Halomethylmetal Compounds. XVII. The Mechanism of Dichlorocarbene Insertion into the Si-H Bond by the Mercurial Route¹

Dietmar Seyferth, Robert Damrauer,^{2a} Jeffrey Yick-Pui Mui,^{2b} and Theodore F. Jula^{2c}

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received October 7, 1967

Abstract: The reaction of phenyl(bromodichloromethyl)mercury with triethylsilane in benzene at 39.0° was found to be about first order in mercurial and zero order in triethylsilane, and the mechanism shown by eq 6 and 7, which involves a dichlorocarbene intermediate, was suggested. A Hammett study of the reaction of this mercurial reagent with substituted aryldimethylsilanes gave relative rate constants which showed good correlation with σ and gave a ρ value of -0.632 ± 0.032 . Electrophilic attack by CCl₂ at the Si-H bond in which there is not high separation of charge in the transition state is indicated. The reaction of triethyldeuteriosilane with PhHgCCl₂Br in benzene and in methylene chloride solution gave only Et₃SiCCl₂D. These observations and others made by Sommer and Ritter and by us in previous studies lead us to favor transition state III for the insertion of CCl₂ into the the Si-H bond.

In a previous investigation it was shown that phenyl-(trihalomethyl)mercury compounds react rapidly and essentially quantitatively with organosilicon hydrides in benzene solution at 80° as shown in eq 1.3

$$PhHgCX_{2}Br + R_{3}SiH \longrightarrow R_{3}SiCX_{2}H + PhHgBr \qquad (1)$$
$$X = Cl \text{ and } Br$$

Germanium hydrides reacted similarly, and triethylgermane was found to be 4.5 times more reactive toward phenyl(bromodichloromethyl)mercury than triethylsilane. Since these reactions are generally applicable and proceed cleanly to give virtually quantitative yields of product, we have expended some effort to learn as much as possible about the mechanism by which such CX_2 insertion into the Si-H bond occurs.

A recent kinetic study of the reaction of phenyl-(bromodichloromethyl)mercury with olefins, which gives gem-dichlorocyclopropanes in high yield,⁴ showed that a free carbene mechanism as indicated in eq 2 and 3 was operative.⁵ Variable concentration competition

PhHgCCl₂Br
$$\frac{k_1 \text{(slow)}}{k_1 \text{(fast)}}$$
 PhHgBr + CCl₂ (2)

$$CCl_2 + C = C \xrightarrow{h_2(fast)} C = C (3)$$

experiments, in which mixtures of triethylsilane and cyclohexene were allowed to compete for a deficiency of phenyl(bromodichloromethyl)mercury, had been carried out, and it was found that the rate constant ratio $k_{\rm Et_{3}SiH}/k_{\rm cyclohexene}$ was 0.8 and that this ratio was independent of the [Et₃SiH]/[cyclohexene] concentration ratio.^{3b} The latter fact indicated that the kinetic order of triethylsilane in its reaction with the mercurial is the same as the kinetic order of cyclohexene in its reaction with PhHgCCl₂Br. Thus a free carbene mechanism for the Et₃SiH-PhHgCCl₂Br reaction seemed likely. However, independent confirmation by means of a kinetic study seemed desirable.

The rate of the Et₃SiH-PhHgCCl₂Br reaction was measured in benzene solution at 39.0° by determining by means of gas-liquid partition chromatography (glpc) the rate of formation of the product, triethyl-(dichloromethyl)silane. The results of these experiments are shown in Table I. As can be seen, doubling

Table I. The Et₃SiH-PhHgCCl₂Br Reaction: Kinetic Runs at 39.0° in Benzene Solution

Run	$[Et_3SiH]^a$	[PhHgCCl₂Br] ^α	$dx/dt \times 10^{5} b$
1	0.20	0.099	8.6
2	0.10	0.099	8.2
3	0.20	0.20	17.8

^a Initial concentration in moles/liter. ^b In moles/liter minute.

