bromide were carefully examined for the formation of ethyltrimethylsilane. From 34 mmoles of tetramethylsilane, 2.9 mmoles of ethyl bromide and 1.87 mmoles of aluminum bromide (as $AlBr_3$) heated at 80° for 24 hr. less than 0.003 mmole of ethyltrimethylsilane (the limit of detection by gas–liquid chromatography) could be found. Propane and other hydrocarbons were found. Addition of traces of water gave a complex mixture of hydrocarbons, but again ethyltrimethylsilane could not be detected.

Acknowledgment.—The vapor fractometers were operated by Dr. E. H. Winslow and Mr. E. M. Hadsell. Mr. D. E. McBournie assisted in some of the experimental work. Ethyltrimethylsilane was prepared by Dr. J. R. Ladd. Rectifications were performed by Mrs. M. M. Grenoble and Mr. E. M. Hadsell.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Catalysis by Metal Halides. II. The Disproportionation of Trimethylsilane, Phenyltrimethylsilane and Bromotrimethylsilane

BY GLEN A. RUSSELL[1]

RECEIVED JANUARY 29, 1959

The relative rates of disproportionation of compounds of the type Me_3SiR indicate the relative intermolecular migratory tendency in the aluminum bromide-catalyzed reactions as $H > C_6H_5 > C_2H_5$. This migratory sequence is identical with the reactivity of R in Me_3SiR toward electrophilic reagents and supports a disproportionation mechanism involving electrophilic attack on carbon or hydrogen and nucleophilic attack on silicon. Side reactions in the disproportionation of trimethylsilane and phenyltrimethylsilane catalyzed by Lewis acids are discussed. It has been found that trimethylsilane will reduce gallium(III) bromide to gallium(II) bromide or gallium(III) chloride to gallium metal. The effects of oxygen and water on the aluminum bromide-catalyzed disproportionation are discussed and the effect of the polar nature of non-migrating groups in these disproportionations is considered.

The preceding and succeeding communications present data from which the mechanism of the metal halide-catalyzed disproportionation of ethyltrimethylsilane in particular, and substituted silanes in general, can be deduced.[2] Additional support for the suggested mechanism, in terms of relative migratory tendencies of R = H, C_2H_5, C_6H_5 and Br in the reaction

$$2Me_2SiR \xrightarrow{MX_3} Me_4Si + Me_2SiR_2$$

and in the reactivity of R toward electrophilic attack in general, is presented in the present work.

Results

Equilibrium.—The aluminum bromide-catalyzed disproportionation of trimethylsilane was studied at 40 and 60°. Results are summarized in Table I.

Table I indicates that the disproportionation of trimethylsilane yields the four methylsilanes and silane in nearly statistical proportions. The methylsilanes essentially reach their equilibrium ratios rapidly, but silane is formed only slowly and the results in Table I do not necessarily indicate that silane has reached its equilibrium concentration.

There is a small but definite trend for the methylsilane system to yield more of the end-products of disproportionation (tetramethylsilane and silane)

---

[1] Department of Chemistry, Iowa State University, Ames, Iowa.

[2] (a) G. A. Russell, THIS JOURNAL, **81**, 4815 (1959); (b) **81**, 4831 (1959).

TABLE I

DISPROPORTIONATION OF TRIMETHYLSILANE[a]

Temp., °C.	Time, hr.	Product, mole % SiH_4	$MeSiH_3$	Me_2SiH_2	Me_3SiH	Me_4Si
40	1	0	0.46	12.1	74.2	13.2
40	18	0.09	5.78	18.2	41.7	34.4
40	42	0.16	6.78	19.3	40.6	33.4
40	114	1.41	6.64	18.7	39.0	34.3
60	87	1.81	6.30	17.6	40.0	34.5
60	162	2.15	6.15	17.3	39.2	35.0
Statistical		0.4	4.7	21.1	42.2	31.6

[a] Approximately 0.5 g. of aluminum bromide/5 ml. of trimethylsilane. No special precautions observed in handling aluminum bromide.

than expected on a statistical basis. This trend is not appreciably affected by temperature, at least between 40 and 60°. At 60° the combined yields of tetramethylsilane, silane and methylsilane were 6.7 mole % greater than expected on a statistical basis while the combined yields of trimethylsilane and dimethylsilane were lower than the statistical yield by the same amount.

Rate Studies, Trimethylsilane.—The effects of catalyst structure, co-catalysis and solvent effects were studied in the disproportionation of trimethylsilane at 40 and 60°. Results are summarized in Table II.

TABLE II

RATE OF DISPROPORTIONATION OF TRIMETHYLSILANE

Catalyst[a]	Me_3SiH, mmoles	Solvent	Temp., °C.	Time, hr.	Mole ratio of products Me_2SiH_2:Me_3SiH:Me_4Si	% reaction/hr.[b]
..	43.8	Me_3SiH	80	48	0.0001:1:<0.0001	<0.0004
..	..	.....	250[c]	48	.0035:1: .0035	.015
BF_3	43.8	Me_3SiH	60	16	.0001:1:< .0001	< .001
BCl_3	43.8	Me_3SiH	60	16	.0293:1:< .0001	< .001
BBr_3	43.8	Me_3SiH	60	16	.0285:1: .0004	.005
Al_2Br_6	43.8	Me_3SiH	40	1	.0059:1: .0056	1.10
$Al_2Br_6 + H_2O$[d]	43.8	Me_3SiH	40	1	.1635:1: .1785	26.5
Al_2Br_6	6.78	C_6H_{12}[e]	40	10	.0233:1: 0.245	0.465
Al_2Br_6	6.78	C_6H_6[e]	40	10	.466 :1: .592	>5.5
Ga_2Br_6	43.8	Me_3SiH	60	16	.0133:1: .0023	0.03
Ga_2Cl_6	43.8	Me_3SiH	60	16	.0004:1: .0008	0.01

[a] 1.87 mmoles as MX_3. [b] $200(Me_4Si/Me_3SiH)/[1 + 2(Me_4Si/Me_3SiH)]$. [c] Vapor phase in Pyrex glass ampoule, approximately 1 atm. pressure at 250°. [d] 0.29 mmole. [e] 5.0 ml. at 25°.

