Halomethylmetal Compounds. XVII. The Mechanism of Dichlorocarbene Insertion into the Si–H Bond by the Mercurial Route[1]

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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 CCl_2 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 $PhHgCCl_2Br$ in benzene and in methylene chloride solution gave only Et_3SiCCl_2D. 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 CCl_2 into the the Si–H bond.

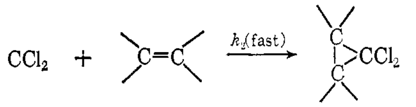
In a previous investigation it was shown that phenyl(trihalomethyl)mercury compounds react rapidly and essentially quantitatively with organosilicon hydrides in benzene solution at 80° as shown in eq 1.[3]

$$PhHgCX_2Br + R_3SiH \longrightarrow R_3SiCX_2H + PhHgBr \qquad (1)$$
$$X = \text{Cl and Br}$$

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

$$PhHgCCl_2Br \underset{k_{-1}\text{(fast)}}{\overset{k_1\text{ (slow)}}{\rightleftharpoons}} PhHgBr + CCl_2 \qquad (2)$$



(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 $k_{Et_3SiH}/k_{cyclohexene}$ was 0.8 and that this ratio was independent of the $[Et_3SiH]/[cyclohexene]$ 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 $PhHgCCl_2Br$. Thus a free carbene mechanism for the Et_3SiH–$PhHgCCl_2Br$ reaction seemed likely. However, independent confirmation by means of a kinetic study seemed desirable.

The rate of the Et_3SiH–$PhHgCCl_2Br$ 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 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–$PhHgCCl_2Br$ reaction and of 9,9-dichlorobicyclo[4.1.0]nonane from the cyclooctene–$PhHgCCl_2Br$ reaction (8.8×10^{-5} mol/l. min) at the same reagent concentrations.[5] The results of our $PhHgCCl_2Br$–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)

Table I. The Et_3SiH–$PhHgCCl_2Br$ Reaction: Kinetic Runs at 39.0° in Benzene Solution

Run	$[Et_3SiH]^a$	$[PhHgCCl_2Br]^a$	$dx/dt \times 10^{5\ b}$
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.

$$\frac{dx}{dt} = \frac{k_1(PhHgCCl_2Br)}{1 + \dfrac{k_{-1}(PhHgBr)}{k_2(\text{olefin})}} \qquad (4)$$

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[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**, 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-

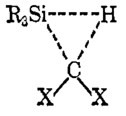
$$dx/dt = k_1(\mathrm{PhHgCCl_2Br}) \qquad (5)$$

silane-PhHgCCl$_2$Br 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

$$\mathrm{PhHgCCl_2Br} \underset{k_{-1}(\mathrm{fast})}{\overset{k_1(\mathrm{slow})}{\rightleftharpoons}} \mathrm{PhHgBr} + \mathrm{CCl_2} \qquad (6)$$

$$\mathrm{CCl_2} + \mathrm{Et_3SiH} \xrightarrow{k_2(\mathrm{fast})} \mathrm{Et_3SiCCl_2H} \qquad (7)$$

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 Et$_3$SiH-CCl$_2$ reaction (eq 7). Ritter and Sommer[6a] have reported that the reaction of phenyl(tribromomethyl)mercury with optically active α-naphthylphenylmethylsilane produced optically active α-naphthylphenylmethyl(dibromomethyl)silane. More recent work has shown that such CX$_2$ insertion into the Si-H bond occurs with retention of configuration.[6b] This is the result expected for the insertion of singlet-state CX$_2$ 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 Prinzbach[7] 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 XC$_6$H$_4$SiMe$_2$H, 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.



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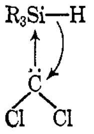

II

Those aryldimethylsilanes, XC$_6$H$_4$SiMe$_2$H, where X = H, m-CF$_3$, p-CH$_3$, p-F, p-Cl, and p-NMe$_2$, 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 ± 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 Henderson[9] and expressed in terms of $k_{\mathrm{PhMe_2SiH}} = 1$. The results are given in Table II.

Table II. Relative Rate Constants for Insertion of PhHgCCl$_2$Br-derived CCl$_2$ into the Si-H Bond of XC$_6$H$_4$SiMe$_2$H

X	σ	$k_{\mathrm{XC_6H_4SiMe_2H}}/k_{\mathrm{PhSiMe_2H}}$ (av)
p-CH$_3$	−0.17	1.25
H	0.00	1.00
p-F	0.06	0.883
p-Cl	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 ArMe$_2$SiCCl$_2$H products were substantially stable to the reaction conditions. Control experiments showed that p-FC$_6$H$_4$SiMe$_2$CCl$_2$H 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_{rel} *vs.* σ, 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-

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[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).

[8] For a brief study of the reaction of PhHgCCl$_2$Br and PhHgCCl$_3$ 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).