the triethylsilane concentration has no effect on the reaction rate. On the other hand, when the mercurial concentration was doubled, the reaction rate was increased by a factor of about 2. Of significance also is the fact that the rate of formation of triethyl(dichloromethyl)silane at 39.0° in benzene solution is, within experimental error, the same as the rate of formation of 1,1-dichloro-2-ethyl-2,3,3-trimethylcyclopropane from the 2,3-dimethyl-2-pentene-PhHgCCl₂Br reaction and of 9,9-dichlorobicyclo[4.1.0]nonane from the cyclooctene-PhHgCCl₂Br reaction (8.8 \times 10⁻⁵ mol/l. min) at the same reagent concentrations.⁵ The results of our PhHgCCl₂Br-olefin reaction study suggested that this was the limiting rate, *i.e.*, the one for which the rate expression for the reaction sequence 2-3 (eq 4)

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_{1}(\mathrm{PhHgCCl}_{2}\mathrm{Br})}{1 + \frac{k_{-1}(\mathrm{PhHgBr})}{k_{2}(\mathrm{olefin})}}$$
(4)

⁽¹⁾ Part XVI: D. Seyferth and H. Dertouzos, J. Organometal. Chem. (Amsterdam), 11, 263 (1968).

^{(2) (}a) National Institutes of Health Predoctoral Fellow, 1964-1967; (b) Postdoctoral Research Associate, 1966-1967; (c) Postdoctoral Research Associate, 1967-1968.

^{(3) (}a) D. Seyferth and J. M. Burlitch, J. Am. Chem. Soc., 85, 2667
(1963); (b) D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, Jr., J. Organometal. Chem. (Amsterdam), 7, 405 (1967).
(4) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, J. Am. Chem. Soc., 87, 1970. (1972).

^{4259 (1965).}

⁽⁵⁾ D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, ibid., 89, 4953 (1967).

simplified to eq 5. These findings, that the triethyl-

$$dx/dt = k_1(PhHgCCl_2Br)$$
 (5)

silane-PhHgCCl₂Br reaction is ca. first order in mercurial and ca. zero order in triethylsilane and that the observed rate is equal to that found previously for olefin-mercurial reactions at comparable reagent concentrations, suggest to us that the mechanism shown in eq 6 and 7 is operative. In other words, in this case

$$PhHgCCl_2Br \xrightarrow{k_1(slow)}_{k_{-1}(fast)} PhHgBr + CCl_2$$
(6)

$$\operatorname{CCl}_2 + \operatorname{Et}_3\operatorname{SiH} \xrightarrow{k_2(\operatorname{fast})} \operatorname{Et}_3\operatorname{SiCCl}_2\operatorname{H}$$
(7)

also we are dealing with a reaction in which free dichlorocarbene is an intermediate. With this established, our further interest centered on the nature of the Et₃SiH-CCl₂ reaction (eq 7). Ritter and Sommer^{6a} have reported that the reaction of phenyl(tribromomethyl)mercury with optically active α -naph-thylphenylmethylsilane produced optically active α -naphthylphenylmethyl(dibromomethyl)silane. More recent work has shown that such CX₂ insertion into the Si-H bond occurs with retention of configuration.^{6b} This is the result expected for the insertion of singlet-state CX₂ into the Si-H bond and it suggests a transition state of type I for the insertion process, which is the



organosilicon analog for the transition state suggested by Doering and Prinzbach⁷ for CH_2 insertion into C-H bonds. In contrast to I, which represents electrophilic attack by CX_2 at the Si-H bond, one can conceive of nucleophilic attack by CX_2 at silicon (as in II) as another possibility, and this could proceed with retention



of configuration at silicon. In order to obtain more information concerning this question, a study of the relative reactivities of a series of substituted aryldimethylsilanes toward phenyl(bromodichloromethyl)mercury by means of competition experiments was carried out. It was hoped that by varying the substituent X in XC₆H₄SiMe₂H, the relative rate constants could be treated by the Hammett equation and that, therefore, the effect of electron donation and withdrawal on the reaction site could be assessed. It was expected that nucleophilic attack at silicon would give a positive ρ value; electrophilic attack, a negative ρ value. The magnitude of this value would be a measure of how much charge separation there was in the transition state.