The data of Table II demonstrate the similarity between the disproportionation of trimethylsilane and the disproportionation of ethyltrimethylsilane discussed previously.[2a] Both reactions will proceed cleanly at elevated temperatures in the vapor phase. In the liquid phase they may be catalyzed by Lewis acids, the catalytic series of $Al_2Br_6 > Ga_2Br_6 > Ga_2Cl_6 > BBr_3 > BCl_3$ or BF_3 being noted for trimethylsilane and the series $Al_2Br_6 > Ga_2Br_6 > Ga_2Cl_6$, BCl_3 or BF_3 for ethyltrimethylsilane. Water serves as a co-catalyst for aluminum bromide in both disproportionations. Finally, the aluminum bromide-catalyzed reaction is much faster in benzene solution than in cyclohexane solution for both silanes.

Some of the results summarized in Table II must be interpreted cautiously since pronounced side reactions were observed when boron and gallium halides were used as catalysts. Boron chloride or bromide was consumed in the reaction as evidenced by the fact that if ethyl ether was added after the reaction mixture had been frozen, the sample would volatilize leaving little residue (*i.e.*, boron halide etherate). Moreover, the trace of residue which did remain instantly inflamed with a green flame when exposed to air. Mixtures of boron chloride or bromide and trimethylsilane gave significant amounts of dimethylsilane but little tetramethylsilane. The results can be explained by the following sequence of reactions where X is chlorine or bromine but not fluorine.

$$>BX + Me_3SiH \longrightarrow Me_3SiX + >BH$$

$$>BH + Me_3SiH \longrightarrow >B\text{-}Me + Me_2SiH_2$$

Trimethylboron does not form a particularly stable etherate and would thus be mainly lost during volatilization. The presence of boron–methyl or boron–hydrogen bonds is confirmed by the oxidative instability of the small amount of residue obtained after treatment with ethyl ether and pumping at 1 mm. at 0°. With gallium chloride reduction occurred rapidly and quantitatively at 60°.[3] Over the first 2-hour period metallic gallium precipitated, after which time no further precipitation was observed. When opened at liquid nitrogen temperature the reaction ampoule contained hydrogen at a pressure above atmospheric. From gallium chloride made from 0.131 g. of gallium a precipitate of 0.121 g. of gallium was recovered after treatment with trimethylsilane at 60° for 16 hours. Under similar conditions gallium(III) bromide is reduced to gallium(II) bromide. Gallium(III) bromide dissolved in trimethylsilane with unusual ease below 0° while at 60° a white precipitate rapidly developed. After 16 hr. at 60° the volatile silanes were removed and the residue washed with *n*-pentane. Gallium(III) bromide from 0.130 g. of gallium gave 0.306 g. of *n*-pentane-washed precipitate having the properties reported for gallium(II) bromide. The material was slightly soluble in benzene, decolorized acidified permanganate and gave a brown precipitate with water which slowly turned white.

Aluminum bromide gave no indication of side reactions in the disproportionation of trimethylsilane. Tetramethylsilane and dimethylsilane were formed in approximately 1:1 ratio in the early stages of the reaction. No products other than the

---

(3) The ability of silicon hydrides to reduce other metal halides is well known [H. Gilman, H. G. Brooks, Jr., and M. B. Hughes, *J. Org. Chem.*, **23**, 1398 (1958); H. H. Anderson, THIS JOURNAL, **79**, 326, 4913 (1957); **80**, 5083 (1958)].

expected silanes were observed in the reactions catalyzed by aluminum bromide.

Rate Studies, Phenyltrimethylsilane.—The rate of disproportionation of phenyltrimethylsilane was complicated by the cleavage of silicon–phenyl bonds by the metal halide. Disproportionation was measured by the quantity of tetramethylsilane formed while cleavage was measured by the yield of benzene and hexamethyldisiloxane after hydrolysis, *e.g.*

$$Al_2Br_6 + C_6H_5SiMe_3 \longrightarrow Al_2Br_5C_6H_5 + Me_3SiBr \xrightarrow{H_2O} C_6H_6 + {}^1/_2Me_3SiOSiMe_3$$

Results summarizing both disproportionation and cleavage are given in Table III.

TABLE III

DISPROPORTIONATION AND CLEAVAGE OF PHENYLTRIMETHYLSILANE[a]

Catalyst[b]	Temp., °C.	Time, hr.	Me_4Si formed mmoles	$C_6H_5SiMe_3$ disproportionated,[c] %	Cleavage, mmoles 2[$Me_3SiOSiMe_3$]	C_6H_6
Al_2Br_6	60	1	5.72	36.4	1.68	1.60
Al_2Br_6	40	1	1.70	10.8	1.34	1.55
Al_2Br_6	40	2	2.67	17.0	1.76	1.63
Al_2Br_6 + O_2[d]	40	1	2.48	15.8	1.00	1.92
Al_2Br_6 + H_2O[e]	40	1	7.80	49.6	1.11	1.85
Al_2Cl_6[f]	40	1.5	0.860	5.47	0.32	0.37
Ga_2Br_6	60	16	.132	0.84	1.50	1.12
Ga_2Cl_6	60	16	< .001	< .008	1.11	0.84
BBr_3	60	16	.0015	.01	2.15	< .01
BCl_3	60	16	< .001	< .008	1.80	< .01
$ZrCl_4$	60	16	< .001	< .008	2.08	2.00
Al_2Br_6[g]	40	16	.026	.75	0.96	..