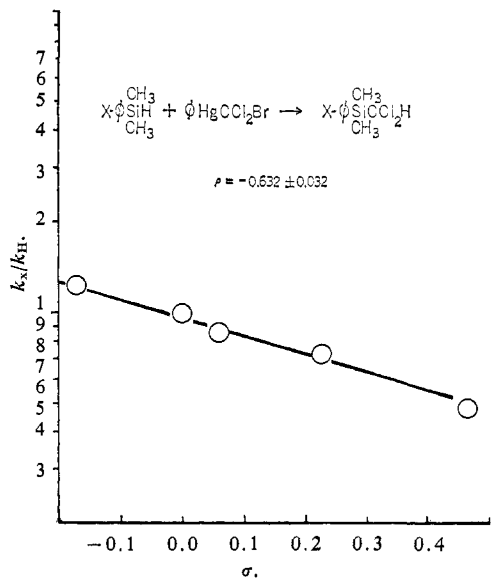
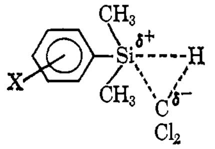


Figure 1.

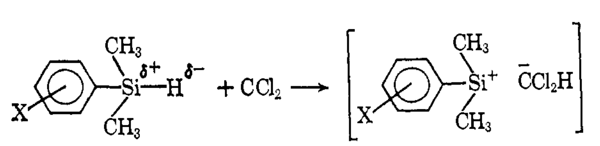
tion indicates clearly that electrophilic attack by dichlorocarbene on the silane is involved; it is clear also that each of the reacting silanes is behaving in a mechanistically similar manner. The value of ρ is small and this suggests that the transition state is not highly charged. In comparison, $\rho^* = -4.2$ for the $R_3Si\text{-}H + Cl_2 \rightarrow R_3Si\text{-}Cl + HCl$ reaction, which presumably involves the attack of chlorine as an electrophilic reagent.[11]

The available data concerning the $R_3SiH\text{-}PhHgCX_2Br$ reaction may be summarized as follows: (1) the reaction involves a dihalocarbene intermediate; (2) CX_2 insertion into the $R_3Si\text{-}H$ bond occurs with retention of configuration at silicon; (3) electrophilic attack by CX_2 is occurring; (4) the transition state of the $R_3SiH\text{-}CX_2$ 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 CCl_2 as is cyclohexene. It may be noted that the $PhHgCCl_2Br$–olefin reaction also involves electrophilic attack by CCl_2, with a ρ value of -0.619 ± 0.045 being obtained in a σ^+ correlation with k_{rel} for substituted styrenes of type $XC_6H_4CH{=}CH_2$.[12]

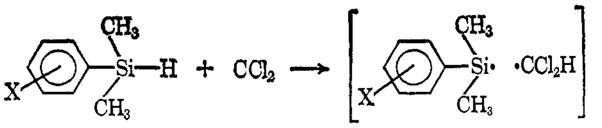
These experimental facts suggest to us three possible mechanisms for the $R_3SiH\text{-}CCl_2$ reaction: (a) insertion of CCl_2 into the Si–H bond with the intervention of a but slightly polar transition state III; (b) hydride abstraction by CCl_2, followed by collapse of the resulting tight ion pair IV to product; (c) radical abstraction of a hydrogen atom followed by a rapid radical coupling step within the solvent cage. Since the rate-determining step of this process is the generation of CCl_2 from the mercurial reagent, any of these three possibilities must occur very rapidly and kinetic experiments cannot distinguish between them. As noted, the $R_3SiH\text{-}PhHgCCl_2Br$ reactions proceed virtually quantitatively without formation of by-products, and this prompts us to remove from further consideration any process in which substantially free CCl_2H radical or anion is involved. Experimental support for this was provided by the observation that Et_3SiD reacted with phenyl(bromodichloromethyl)mercury in benzene, and more significantly, in methylene chloride solution to give only Et_3SiCCl_2D. If free dichloromethyl-*d* anion had been involved as an intermediate, exchange with the methylene chloride solvent should have produced some CCl_2H^- and thus a mixture of Et_3SiCCl_2D and Et_3SiCCl_2H 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 CCl_2 have been reported to date.



III



IV



V

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, Me_2HSiCl. 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-

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[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 Technology, Cambridge, Mass., 1967; D. Seyferth, J. Y.-P. Mui, and R. Damrauer, paper in preparation.