(6) (a) A. Ritter and L. H. Sommer, Scientific Communications, International Symposium on Organosilicon Chemistry, Prague, Sept 1965, p 279;
(b) L. H. Sommer, private communication, Jan. 1967.
(7) W. von E. Doering and H. Prinzbach, *Tetrahedron*, 6, 24 (1959). Those aryldimethylsilanes, $XC_6H_4SiMe_2H$, where X = H, *m*-CF₃, *p*-CH₃, *p*-F, *p*-Cl, and *p*-NMe₂, were prepared and their reactions with phenyl(bromodichloromethyl)mercury studied. With the exception of the *p*-dimethylaminophenyl derivative, all gave the expected aryldimethyl(dichloromethyl)silane in high yield. *p*-Dimethylaminophenyldimethylsilane gave no isolable product on reaction with phenyl(bromodichloromethyl)mercury in benzene, only rapid darkening of the reaction mixture and resinification being discernible.⁸

In the competition study a mixture of two aryldimethylsilanes and phenyl(bromodichloromethyl)mercury in *ca.* 5:5:1 molar ratio in benzene solution was stirred and heated at 79 \pm 1° for 2 hr. Glpc analysis of the reaction mixtures served to determine the yields of the two aryldimethyl(dichloromethyl)silanes produced. The relative rate constants then were calculated by the method of Doering and Henderson⁹ and expressed in terms of $k_{\rm PhMe_2SiH} = 1$. The results are given in Table II.

Table II. Relative Rate Constants for Insertion of PhHgCCl₂Br-derived CCl₂ into the Si-H Bond of $XC_6H_4SiMe_2H$

Х	σ	$k_{ ext{XC}6 ext{H}4 ext{SiMe}2 ext{H}}/ \ k_{ ext{PhSiMe}2 ext{H}}$ (av)
p-CH ₃	-0.17	1.25
H	0.00	1.00
p-F	0.06	0.883
p-C1	0.23	0.733
m-CF ₃	0.47	0.482

In a separate control experiment it was shown that the excess silanes present under the conditions of the competition experiments were stable to these reaction conditions. It is, therefore, valid to follow only the production of the dichloromethylsilanes in these competition experiments. The ArMe₂SiCCl₂H products were substantially stable to the reaction conditions. Control experiments showed that p-FC₆H₄SiMe₂CCl₂H remained undecomposed on being heated at 78° with phenylmercuric bromide in benzene for 4 hr, while the other aryldimethyl(dichloromethyl)silanes decomposed at the most to the extent of 4-5% under these conditions. This represents twice the reaction time used in the competition studies, and so it was felt that product decomposition would be neglible in the competition studies.

Table II shows clearly that an electron-donating substituent increases the relative rate constant of insertion. Figure 1, a plot of log $k_{\rm rel} vs. \sigma$, shows that the values obtained fit the Hammett equation quite well. The slope of the line obtained gave a ρ value of -0.632 ± 0.032 . This value was calculated using a least-squares program on an IBM 1620 computer using σ constants compiled by Barlin and Perrin.¹⁰ (Somewhat poorer correlations were obtained with σ^0 ($\rho = -0.632 \pm 0.07$) and with σ^+ ($\rho = -0.493 \pm 0.066$).) This correlation of these data with the Hammett equa-

⁽⁸⁾ For a brief study of the reaction of PhHgCCl₂Br and PhHgCCl₂ with tertiary amines, see D. Seyferth, M. E. Gordon, and R. Damrauer, J. Org. Chem., 32, 469 (1967).

⁽⁹⁾ W. von E. Doering and W. A. Henderson, J. Am. Chem. Soc., 80, 5274 (1958).