[a] 5.0 ml. at 0° (31.5 mmoles) of phenyltrimethylsilane served as solvent and reactant. [b] 1.87 mmoles as MX_3 or MX_4. [c] 200(mmoles Me_4Si)/31.5. [d] 0.24 mmole. [e] 0.29 mmole. [f] Heterogeneous. [g] 6.92 mmoles of phenyltrimethylsilane, 5.0 ml. (at 10°) of cyclohexane as solvent.

The interpretation of the data in Table III is difficult in view of the simultaneous cleavage and disproportionation reactions. In most cases nearly one silicon–phenyl bond was cleaved per mole of catalyst (as MX_3 or MX_4). In the case of aluminum bromide the amount of cleavage increased only slightly between one and two hours at 40° or between 2 hours at 40 or 60°. Thus for the aluminum bromide-catalyzed disproportionation the structure of the catalyst was nearly $(C_6H_5AlBr_2)_2$. The rate of the aluminum bromide-catalyzed reaction appears to be fairly independent of time so either the equilibrium

$$(AlBr_3)_2 + 2C_6H_5SiMe_3 \rightleftarrows (C_6H_5AlBr_2)_2 + 2Me_3SiCl$$

is rapidly established or else phenylaluminum bromide and aluminum bromide have similar catalytic efficiencies. For example, in 1 hr. at 40° (see Table III) aluminum bromide disproportionated 10.8% of the original phenyltrimethylsilane (no correction has been made for phenyltrimethylsilane destroyed by cleavage) while in 2 hr. at 40° 17.0% of the original silane had been disproportionated. Considering the extent of disproportionation and the fact that the disproportionation reaction is reversible, there appears to be no significant decrease in rate between 1 and 2 hours reaction period.

The data of Table III indicate that another possible disproportionation does not occur under the

$$2C_6H_5SiMe_3 \longrightarrow C_6H_6 + C_6H_4(SiMe_3)_2$$

reaction conditions since the yield of benzene after hydrolysis was never much greater than twice the yield of hexamethyldisiloxane. Moreover, in cases when the phenyl derivatives of the catalyst are stable to hydrolysis (*i.e.*, phenylboronic acids), no benzene could be detected.

There is apparently little correlation between catalytic activity in disproportionation and in the extent of cleavage. Aluminum bromide, gallium halides, boron halides and zirconium chloride all cleave the silicon–phenyl bond readily,[4] whereas large differences in the ability of these metal halides to catalyze disproportionation are observed. The catalytic abilities associated with the various metal halides are $Al_2Br_6 > Al_2Cl_6 > Ga_2Br_6 > BBr_3 > Ga_2Cl_6$, BCl_3, $ZrCl_4$. This sequence is the same as was observed in the disproportionations of trimethylsilane and ethyltrimethylsilane. The aluminum bromide-catalyzed reaction is strongly accelerated by water, as were the disproportionations of trimethylsilane and ethyltrimethylsilane. Finally, the disproportionation is much faster in an aromatic solvent (phenyltrimethylsilane) than in cyclohexane, a phenomenon also observed for trimethylsilane and ethyltrimethylsilane. The effect of oxygen is small in the disproportionation of phenyltrimethylsilane, at least when compared with the effect in ethyltrimethylsilane disproportionations. Possibly oxidation of the phenylaluminum bromide is involved.

$$C_6H_5AlBr_2 + {}^1/_2O_2 \longrightarrow C_6H_5OAlBr_2$$

Rate Studies, Bromotrimethylsilane.—Table IV outlines the results obtained in a study of the rate of disproportionation of bromotrimethylsilane.

TABLE IV

DISPROPORTIONATION OF BROMOTRIMETHYLSILANE AT 80°

Catalyst[a]	Me_3SiBr mmoles	Solvent	Time, hr.	Me_4Si formed mmole	% Me_3SiBr disproportionated/hr.[b]
....	38.6	Me_3SiBr	90	<0.01	<0.0005
Al_2Br_6	38.6	Me_3SiBr	16	.770	.250
Al_2Br_6 + O_2[c]	38.6	Me_3SiBr	16	.194	.063
Al_2Br_6 + H_2S[d]	38.6	Me_3SiBr	3	.110	.190
Ga_2Br_6	38.6	Me_3SiBr	90	.382	.022
Al_2Br_6	4.65	C_6H_{12}[e]	20	.049	.105
Al_2Br_6	4.65	C_6H_6[e]	2	.0535	1.15

[a] 1.87 mmoles as MX_3. [b] 200(Me_4Si)/Me_3SiBr used. [c] 0.24 mmole. [d] 0.29 mmole, heterogeneous. [e] 5.0 ml. at 10°.

The data of Table IV indicate that aluminum bromide is a much better catalyst than gallium bro-

---

[4] Similar cleavage reactions by aluminum bromide at 30° [W. E. Evison and F. S. Kipping, *J. Chem. Soc.*, 2774 (1931); A. Y. Yakubovich and G. V. Motsarev, *J. Gen. Chem.* (*U.S.S.R.*), **23**, 771 (1953); Z. M. Manulkin, *ibid.*, **18**, 299 (1948); B. N. Dolgov and O. K. Panina, *ibid.*, **18**, 1293 (1948)], ferric chloride at −80° [A. Y. Yakubovich and G. V. Motsarev, *ibid.*, **23**, 1059 (1953)], antimony pentachloride at −20° [A. Y. Yakubovich and G. V. Motsarev, *ibid.*, **23**, 1414 (1953)], bismuth chloride at 140–150° [Z. M. Manulkin, *ibid.*, **20**, 2004 (1950)] or mercuric chloride at 140–150° [Z. M. Manulkin, *ibid.*, **16**, 235 (1946)] have been reported.

