

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.<sup>2a</sup>

**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,  $n_D^{20}$  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]

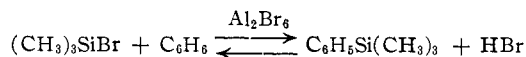
### Catalysis by Metal Halides. III. The Question of the Existence of Siliconium Ions

BY GLEN A. RUSSELL<sup>1</sup>

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 acylium 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.

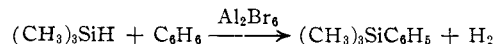
The question of the formation of siliconium ions from the interaction of Lewis acids with substituted silanes was investigated using the isomerization of methylcyclopentane and the silylation of benzene as criteria. It is well known that a halosilane, such as trimethylbromosilane, will not react with benzene in the presence of aluminum bromide to produce a significant amount of trimethylsilylbenzene.<sup>2</sup> 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.<sup>2</sup>



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-co-catalyst system of aluminum bromide-trimethylbromosilane is completely inactive in the isomerization of methylcyclopentane to cyclohexane at 25°.<sup>3</sup> At 80° isomerization of cyclohexane by this system could not be detected under conditions wherein trimethylbromosilane was disproportionated.<sup>4</sup> More-

over, 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.<sup>4,5</sup> 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



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°.<sup>6</sup>

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

(6) Similar reactions between silicochloroform or methylchlorosilane 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)].

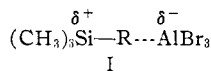
(1) Iowa State University, Ames, Iowa.

(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).

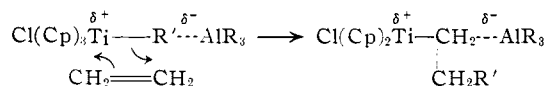
All of these results are consistent with an interpretation of the disproportionation reaction of silanes as a reaction which does not involve a siliconium ion, an interpretation consistent with all facts known about the disproportionation reaction itself.<sup>4,5</sup> The failure to observe hydrocarbon isomerization or the silylation of benzene, under conditions where disproportionation occurs readily, can be taken as support for this interpretation since a siliconium ion would be expected to display a reactivity similar to a carbonium ion. The experiments with tetramethylsilane and trimethylsilane, as well as the inability of mixtures of bromotrimethylsilane and aluminum bromide to isomerize methylcyclopentane, indicate that a reversal of the silylation reaction is probably not the proper explanation for the absence of silylation in the reaction of a halosilane with benzene in the presence of a Lewis acid at moderate temperatures. Hydrogen or methane formed in the trimethylsilylation reactions of trimethylsilane or tetramethylsilane would hardly be expected to cleave a silicon-phenyl bond. These results force us to conclude that the interaction of aluminum bromide with bromotrimethylsilane, tetramethylsilane or trimethylsilane does not produce an intermediate analogous to a carbonium ion. Evidently a slight polarization of a silicon-halogen, silicon-methyl or silicon-hydrogen bond is produced, to yield an intermediate which has suf-



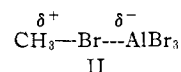
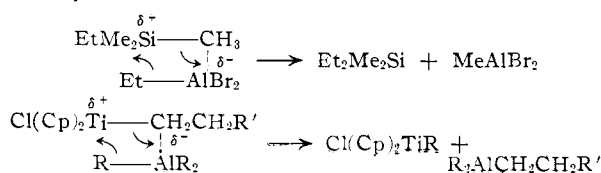
ficient reactivity to attack another silane molecule thereby producing disproportionation products.<sup>6a</sup> However, I does not possess the reactivity of a carbonium ion, and can neither abstract a hydrogen atom from methylcyclopentane nor substitute in the benzene ring.

The conclusion that substituted silanes are more reactive than benzene toward intermediates similar to I suggested that tetramethylsilane also would be more reactive than benzene toward intermediates with structures similar to II.

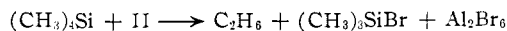
(6a) ADDED IN PROOF.—There are some similarities between I and certain structures suggested for soluble Ziegler catalysts [D. S. Breslow and N. R. Newburg, *THIS JOURNAL*, **81**, 81 (1959), J. C. W. Chien, *ibid.*, **81**, 86 (1959)]. However, mixtures of tetramethylsilane and aluminum bromide will not polymerize ethylene. The relative ease of disproportionation of bromotrimethylsilane and ethyltrimethylsilane<sup>4</sup> suggests that interaction between aluminum alkyls and alkyltitanium chlorides does not necessarily involve exclusively bond formation between the aluminum and chlorine atoms but could also be formulated as  $\text{Cl}(\text{Cp})_2\text{Ti}^{\delta+}-\text{R}^{\delta-}-\text{AlR}_3$ . The polymerization of ethylene could then be formulated