⁽¹⁰⁾ G. B. Barlin and D. D. Perrin, Quart. Rev. (London), 20, 75 (1966).





tion indicates clearly that electrophilic attack by dichlorocarbene on the silane is involved; it is clear also that each of the reacting silanes is behaving in a mechanistically similar manner. The value of ρ is small and this suggests that the transition state is not highly charged. In comparison, $\rho^* = -4.2$ for the R₃Si-H + Cl₂ \rightarrow R₃Si-Cl + HCl reaction, which presumably involves the attack of chlorine as an electrophilic reagent.¹¹

The available data concerning the R₃SiH-PhHg-CX₂Br reaction may be summarized as follows: (1) the reaction involves a dihalocarbene intermediate; (2) CX₂ insertion into the R₃Si-H bond occurs with retention of configuration at silicon; (3) electrophilic attack by CX₂ is occurring; (4) the transition state of the R₃SiH-CX₂ reaction is not highly charged; (5) the Ge-H bond is 4.5 times more reactive than the Si-H bond; (6) the Si-H bond is almost as reactive toward CCl₂ as is cyclohexene. It may be noted that the Ph-HgCCl₂Br-olefin reaction also involves electrophilic attack by CCl₂, with a ρ value of -0.619 ± 0.045 being obtained in a σ^+ correlation with k_{rel} for substituted styrenes of type XC₆H₄CH=CH₂.¹²

These experimental facts suggest to us three possible mechanisms for the $R_3SiH-CCl_2$ reaction: (a) insertion of CCl_2 into the Si-H bond with the intervention of a but slightly polar transition state III; (b) hydride



abstraction by CCl_2 , followed by collapse of the resulting tight ion pair IV to product; (c) radical abstraction of a hydrogen atom followed by a rapid radical

(12) R. Damrauer, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1967; D. Seyferth, J. Y.-P. Mui, and R. Damrauer, paper in preparation.



coupling step within the solvent cage. Since the rate-



determining step of this process is the generation of CCl₂ from the mercurial reagent, any of these three possibilities must occur very rapidly and kinetic experiments cannot distinguish between them. As noted, the R₃SiH-PhHgCCl₂Br reactions proceed virtually quantitatively without formation of by-products, and this prompts us to remove from further consideration any process in which substantially free CCl₂H radical or anion is involved. Experimental support for this was provided by the observation that Et₃SiD reacted with phenyl(bromodichloromethyl)mercury in benzene, and more significantly, in methylene chloride solution to give only Et₃SiCCl₂D. If free dichloromethyl-d anion had been involved as an intermediate, exchange with the methylene chloride solvent should have produced some CCl₂H⁻ and thus a mixture of Et₃SiCCl₂D and Et₃SiCCl₂H would have been formed. Since IV and V must then be considered as tightly bound species, we tend to favor transition-state III because of its simplicity. We feel that adding the stipulation of tight binding to IV and V makes them virtually identical with III, the only differences between III, IV, and V being where we decide to place the electrons which bind hydrogen to silicon. Our experiments certainly cannot distinguish between these subtle features. In any case, possibility c is the least attractive in view of the fact that strict retention of configuration is observed in these reactions and since no radical-type reactions of CCl₂ have been reported to date.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry prepurified nitrogen or argon. Elemental analyses were performed by Dr. S. M. Nagy, MIT Microchemical Laboratory, and by the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded using either a Perkin-Elmer 237 or 337 grating infrared spectrophotometer. Unless otherwise stated, spectra were taken of neat liquids. The nmr spectra were recorded using a Varian Associates A-60 nmr spectrometer. Chemical shifts are given in δ units (ppm) downfield from internal TMS. Mass spectra were recorded using a Hitachi-Perkin-Elmer RMU6D mass spectrometer.