mide for the disproportionation of bromotrimethylsilane. This result is consistent with observations made on the disproportionation of ethyltrimethylsilane and phenyltrimethylsilane. Moreover, the disproportionation proceeds more rapidly in benzene than in cyclohexane as was observed for the other three silanes. However, whereas oxygen or water promotes the aluminum bromide-catalyzed disproportionation of the other three silanes and hydrogen sulfide promotes the disproportionation of ethyltrimethylsilane, both oxygen and hydrogen sulfide retarded the aluminum bromide disproportionation of bromotrimethylsilane. In the presence of oxygen the catalyst was left as a black oil instead of the white, crystalline residue observed under anerobic conditions. Evidence that oxygen reacted with the aluminum bromide to produce bromine which then cleaved silicon–methyl bonds

$$Al_2Br_6 + {}^1/_2O_2 \longrightarrow Al_2Br_4O + Br_2$$

$$Br_2 + Me_3SiBr \xrightarrow{Al_2Br_6} MeBr + Me_2SiBr_2$$

was furnished by the isolation of methyl bromide. No methyl bromide was found in the absence of oxygen. In the experiment recorded in Table IV, 0.24 mmole of oxygen gave 0.20 mmole of recovered methyl bromide. Thus, at least 41% of the oxygen supplied was consumed by reaction with aluminum bromide.

Discussion

Relative Migratory Aptitudes.—The similarities between the effects of catalyst structures, the effects of solvent and the effects of water on the rate of disproportionation suggest that the disproportionation of ethyltrimethylsilane, trimethylsilane, phenyltrimethylsilane and bromotrimethylsilane all proceed by a similar mechanism. It is thus of interest to compare the rate of these reactions which, to a first approximation, are measures of the relative rates of methyl–ethyl, methyl–phenyl, methyl–hydrogen and methyl–bromine intermolecular migration. Table V summarizes data for the aluminum bromide-catalyzed disproportionation of the four silanes in cyclohexane and benzene solution and in the absence of added solvent.

TABLE V

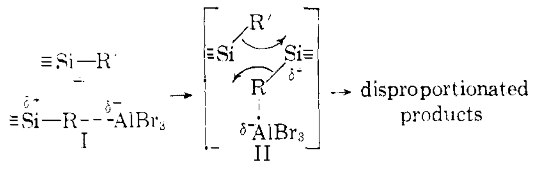
RATES OF ALUMINUM BROMIDE-CATALYZED DISPROPORTIONATION OF $RSiMe_3$

R	Solvent	$[Al_2Br_6]^a$	$[RSiMe_3]^a$	Temp., °C.	10^7 Rate mole/l. sec.	10^6k in mole l. and sec.^{b}
H	C_6H_6	0.149	1.08	40	> 160	>100
H	C_6H_{12}	.148	1.08	40	13.7	8.60
H	Me_3SiH	.162	7.60	40	232	6.83
C_6H_5	$C_6H_5SiMe_3$	.170	5.71	40	>1700	>74
C_6H_5	C_6H_{12}	.141	1.04	40	1.08	0.72
Et	C_6H_6	.156	0.238	80	25	138^c
Et	C_6H_6	.156	.250	40	4.41	22.7^c
Et	C_6H_{12}	.156	.230	80	0.51	2.96^d
Et	C_6H_{12}	.143	.742	80	2.48	2.96^d
Et	C_6H_{12}	...	...	40	...	$0.17^{c,e}$
Et	Me_3SiEt	.159	5.84	80	34.8	1.57^c
Et	Me_3SiEt	...	...	40	...	$0.089^{c,e}$
Br	C_6H_6	.146	0.725	80	23.0	25.6
Br	C_6H_{12}	.144	0.715	80	2.11	2.38
Br	Me_3SiBr	.161	6.65	80	45.3	1.67

[a] Mole/l. [b] $-d[RSiMe_3]/dt = k[Al_2Br_6][RSiMe_3]^{1.5}$. [c] Ref. 2a. [d] From Fig. 2, ref. 2a. [e] Calcd. on the basis of the energy of activation found in ethyltrimethylsilane solution.

The data of Table V indicate the relative migratory sequence of methyl–hydrogen > methyl–phenyl > methyl–ethyl > methyl–bromine. This sequence is observed in both benzene and cyclohexane solution and can be deduced from a consideration of either the specific rate constants based on the kinetic expression previously found for ethyltrimethylsilane[2a] or from the rates of silane disproportionation under conditions of constant catalyst and silane concentration.

According to the mechanism developed in the previous paper, the effect of the structure of the migrating group on the rate of migration should be connected with either the ease of formation of complex I or the stability of the transition state II



Both I and II involve an electron-deficient species ($AlBr_3$ on an incipient $\equiv Si^+$) attacking R or R′. It is therefore interesting to consider the migratory series of $H > C_6H_5 > C_2H_5$ as being due to the ease of electrophilic attack upon these groups when they are attached to a silicon atom. The greater reactivity of hydrogen and phenyl relative to ethyl is consistent with recognized behavior in the chemistry of carbon compounds. Strong electrophiles, such as a carbonium ion, will attack the hydrogen atom of a hydrocarbon whereas weaker electrophiles, such as a proton, will attack an aromatic nucleus. Attack of an electrophile on a saturated carbon atom is not observed for hydrocarbons. In the silane series we might have expected phenyl migration to have proceeded more readily than hydrogen migration by analogy with the chemistry of hydrocarbons. However, there is abundant independent evidence that in the reactions of silanes the ease of electrophilic attack on a silicon–R bond decreases in the order $H > C_6H_5 > CH_3$. For example, the dark reaction of chlorine with phenyldimethylsilane results in exclusive silicon–hydrogen cleavage by a heterolytic process[5]

$$C_6H_5Si(CH_3)_2H + Cl_2 \longrightarrow C_6H_5Si(CH_3)_2Cl + HCl$$

and bromine reacts with phenylsilane to give phenyltribromosilane in high yield.[6] There is abundant evidence that electrophilic species attack silicon–phenyl bonds or silicon–hydrogen bonds in preference to silicon–alkyl bonds. Hydrogen cleavage is observed exclusively in the reactions of bromine,[7a] iodine or iodine monochloride[7a,b] or iodine plus aluminum iodide[7c] with alkylsilanes. Similarly, exclusive silicon–phenyl bond cleavage is noted in the reaction of phenyltrimethylsilane with hydrogen chloride,[8a] aqueous acid,[8b] bromine or iodine,[9] while

---

[5] G. A. Russell, *J. Org. Chem.*, **21**, 1190 (1956).