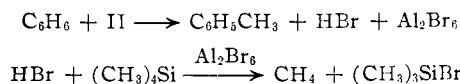
The chain transfer reaction documented by Chien now becomes easily understood and analogous to reactions observed between alkylsilanes and alkylaluminum halides.<sup>3</sup>



To test this idea methyl bromide, in the presence of aluminum bromide, was allowed to react with tetramethylsilane and with a mixture of tetramethylsilane and benzene. Reaction of the methyl bromide-aluminum bromide complex (II) with tetramethylsilane should produce ethane

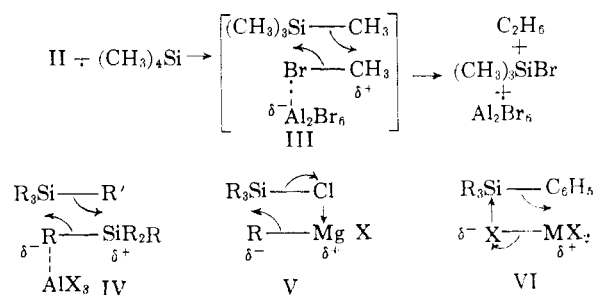


while reaction with benzene should eventually produce methane.



At 60° mixtures of methyl bromide and aluminum bromide in tetramethylsilane did produce ethane, although slowly. Addition of benzene resulted in a rapid destruction of methyl bromide, ethane being formed in a quantitative yield. Apparently tetramethylsilane is more reactive toward II than is benzene while benzene exerts a powerful solvent effect on the rate of the reaction of II with tetramethylsilane. This solvent effect is consistent with the effect of benzene in the disproportionation of substituted silanes.<sup>4,5</sup>

In view of these findings it became of interest to determine whether a carbonium ion would attack tetramethylsilane in preference to benzene. Reaction of benzoyl chloride with a mixture of tetramethylsilane and benzene in the presence of aluminum chloride produced benzophenone and very little acetophenone. Moreover, a mixture of 1-bromohexane, aluminum bromide, tetramethylsilane and benzene gave only hexylbenzenes and no heptane could be detected. These results suggest that a carbonium ion, or an acylium ion, prefers to attack benzene in preference to tetramethylsilane. The reverse order of reactivity, which is displayed by I or II, undoubtedly results because I or II can react with tetramethylsilane without the formation of a siliconium ion.<sup>7</sup>



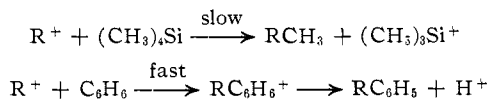
On the other hand, the reaction of a carbonium ion with tetramethylsilane would lead to the formation of a siliconium ion, an intermediate of high energy content.<sup>8</sup>

(7) Transition state III is similar to the transition state suggested for the disproportionation of silanes (IV) and not unlike possible transition states for the reaction of organometallic reagents with silicon-halogen bonds (V) or the reaction of metal halides with silicon-phenyl bonds (VI).<sup>4</sup>

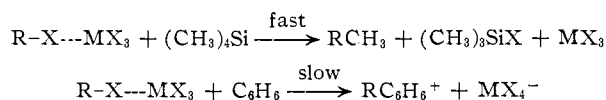
(8) J. A. Cade, *Tetrahedron*, **2**, 322 (1958); R. H. Prince, *J. Chem. Soc.*, 1783 (1959); A. B. Thomas and E. G. Rochow, *THIS JOURNAL*, **79**, 1843 (1957).

In view of these results the reduction of alkyl chlorides to alkanes<sup>9</sup> or acyl halides to aldehydes<sup>10</sup> by trialkylsilanes in the presence of aluminum halides probably should be formulated as occurring by a process not involving the formation of siliconium ions. Since neopentyl and neopentylcarbinyl chlorides yield isopentane and 2,3-dimethylbutane, respectively, these reductions undoubtedly involve a carbonium ion, possibly in equilibrium with a complex similar to II.

It is suggested that a delicate test of whether a carbonium ion or a complex (I or II) is an intermediate in a reaction can be made on the basis of the products of the competitive reaction of the intermediate with a mixture of tetramethylsilane and benzene. A carbonium ion will be phenylated by the benzene



whereas a complex will be methylated by the tetramethylsilane.



The consequences of these observations, particularly from a synthetic point of view, are being explored further.

### Experimental

**Attempted Trimethylsilylations of Benzene.**—In the preceding papers the rates of disproportionation of ethyltrimethylsilane, bromotrimethylsilane and trimethylsilane in benzene solution and in the presence of aluminum bromide were reported.<sup>4,5</sup> The reaction products also were examined for the formation of phenyltrimethylsilane by g.l.c. Trial experiments indicated that one part of phenyltrimethylsilane could be detected in 4000 parts of benzene. In no case was phenyltrimethylsilane formed in an amount that could be detected even though the silanes underwent extensive disproportionation (see Table I).