Starting Materials. Phenyl(bromodichloromethyl)mercury was prepared using our previously published directions.¹³ Dimethylphenylsilane was prepared by lithium aluminum hydride reduction of dimethylphenylchlorosilane, the remaining dimethylarylsilanes by reaction of the appropriate Grignard reagent with dimethylchlorosilane, Me₂HSiCl. The infrared, nmr, and mass spectra of these silanes are recorded in the Ph.D. thesis of R. Damrauer (MIT, 1967). The refractive indices and spectral properties of the known silanes agreed well with literature data. All were available for further experiments in 99+% purity. Triethylsilane was purchased from Peninsular ChemResearch, Inc. and was purified by distilla-

⁽¹¹⁾ L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 107, 128.
(12) R. Damrauer, Ph.D. Thesis, Massachusetts Institute of Tech-

⁽¹³⁾ D. Seyferth and J. M. Burlitch, J. Organometal. Chem. (Amsterdam), 4, 127 (1965).

Table III. Physical Properties of Aryldichloromethyldimethylsilanes

$-\mathrm{Si}(\mathrm{CH}_3)_2\mathrm{CO}$	l₂H		20		- Found (calcd), % -	
<u>x'</u>	Bp, °C (mm)	oCCl₂H, ppm	<i>n</i> ²⁰ D	C	Н	Ci
Н	128 (20)	5.28	1.5358	49.08 (49.32)	5.50 (5.52)	32.75 (32.36)
m-CF ₃	64-65 (0.3)	5.30	1.4858	42.15 (41.82)	4.03 (3.86)	25.09 (24.69)
$p-CH_3$	79-80 (0.25)	5.24	1.5347	51.19 (51.50)	6.10 (6.05)	30.74 (30.41)
p-F	69-70 (0.2)	5.32	1.5209	45.49 (45.58)	4.41 (4.68)	30.11 (29.90)
p-CH ₂ SiMe ₃	115-120 (0.15)	5.37	1.5244	51.25 (51.13)	7.48 (7.26)	23.45 (23.22)
p-Cl	79 (0.1)	5.34	1.5513	42.50 (42.62)	4.74 (4.37)	41.41 (41.94)

Table IV. Reactions of Phenyl(bromodichloromethyl)mercury (0.0995 M) with Triethylsilane (0.20 M) in Benzene at 39.0°: Kinetic Run

	Sample no.	CeH CClaa	area Et ₃ SiCCl ₂ H	Cor peak area, $C_{4}H_{5}CCl_{3} \equiv 360$	Concn of Et ₈ SiCCl ₂ H, $M \times 10^2$	Concn of Et ₃ SiH, $M \times 10^2$	Time,	
<u> </u>								
	1	340	31	31.9	0.0428	19.957	5	
	2	306	57	67	0.090	19.910	10	
	3	340	95	101	0.136	19.864	15	
	4	334	127	137	0.184	19.816	20	
	5	353	168	171	0.230	19.770	25	
	6	347	190	197	0.265	19.735	30	
	7	354	230	234	0.314	19.686	35	
	8	374	269	259	0.348	19.652	40	
	9	373	299	288	0.387	19.613	45	
	10	367	324	318	0.427	19.573	50	
	11	348	331	342	0.460	19.540	55	
	12	351	356	365	0.490	19.510	60	

^a Internal standard.

tion. Also prepared (but not used in the competition study) was dimethyl(*p*-trimethylsilylmethylphenyl)silane, *p*-Me₃SiCH₂C₆H₄Si-Me₂H, n^{20} D 1.4991, by the reaction of the Grignard reagent prepared from *p*-chlorobenzyltrimethylsilane and dimethylchlorosilane in THF (59% yield). The boiling point of 90% pure material was 79–83° (2 mm).

Anal. Calcd for $C_{12}H_{22}Si_2$ (material purified by glpc): C, 64.80; H, 9.97. Found: C, 64.88; H, 9.89.

Preparation of Aryldimethyl(dichloromethyl)silanes. These compounds were prepared by the reaction of phenyl(bromodichloromethyl)mercury with the appropriate aryldimethylsilane in benzene solution at reflux using the procedure described previously.^{2b} Larger scale runs (15–20 mmol) were carried out using only a slight excess of mercurial; the product was isolated by distillation and characterized, in most cases after another purification by glpc. No attempt was made to maximize yields, which ranged from 42 to 96%. Separate, small-scale preparations were carried out using a three- to fourfold excess of the mercurial reagent. In these experiments, the yields, determined by glpc, were in the range 83-96%. Pertinent physical, spectral, and analytical data for these compounds are given in Table III. The infrared, nmr, and mass spectra of these compounds are given in the thesis of R. Damrauer.