[6] W. H. Nebergall, THIS JOURNAL, **72**, 4702 (1950).

[7] (a) W. H. Nebergall and O. H. Johnson, *ibid.*, **71**, 4022 (1949); (b) D. R. Deans and C. Eaborn, *J. Chem. Soc.*, 3169 (1954); (c) M. G. Voronkov and Y. I. Khudobin, *Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci.*, 805 (1956).

[8] (a) H. Gilman and F. J. Marshall, THIS JOURNAL, **71**, 2066 (1949); (b) C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

[9] B. O. Pray, L. H. Sommer, G. M. Goldenberg, K. T. Ken, P. A. DiGiorgio and F. C. Whitmore, THIS JOURNAL, **70**, 433 (1948).

toward aluminum iodide and iodine the relative rates of cleavage of $C_6H_5 >> CH_3 > C_2H_5$ have been observed in phenylalkylsilanes.[10] The ease of electrophilic attack of $H > C_6H_5 >$ alkyl is quite general for metal hydrides and organometallic materials. For example, the reactions of alkyl and aryl mercury, tin, germanium and lead compounds all indicate the reactivity sequence of $C_6H_5 > CH_3 > C_2H_5$ toward acidic species such as hydrogen chloride, bromine or iodine.[11]

Methyl–bromine migration in bromotrimethylsilane is somewhat slower than methyl–ethyl migration in ethyltrimethylsilane. This is surprising in view of the high reactivity of halogen atoms toward electrophilic attack in the halogen derivative of hydrocarbons. Moreover, since halogen–halogen exchange in the silicon tetrahalides occurs fairly easily in a thermal reaction[12] but alkyl–alkyl exchange occurs thermally only under drastic conditions,[2a] the migratory sequence halogen–halogen > halogen–alkyl > alkyl–alkyl might have been expected.

The rate of disproportionation of bromotrimethylsilane may not be a fair measure of methyl–bromine migration, at least when compared to the rate of disproportionation of ethyltrimethylsilane, because the non-migrating bromine atoms may have a large effect on the reactivity of the migrating methyl group.

$$Me_2BrSi\text{-}Me + Br\text{-}SiMe_3 \longrightarrow Me_2BrSiBr + Me_4Si$$

Similarly, the finding that in the reaction of triethylsilane with dichlorodiethylsilane, hydrogen–chlorine shifts occur exclusively,[13] does not necessarily indicate that hydrogen–chlorine shifts intrinsically occur more readily than hydrogen–ethyl shifts. Alternately, the products can be explained on the basis that an ethyl group of dichlorodiethylsilane activates a chlorine atom whereas a non-migrating chlorine atom deactivates an ethyl group in the disproportionation reaction.[14] However, the report that alkylhydrogendichlorosilanes disproportionate in the presence of aluminum chloride to alkyltrichlorosilane and monoalkylmonochlorosilane, or under more drastic conditions to monoalkylsilane,[15] apparently indicates that hydrogen–chlorine migration does occur more readily than alkyl–chlorine exchange.

$$2RSiHCl_2 \xrightarrow{Al_2Cl_6} RSiCl_3 + RSiH_2Cl$$

$$3RSiHCl_2 \xrightarrow{Al_2Cl_6} 2RSiCl_3 + RSiH_3$$

The migratory tendencies in the disproportionation of boron compounds appear to be similar to the analogous silanes, since, in the boron series, halogen–halogen exchange occurs with great rapidity,[16] alkyl–alkyl interchange occurs readily,[17] but alkyl–halogen shifts occur only with great difficulty.[18] Again, in the boron series hydrogen–halogen shifts[19a] and hydrogen–methyl shifts[19b] occur readily whereas alkyl–halogen shifts do not.[18,20] For mercury compounds the intermolecular migratory sequence of halogen–halogen > halogen–alkyl[21] > alkyl–alkyl[22] seems well established.[23]

It is concluded that the rate data for the disproportionation of trimethylsilane, phenyltrimethylsilane and ethyltrimethylsilane are consistent with a reaction involving electrophilic attack on a hydrogen atom, a phenyl group or an alkyl group, the reactivities of these groups in electrophilic substitution being $H > C_6H_5 > C_2H_5$.[24] The rate of disproportionation of bromotrimethylsilane probably should not be compared with the rate of disproportionation of the other three silanes because of the possibility of a pronounced polar effect for the non-migrating bromine atom in this reaction. In the case of the other three silanes the non-migrating hydrogen, phenyl or alkyl groups do not vary greatly in their inductive effect and a comparison of the rate data is more valid, although admittedly a better measure of these intermolecular migratory

---

R. A. Benkeser and A. Torkelson, THIS JOURNAL, **76**, 1252 (1954); C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 4449 (1957).

(10) C. Eaborn, *ibid.*, 2755 (1949).

(11) M. S. Kharasch and A. L. Flenner, THIS JOURNAL, **54**, 674 (1932); R. H. Bullard, *ibid.*, **51**, 3065 (1929); H. Gilman, E. B. Towne and H. L. Jones, *ibid.*, **55**, 4689 (1933); A. E. Flood, *ibid.*, **54**, 1663 (1932); Z. M. Manulkin, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 386 (1941); **13**, 42, 46 (1943); **14**, 1047 (1944); **16**, 235 (1946); E. Krause and O. Schlöttig, *Ber.*, **58**, 429 (1925); R. E. Dessy, G. F. Reynolds and J.-Y. Kim, THIS JOURNAL, **81**, 2683 (1959).