Silane	Temp., °C.	Time, hr.	% Silane disproportionated
(CH <sub>3</sub> ) <sub>3</sub> SiC <sub>2</sub> H <sub>5</sub>	80	16	46
(CH <sub>3</sub> ) <sub>3</sub> SiBr	80	2	2.3
(CH <sub>3</sub> ) <sub>3</sub> SiH	40	10	55

<sup>a</sup> 0.15 *M* aluminum bromide, approximately 1 *M* in silane.

(9) F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, THIS JOURNAL, **69**, 2108 (1947); B. N. Dolgor, S. N. Borisov and M. G. Voronkov, *J. Gen. Chem. (U.S.S.R.)*, **27**, 716 (1957).

(10) J. W. Jenkins and H. W. Post, *J. Org. Chem.*, **15**, 556 (1950).

In another experiment tetramethylsilane (5.0 ml.) and benzene (5.0 ml.) were held for 90 hr. at 80° in the presence of 1 g. of aluminum bromide. Analysis of the reaction products indicated that phenyltrimethylsilane was not present to the extent of 0.025%.

Trimethylsilane (1 *M*) and aluminum bromide (0.15 *M*) in benzene were held at 40° for 10 hours in an ampoule containing a break-off tip. The ampoule was sealed to a Toeppler pump and the contents transferred through a liquid nitrogen trap. Non-condensable gas totaled 855 mm.-ml. at 28°. The mass spectrum of this gas indicated hydrogen containing 1–2% of methane. The hydrogen was equivalent to 0.76% of the theoretical amount expected for a reaction between trimethylsilane and benzene yielding phenyltrimethylsilane and hydrogen. Alternately the hydrogen may have resulted from impurities which could have given rise to hydrogen bromide. Repetition of this experiment using tetramethylsilane in place of the trimethylsilane and reaction conditions of 24 hours at 80° did not yield any non-condensable gas (*i.e.*, methane).<sup>11</sup>

**Competitive Reactions Involving Tetramethylsilane and Benzene.**—Methyl bromide (1.57 mmoles) was allowed to react with tetramethylsilane (34.1 mmoles) in the presence of 1.87 mmoles of aluminum bromide (AlBr<sub>3</sub>) for 12 hours at 60°. The reaction ampoule contained a break-off tip and the entire sample was vaporized into a 3-l. bulb after the reaction period. Analysis by g.l.c. indicated that only a small amount of the methyl bromide had been consumed. Ethane was formed to the extent of 0.068 mmole indicating that only 4.35% of the methyl bromide had reacted with the tetramethylsilane. Methane was not detected.

The above experiment was repeated using the same quantities of reactants, but in addition 11.5 mmoles of benzene. Analysis by gas-solid chromatography indicated the complete absence of methane after a 12-hour reaction period at 60°. Analysis of the vaporized reaction product by g.l.c. indicated the presence of 0.024 mmole of unreacted methyl bromide and 1.50 mmoles of ethane. The amount of methane formed must have been less than 0.005 mmole.

The reaction of *n*-hexyl bromide (0.1 mole) with a mixture of 25 ml. of tetramethylsilane and 25 ml. of benzene in the presence of 0.50 g. of aluminum bromide was investigated. After 30 hr. at 40° the reaction product was hydrolyzed and distilled. No heptane, hexamethyldisiloxane or hexyl bromide was found. A hexylbenzene, b.p. 130–140° at 53 mm., was found (7.5 g.) and 5.4 g. of a dihexylbenzene mixture was obtained. The yields of the mono- and dihexylbenzenes were 46 and 44%, respectively, based on *n*-hexyl bromide.

Benzoyl chloride (0.10 mole), aluminum chloride (0.10 mole as Al<sub>2</sub>Cl<sub>6</sub>), tetramethylsilane (20 ml.) and benzene (20 ml.) were stirred for 16 hr. at 25°. The reaction mixture contained a solid residue after this reaction period.

The reaction mixture was hydrolyzed and extracted with aqueous base until acidification of the aqueous extract no longer gave benzoic acid. A total of 0.031 mole of benzoic acid was obtained. The organic phase was diluted with more benzene and analyzed for acetophenone and benzophenone by infrared absorption using a Perkin-Elmer model 21 spectrometer equipped with calcium fluoride optics. Carbonyl absorbance indicated the formation of 0.055 mole of benzophenone (6.00 μ) and 0.002 mole of acetophenone (5.91 μ). The yield of benzoic acid, acetophenone and benzophenone accounted for only 88% of the benzoyl chloride used. However, the results clearly indicate that a benzoyl cation attacks benzene to give benzophenone in preference to attacking tetramethylsilane to give acetophenone.

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(11) Drs. H. Dewhurst and F. Norton provided valuable assistance in these experiments.