The reaction of 1 mmol of dimethyl(*p*-dimethylaminophenyl)silane with 4 mmol of PhHgCCl₂Br in 5 ml of dry benzene at 80° for 2 hr gave none of the expected dichloromethylsilane. The reaction mixture rapidly turned brown on warming, and no volatile products could be detected in the benzene solution by glpc upon completion of the reaction.

Rate Measurements of the Reaction of Phenyl(bromodichloromethyl)mercury with Triethylsilane in Benzene at 39.0°. The apparatus and procedure used were identical with apparatus and procedure used in our study of the PhHgCCl₂Br-olefin reaction as described in ref 5 and thus need not be repeated here. Benzotrichloride was used as the internal standard. In view of the instability of the product, dichloromethyltriethylsilane, to base, all glassware was washed with 3% H₂SO₄ and dried thoroughly before use. Triethylsilane was distilled from calcium hydride immediately before use. The rate of the reaction was followed by glpc determination of the dichloromethyltriethylsilane formed in aliquots of the reaction mixture taken in 5-min intervals. A F & M Model 700 gas chromatograph equipped with a dual-flame ionization detector was used. The analysis was carried out at oven temperature 140°, a helium flow rate of 40 cc/min, with a 20-ft (${}^{1}/_{8}$ in. o.d.) aluminum column packed with 20% General Electric Co. SE-30 silicone rubber gum on Johns Manville Chromosorb P. The raw data from one such run are given in Table IV. Plots of the Et₃SiCCl₂H concentration *vs.* time in minutes gave straight lines, the slopes of which gave the initial rate, dx/dt, in moles/liter minute. The results are summarized in Table I. One such plot is shown in Figure 2.



Figure 2. Plot of Et_3SiCCl_2H concentration vs. time: (PhHg-CCl_2Br)_{initial} = 0.0995 M; (Et_3SiH)_{initial} = 0.020 M.

Competition Studies. All glassware used was washed with 5% H₂SO₄, water, and acetone and dried thoroughly. Runs were carried out in duplicate simultaneously in a large oil bath whose temperature was regulated to $79 \pm 1^{\circ}$. The reaction flasks were evacuated to 0.1 mm and at the same time flame dried before being charged with reactants under prepurified nitrogen. Glpc analysis was carried out using an F & M Model 700 gas chromatograph with a 12-ft ($\frac{1}{4}$ in. o.d.) aluminum column filled with 20% LAC