(12) G. S. Forbes and H. H. Anderson [*ibid.*, **66**, 931 (1944)] report a spontaneous thermal disproportionation of silicon tetrachloride and tetrabromide at 170°. M. L. Delwaulle and M. F. Francois [*Comp. rend.*, **219**, 335 (1944); **220**, 173 (1945)] could not detect a thermal reaction at room temperature.

(13) F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, THIS JOURNAL, **69**, 2108 (1947).

(14) Similarly, the silicon–hydrogen bond of the triethylsilane is cleaved much more readily by iodine than the silicon–hydrogen bond of trichlorosilane.[6b]

(15) B. N. Dolgov, M. G. Voronkov and S. N. Borisov, *J. Gen. Chem.* (*U.S.S.R.*), **27**, 709 (1957).

(16) R. E. Nightingale and B. Crawford, Jr., *J. Chem. Phys.*, **22**, 1468 (1954); L. H. Long and D. Dillimore, *J. Chem. Soc.*, 4457 (1954); J. Goubeau, D. E. Richter and H. J. Recher, *Z. anorg. allgem. Chem.*, **278**, 12 (1955).

(17) T. D. Parsons and D. M. Ritter, THIS JOURNAL, **76**, 1710 (1954); T. D. Parsons, M. B. Silverman and D. M. Ritter, *ibid.*, **79**, 5091 (1957).

(18) H. J. Becher, *Z. anorg. allgem. Chem.*, **271**, 243 (1953); E. Wiberg and G. Horeld, *Z. Naturforsch.*, **6B**, 338 (1951); P. A. McCusker, G. F. Hennion and E. C. Ashby, THIS JOURNAL, **79**, 5192 (1957).

(19) (a) H. I. Schlesinger, H. C. Brown, *et al.*, *ibid.*, **75**, 191, 195 (1953); (b) H. I. Schlesinger and A. O. Walker, *ibid.*, **57**, 621 (1935); H. I. Schlesinger, L. Howitz and A. B. Burg, *ibid.*, **58**, 407 (1936).

(20) A further indication of the ease of migration of hydrogen atoms in the boranes is the reported catalysis of alkyl–bromine shifts [F. L. McKennon, Ph.D. Dissertation, Univ. of Chicago Libraries, 1936] and other disproportionations [A. B. Burg and F. M. Graber, THIS JOURNAL, **78**, 1523 (1956)] by traces of materials containing a boron-hydrogen bond.

(21) S. Winstein, T. G. Traylor and C. S. Garner, *ibid.*, **77**, 3741 (1955).

(22) S. Hilpert and G. Gruttner, *Ber.*, **48**, 906 (1915); M. S. Kharasch and M. W. Grafflin, THIS JOURNAL, **47**, 1948 (1925).

(23) This sequence may result in part from a considerable thermochemical driving force for alkyl–chlorine shifts in many mercuryl compounds [K. Hartley, H. Prichard and H. Skinner, *Trans. Faraday Soc.*, **146**, 1019 (1950)]. For example: $^1/_2HgEt_2 + {}^1/_2HgCl_2 = EtHgCl +$ 7.3 kcal.

(24) It is thus not surprising that some of the most facile disproportionations of silanes involve hydrogen–phenyl shifts [J. L. Speier and R. E. Zimmerman, THIS JOURNAL, **77**, 6395 (1955); H. Gilman and D. H. Miles, *J. Org. Chem.*, **23**, 326 (1958)]. In view of these relative migratory aptitudes it is also apparent why traces of a compound containing silicon–hydrogen bonds will serve as co-catalysts in the disproportionation of alkylchlorosilane [H. R. McEntee, U. S. Patent 2,786,861 (1957)] and why the disproportionation of phenyldichlorosilane [G. H. Wagner and M. M. Burnham, U. S. Patent 2,746,981 (1956)] occurs more readily than the disproportionation of phenylmethyldichlorosilane [Dow Corning Ltd., British Patent 663,698 (1951)].

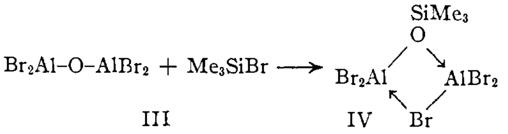
tendencies would be the relative rates of the reactions

$$Me_3SiY + MeSiR_3 \longrightarrow Me_4Si + YSiR_3$$

as Y is varied from hydrogen to phenyl, ethyl or bromine.

The Oxygen Effect.—In the preceding paper the pronounced effect of oxygen, water or hydrogen sulfide on the rate of ethyltrimethylsilane disproportionation was discussed in terms of the formation of aluminum oxybromide, possibly $Br_2AlOAlBr_2$, or its sulfur analog.[2a] In the present work a pronounced accelerating effect of water on the aluminum bromide-catalyzed disproportionation of trimethylsilane and phenyltrimethylsilane also was observed, indicating that the oxygen effect discussed previously is quite general. It was thus surprising to find that oxygen, water or hydrogen sulfide did not accelerate the aluminum bromide-catalyzed disproportionation of bromotrimethylsilane. Actually, a considerable retardation in the rate of reaction was observed in the presence of these materials. In the case of oxygen there is ample evidence for the reaction with aluminum bromide in the presence of bromotrimethylsilane (*e.g.*, the formation of methyl bromide).

The best explanation of these observations appears to be that bromotrimethylsilane can somehow destroy the effective catalyst in aluminum oxybromide whereas the non-halogen containing silanes cannot. In particular, the following reaction suggests itself


III IV

In the presence of a large excess of bromotrimethylsilane, III may be destroyed completely giving IV. If IV is a less effective catalyst than aluminum bromide itself, the observed retardation can be explained. It is not unreasonable that IV would be a weaker Lewis acid than aluminum bromide because the oxygen bridge would be expected to be more stable than a bromine bridge and, as pointed out previously,[2a] for dimeric aluminum bromide to function as an acid there must be either dissociation or a molecular reorganization.

Experimental

General Procedure.—The procedure for preparing catalysts and reaction mixtures was the same as described previously.[2a] Bromotrimethylsilane was introduced into the vacuum line by distillation from aluminum bromide. Trimethylsilane was introduced directly after distillation through a low temperature Podbielniak column. Phenyltrimethylsilane was stored in the vacuum line over a sodium mirror. The quantities of reagents used in preparing a reaction mixture were carefully measured, but the actual molar concentration at the reaction temperature was calculated. The densities of trimethylsilane, phenyltrimethylsilane and bromotrimethylsilane between 0 and 80° were found to follow the relationship

trimethylsilane, g./ml. $= 0.648 - 0.0013t$
phenyltrimethylsilane, g./ml. $= 0.943 - 0.0009t$
bromotrimethylsilane, g./ml. $= 1.18 - 0.0014t$

where t is the temperature in °C. Final volumes were calculated on the basis of no changes in volume upon mixing and on the basis that the volume correction for dissolution of aluminum bromide followed the equation $V_f = V_i + 320$ (mole Al_2Br_6), where V_f and V_i are the initial and final volumes at the temperature in question. The equation was found to apply experimentally for the solution of aluminum bromide in ethyltrimethylsilane.[2a] Pertinent data, required for the calculation of the concentrations given in Table V, are given in Table VI.

TABLE VI

CALCULATED VOLUMES FOR REACTION MIXTURES CONTAINING Me_3SiR[a]

R	Me_3SiR[b]	Solvent[c] C_6H_{12}	Solvent[c] C_6H_6	Final volume ml.	Final volume temp., °C.
H	43.8	..	..	5.74	(40)
H	6.78	5.0[d]	..	6.29	(40)
H	6.78	..	5.0[d]	6.27	(40)
C_6H_5	31.5	..	..	5.51	(40)
C_6H_5	6.92	5.0	..	6.64	(40)
Br	38.60	..	..	5.80	(80)
Br	4.65	5.0	..	6.50	(80)
Br	4.65	..	5.0	6.42	(80)

[a] 1.87 mmoles of $AlBr_3$ in all experiments. [b] Mmoles. [c] Ml. at 10°. [d] At 25°.

Analysis.—Trimethylsilane disproportionations were analyzed by opening the sealed ampoules at liquid nitrogen temperature, attaching the ampoule to a 3-l. bulb, evacuating the bulb and ampoule and then allowing the silanes to vaporize into the bulb. The gaseous silanes were mixed by shaking the bulb which contained a number of strips of Teflon. Samples of vapor were injected into a Perkin-Elmer model 154B vapor fractometer. The vapor fractometer employed a 4 m. "D"-column (purportedly tetraisobutylene) and used helium carrier gas at 30°. Under these conditions the relative retention times of SiH_4:SiH_3Me:SiH_2Me_2:$SiHMe_3$:$SiMe_4$ of 0.27:0.36:0.59:1.0:1.63 were observed. Relative molar concentrations were calculated from the various peak areas by means of the experimental relationships

$$\frac{\text{mole } Me_3Si}{\text{mole } Me_3SiH} = 0.82\,\frac{\text{area } Me_4Si \text{ peak}}{\text{area } Me_3SiH \text{ peak}}$$

$$\frac{\text{mole } Me_2SiH_2}{\text{mole } Me_3SiH} = 1.00\,\frac{\text{area } Me_2SiH_2 \text{ peak}}{\text{area } Me_3SiH \text{ peak}}$$

$$\frac{\text{mole } MeSiH_3}{\text{mole } Me_3SiH} = 1.08\,\frac{\text{area } MeSiH_3 \text{ peak}}{\text{area } Me_3SiH \text{ peak}}$$

The relative molar ratios of silane and methylsilane were calculated on the basis that the thermal conductivities were inversely proportional to the molecular weight.

When the volatile boron halides were used, the procedure was modified in that 2-ml. of ethyl ether was added before the sample was allowed to volatilize. For boron trifluoride the appropriate quantity of boron trifluoride etherate remained after volatilization of the methylsilanes. However, when boron chloride or bromide was used as catalyst, only a small amount of residue remained after vaporization of the silanes and upon exposure to air this residue immediately burned with a green flame.

The products of the disproportionation of phenyltrimethylsilane were analyzed by opening the reaction ampoules at liquid nitrogen temperature and slowly adding 2 ml. of 10% aqueous sodium hydroxide. The ampoules were cautiously warmed to 0° and shaken to ensure hydrolysis. An aliquot of a standard solution of ethyltrimethylsilane in carbon tetrachloride was added and the mole ratio of tetramethylsilane and ethyltrimethylsilane in the organic phase determined as described previously.[2a] Benzene and hexamethyldisiloxane in the hydrolysate were also determined in this analysis by using the experimentally determined equations

$$\frac{\text{mole } Me_3SiOSiMe_3}{\text{mole } Me_3SiEt} = 0.928\,\frac{\text{area } Me_3SiOSiMe_3 \text{ peak}}{\text{area } Me_3SiEt \text{ peak}}$$

$$\frac{\text{mole } C_6H_6}{\text{mole } Me_3SiEt} = 1.42\,\frac{\text{area } C_6H_6 \text{ peak}}{\text{area } Me_3SiEt \text{ peak}}$$

Disproportionation products of bromotrimethylsilane were analyzed by collection of the vacuum distillate at liquid nitrogen temperature. To the distillate a standard solution of ethyltrimethylsilane in carbon tetrachloride was added and the mixture injected into a vapor fractometer. The vapor fractometer employed, in series, a 2-m. column packed with Tide, which effectively removed traces of hydrogen bromide from the samples, and a 2-m. "A"-column (di-*n*-decyl phthalate). The mole ratio of tetramethylsilane and ethyltrimethylsilane was calculated as described previously.[2a]

Reagents.—Trimethylbromosilane was prepared by the reaction of aluminum bromide with purified hexamethyldisiloxane. The silane was distilled through a packed column of approximately 25 theoretical plates and constant boiling material introduced into the vacuum line by distillation from aluminum bromide. Tetramethylsilane could not be detected as an impurity by gas-liquid chromatography and the material used for disproportionation was tensiometrically homogeneous.