		х	CH₃ ∣ ₁C₅H₄SiH └ CH₃ I	$+ X_2C_6H_4$	CH ₃ SiH CH ₃ II	₅HgCCl₂Br	CH │ X₁C₀H₄SiC │ CH Ⅲ	I3 CCl2H + I3	CH X₂C₅H₄SiC CH IV	I₃ CCl₂H I₃			
 X1	X_2	Amt of I, g	$\begin{array}{c} \text{Mmoles} \\ \text{of I,} \\ I_{\text{I}} \end{array}$	Amt of II, g	Mmoles of II, <i>I</i> _{II}	Amt of C ₆ H ₅ Hg- CCl ₂ Br, g	Mmoles of C ₆ H ₅ - HgCCl ₂ Br	Yield, % III	$\begin{array}{c} \text{Mmoles} \\ \text{of III,} \\ P_{\text{I}} \end{array}$	Yield, % IV	Mmoles of IV, P ₁₁	k _{x1} / k _{x2}	
<i>m</i> -CF ₃ <i>m</i> -CF ₃ <i>p</i> -CH ₃ <i>p</i> -CH ₃ <i>p</i> -F <i>p</i> -F <i>p</i> -Cl <i>p</i> -Cl	H H H <i>m</i> -CF₃ <i>m</i> -CF₃ H H	0.9838 0.9839 0.3565 0.3625 0.7713 0.7398 0.8851 0.8632	$\begin{array}{r} 4.82 \\ 4.82 \\ 2.93 \\ 2.41 \\ 5.00 \\ 4.80 \\ 5.19 \\ 5.06 \end{array}$	$\begin{array}{c} 0.\ 6399\\ 0.\ 6349\\ 0.\ 3251\\ 0.\ 3328\\ 1.\ 0107\\ 0.\ 9990\\ 0.\ 5910\\ 0.\ 6522 \end{array}$	$\begin{array}{c} 4.70^{a} \\ 4.66 \\ 2.39^{b} \\ 2.44 \\ 4.95^{b} \\ 4.89 \\ 4.34^{c} \\ 4.79 \end{array}$	$\begin{array}{c} 0.4402\\ 0.4432\\ 0.2334\\ 0.2252\\ 0.4430\\ 0.4407\\ 0.4458\\ 0.4434\\ \end{array}$	1.00 1.01 0.530 0.511 1.01 1.00 1.01 1.01	31.9 33.9 51.7 54.4 62.4 67.3 42.2 41.8	$\begin{array}{c} 0.319\\ 0.340\\ 0.274\\ 0.278\\ 0.629\\ 0.673\\ 0.426\\ 0.422\\ \end{array}$	64.2 68.1 41.9 44.1 34.8 36.0 48.3 53.7	0.642 0.687 0.222 0.225 0.352 0.360 0.488 0.541	0.485 0.478 1.24 1.25 1.77 1.90 0.729 0.737	0.482 1.25 0.883 0.733
a Interi	nal standard	d: ethyl c	innamate.	^b Interna	l standard	l: chlorob	enzene. °	Internal	standard:	1-chlor	onaphthale	ne.	

728 on Chromosorb W at 195°. Yield determinations were carried out using the internal standard method.

2948

The competition reaction between dimethylphenylsilane and dimethyl(*m*-trifluoromethylphenyl)silane is described as an example of the procedure used. Into a dry, 50-ml, three-necked flask equipped with a magnetic stirring bar and a reflux condenser topped with a nitrogen inlet tube was charged, under nitrogen, 0.6399 g (4.70 mmol) of dimethylphenylsilane, 0.9838 g (4.82 mmol) of dimethylphenylsilane, 0.4402 g (1.00 mmol) of phenyl(*m*-trifluoromethylphenyl)silane, 0.4402 g (1.00 mmol) of phenyl(bromodichloromethylphenyl)silane, 0.4402 g (1.00 mmol) of phenyl(bromodichloromethylphenyl) and 5.0 ml of dry benzene. The mixture was stirred and heated at 79 ± 1° for 2 hr. Direct glpc analysis using ethyl cinnamate as internal standard gave the following yields: *m*-CF₄C₆H₄SiMe₂CCl₂H, 31.9%, and C₆H₄SiMe₂CCl₂H, 64.2%.

Experimental data on all competition reactions carried out are presented in Table V. The relative rate constants were calculated from these data using the equation⁹

$$k_{\rm rel} = \frac{k_{\rm x_1}}{k_{\rm x_2}} = \frac{P_{\rm I}I_{\rm II}}{P_{\rm II}I_{\rm I}}$$

where $P_{\rm I}$ and $P_{\rm II}$ are the number of mmoles of product derived from silanes I and II, respectively, and $I_{\rm I}$ and $I_{\rm II}$ are the number of mmoles of starting silanes I and II present at the beginning of the competition reaction.

Reaction of Triethyldeuteriosilane with Phenyl(bromodichloromethyl)mercury. Triethyldeuteriosilane was prepared by reduction of triethylchlorosilane with lithium aluminum deuteride (Metal Hydrides, Inc.) in diethyl ether. The product, bp 105–110° (lit.¹⁴ bp 107°), had an infrared spectrum (in CCl₄) in which the absence of $\nu_{\rm Si-H}$ at 2100 cm⁻¹ and the presence of $\nu_{\rm Si-D}$ at 1535 cm^{-1 15} were notable.

a. Reaction in Benzene. The usual procedure was used.^{3b} All glassware used in reactions with triethyldeuteriosilane was first acid washed and then rinsed repeatedly with distilled water before drying. A reaction with 4.41 g (10 mmol) of PhHgCCl₂Br and 1.66 g (14.2 mmol) of Et₃SiD in 20 ml of benzene at reflux for 4 hr gave phenylmercuric bromide in 95% yield and Et₃SiCCl₂D in about

85% yield. Pure samples (n^{25} D 1.4662) were collected by glpc (3.5 ft \times 10 mm i.d. glass column packed with Dow Corning 710 silicone oil on Chromosorb P, 140°, 15 psi of helium).

Anal. Calcd for $C_7H_{13}DCl_2Si$: C, 41.99; H + D, 8.06; Cl, 35.42. Found: C, 42.23; H + D, 8.09; Cl, 35.45.

The infrared spectrum of Et₃SiCCl₂D (pure liquid) showed absorption at 2940 (s), 2910 (s), 2880 (s), 2800 (sh), 2730 (w), 2200 (w), 1460 (m), 1418 (m), 1380 (w), 1238 (m), 1015 (sh), 1005 (s), 970 (sh), 910 (w), 875 (s), 730 (s), 715 (sh), 680 (s), and 580 (sh) cm⁻¹. The nmr spectrum (in CCl₄) showed only a complex pattern from 0.5 to 1.2 ppm, which was identical with the C₂H₃ resonance due to CCl₂H was observed when the spectrum amplitude was increased tenfold.

The mass spectrum (Hitachi-Perkin-Elmer RMU6D, 80 V) of a collected sample showed the following pattern (m/e 115 (Et₃-Si⁺ == 100)): 131 (4), 129 (14), 127 (18), 123 (5), 121 (11), 117 (7), 116 (7), 115 (100), 103 (4), 101 (15), 99 (2), 95 (6), 93 (16), 89 (4), 88 (4), 87 (65), 86 (3), 85 (2), 79 (6), 65 (11), 63 (15), 59 (27), 58 (5), 57 (4), 43 (5). The intensity of the molecular ion ((C_2H_6)₃Si²⁸-CCl³⁵Cl³⁵D, m/e 199) at 80 V was <1%, but at 8.3 V, the following pattern was observed: 204 (5), 203 (14), 202 (12), 201 (68), 200 (16), 199 (100), 198 (<2).

b. Reaction in Methylene Chloride. A mixture of 10.1 mmol of phenyl(bromodichloromethyl)mercury and 13.1 mmol of triethyldeuteriosilane in 20 ml of methylene chloride (reagent grade, distilled from P_2O_5 under nitrogen directly into the reaction flask) was heated at an oil bath temperature of $50-55^\circ$ with stirring for 30 hr. All volatiles were removed by a trap-to-trap distillation at 0.07 mm. Analysis of the distillate by glpc after removal of most of the solvent showed the Et_8SiCCl_2D yield to be 78%. Infrared, nmr, and mass spectrometry showed the product to be identical in all respects with that obtained in the reaction carried out in benzene solution.

Acknowledgments. The authors are grateful to the U. S. Air Force Office of Scientific Research ((SRC)-OAR) for generous support of this work (Grant No. AFOSR-68-1350) and to M & T Chemicals, Inc., and the Dow Corning Corporation for gifts of chemicals. This investigation was supported in part by U. S. Public Health Service Fellowship 5-F1-GM-24,781-03 (to R. D.). Our thanks also are due to Professor L. H. Sommer for communicating his results on the stereochemistry of the $R_3SiH-CX_2$ reaction prior to publication.

⁽¹⁴⁾ V. A. Ponomarenko, Yu. P. Egorov and G. Ya. Vzenkova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 54 (1958); *Chem. Abstr.*, 52, 11735 (1958).

⁽¹⁵⁾ V. A. Ponomarenko and Yu. P. Egorov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1133 (1960); Chem. Abstr., 54, 22005 (1960).