Trimethylsilane, Peninsular ChemResearch, Inc., was rectified in a low temperature Podbielniak column of about 100 theoretical plates. Constant boiling material with a constant thermal conductivity was introduced into the vacuum line without exposure to air. Two different samples were used, one containing about 0.4% tetramethylsilane as an impurity and one containing 0.4% dimethylsilane as an impurity. Corrections for these impurities were applied. Pure samples of methylsilane and dimethylsilane, originally purified by rectification in the Podbielniak column, were obtained from Dr. G. D. Cooper.

Their purity was estimated to be greater than 99.5% by gas-liquid chromatography and trimethylsilane was not an impurity.

Phenyltrimethylsilane was rectified in a column of about 20 theoretical plates. The material used, $n^{20}\text{D}$ 1.4902, contained no detectable impurities by gas-liquid chromatography.

Acknowledgment.—The vapor fractometer and low temperature Podbielniak column were operated by Mr. E. M. Hadsell. Phenyltrimethylsilane and bromotrimethylsilane were prepared by Dr. J. R. Ladd. Mr. D. E. McBournie assisted in certain phases of the experimental work.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Catalysis by Metal Halides. III. The Question of the Existence of Siliconium Ions

BY GLEN A. RUSSELL[1]

RECEIVED APRIL 8, 1959

The interaction of various substituted silanes with aluminum bromide does not produce intermediates capable of silylating benzene or catalyzing the rearrangement of cyclohexane to methylcyclopentane. These data are taken as evidence against the formation of siliconium ions. Complexes between aluminum bromide and substituted silanes or between aluminum bromide and methyl bromide attack tetramethylsilane in preference to benzene. On the other hand, carbonium ions or acylonium ions attack benzene in preference to tetramethylsilane. On this basis a distinction can be made between carbonium ions and alkyl halide–metal halide complexes as reaction intermediates.

The question of the formation of siliconium ions from the interaction of Lewis acids with substituted silanes was investigated using the isomerization of methylcyclopentane and the silylation of benzene as criteria. It is well known that a halosilane, such as trimethylbromosilane, will not react with benzene in the presence of aluminum bromide to produce a significant amount of trimethylsilylbenzene.[2] The failure of silicon compounds to undergo reactions analogous to the Friedel–Crafts reaction can be explained in several different ways. The halosilane may not produce a siliconium ion upon interaction with Lewis acids. Alternately, the siliconium ion may be ineffective in the attack upon a benzene ring. Finally, the silylation reaction, if it occurs, must be reversible.[2]

$$(CH_3)_3SiBr + C_6H_6 \overset{Al_2Br_6}{\rightleftarrows} C_6H_5Si(CH_3)_3 + HBr$$

All evidence that we have obtained points to the conclusion that siliconium ions, or even incipient siliconium ions, are not formed by the interaction of aluminum halides with substituted silanes, at least below temperatures of 80°. Thus, the catalyst-cocatalyst system of aluminum bromide–trimethylbromosilane is completely inactive in the isomerization of methylcyclopentane to cyclohexane at 25°.[3] At 80° isomerization of cyclohexane by this system could not be detected under conditions wherein trimethylbromosilane was disproportionated.[4] Moreover, at 80° in benzene solution bromotrimethylsilane was disproportionated by aluminum bromide but phenyltrimethylsilane could not be detected (<1 part/4000) by g.l.c.

Tetramethylsilane, aluminum bromide and benzene also gave no detectable amount of phenyltrimethylsilane at 80° under conditions where ethyltrimethylsilane was extensively disproportionated. Analysis of the reaction product indicated the complete absence of methane, a necessary by-product of trimethylsilylation of benzene by tetramethylsilane. The disproportionation of ethyltrimethylsilane by aluminum bromide in cyclohexane solution at 80°, or of trimethylsilane at 40°, also failed to produce any isomerization of the cyclohexane.[4,5] Phenyltrimethylsilane could not be detected in the aluminum bromide-catalyzed disproportionation of trimethylsilane in benzene solution at 60° even when the disproportionation of trimethylsilane had reached equilibrium. A trace of hydrogen was formed in this reaction, possibly suggesting trimethylsilylation but also explicable on the basis of a

$$(CH_3)_3SiH + C_6H_6 \xrightarrow{Al_2Br_6} (CH_3)_3SiC_6H_5 + H_2$$

trace impurity. A solution 1 *M* in trimethylsilane and 0.15 *M* in aluminum bromide in benzene yielded hydrogen equivalent to reaction of only 0.76% of the trimethylsilane after 10 hours at 60°.[6]

---

(1) Iowa State University, Ames, Iowa.

(2) H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

(3) G. A. Russell, THIS JOURNAL, **81**, 4834 (1959).

(4) G. A. Russell, *ibid.*, **81**, 4825 (1959).

(5) G. A. Russell, *ibid.*, **81**, 4815 (1959).

(6) Similar reactions between silicochloroform or methyldichlorosilane and aromatic materials at 200–300° are well known [A. J. Barry, *et al.*, U. S. Patents 2,499,561 (1950), 2,591,668, 2,611,775 (1952), 2,626,266 (1953), 2,788,357 (1957); C. H. Wagner and P. W. Shafer, U. S. Patent 2,775,606 (1956)].