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

Table III. Physical Properties of Aryldichloromethyldimethylsilanes

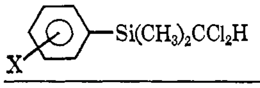
	Bp, °C (mm)	δCCl_2H, ppm	$n^{20}D$	Found (calcd), % C	H	Cl
H	128 (20)	5.28	1.5358	49.08 (49.32)	5.50 (5.52)	32.75 (32.36)
m-CF_3	64–65 (0.3)	5.30	1.4858	42.15 (41.82)	4.03 (3.86)	25.09 (24.69)
p-CH_3	79–80 (0.25)	5.24	1.5347	51.19 (51.50)	6.10 (6.05)	30.74 (30.41)
p-F	69–70 (0.2)	5.32	1.5209	45.49 (45.58)	4.41 (4.68)	30.11 (29.90)
p-CH_2SiMe_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.	Peak area $C_6H_5CCl_3$[a]	Et_3SiCCl_2H	Cor peak area, $C_6H_5CCl_3 \equiv 360$	Concn of Et_3SiCCl_2H, $M \times 10^2$	Concn of Et_3SiH, $M \times 10^2$	Time, min
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*-$Me_3SiCH_2C_6H_4SiMe_2H$, $n^{20}D$ 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.[3b] 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 $PhHgCCl_2Br$ 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 $PhHgCCl_2Br$–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% H_2SO_4 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 Et_3SiCCl_2H concentration *vs.* time in minutes gave straight lines, the slopes of which gave the initial rate, d*x*/d*t*, in moles/liter minute. The results are summarized in Table I. One such plot is shown in Figure 2.

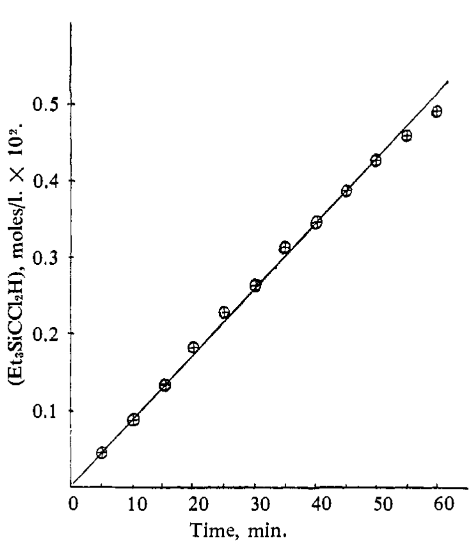
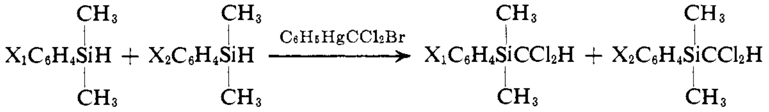


Figure 2. Plot of Et_3SiCCl_2H concentration *vs.* time: $(PhHgCCl_2Br)_{initial}$ = 0.0995 *M*; $(Et_3SiH)_{initial}$ = 0.020 *M*.

Competition Studies. All glassware used was washed with 5% H_2SO_4, water, and acetone and dried thoroughly. Runs were carried out in duplicate simultaneously in a large oil bath whose temperature was regulated to 79 ± 1°. 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 (1/4 in. o.d.) aluminum column filled with 20% LAC

Table V. Data from Competition Study of Dichlorocarbene Insertion into Aryldimethylsilanes



$$X_1C_6H_4\overset{CH_3}{\underset{CH_3}{Si}}H + X_2C_6H_4\overset{CH_3}{\underset{CH_3}{Si}}H \xrightarrow{C_6H_5HgCCl_2Br} X_1C_6H_4\overset{CH_3}{\underset{CH_3}{Si}}CCl_2H + X_2C_6H_4\overset{CH_3}{\underset{CH_3}{Si}}CCl_2H$$

I II Ill IV

X_1	X_2	Amt of I, g	Mmoles of I, I_I	Amt of II, g	Mmoles of II, I_{II}	Amt of C_6H_5Hg-CCl_2Br, g	Mmoles of C_6H_5-$HgCCl_2Br$	Yield, % III	Mmoles of III, P_I	Yield, % IV	Mmoles of IV, P_{II}	k_{X_1}/k_{X_2}	Av k_{X_1}/k_H
m-CF_3	H	0.9838	4.82	0.6399	4.70[a]	0.4402	1.00	31.9	0.319	64.2	0.642	0.485	0.482
m-CF_3	H	0.9839	4.82	0.6349	4.66	0.4432	1.01	33.9	0.340	68.1	0.687	0.478	
p-CH_3	H	0.3565	2.93	0.3251	2.39[b]	0.2334	0.530	51.7	0.274	41.9	0.222	1.24	1.25
p-CH_3	H	0.3625	2.41	0.3328	2.44	0.2252	0.511	54.4	0.278	44.1	0.225	1.25	
p-F	*m*-CF_3	0.7713	5.00	1.0107	4.95[b]	0.4430	1.01	62.4	0.629	34.8	0.352	1.77	0.883
p-F	*m*-CF_3	0.7398	4.80	0.9990	4.89	0.4407	1.00	67.3	0.673	36.0	0.360	1.90	
p-Cl	H	0.8851	5.19	0.5910	4.34[c]	0.4458	1.01	42.2	0.426	48.3	0.488	0.729	0.733
p-Cl	H	0.8632	5.06	0.6522	4.79	0.4434	1.01	41.8	0.422	53.7	0.541	0.737	

[a] Internal standard: ethyl cinnamate. [b] Internal standard: chlorobenzene. [c] Internal standard: 1-chloronaphthalene.

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

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 dimethyl(*m*-trifluoromethylphenyl)silane, 0.4402 g (1.00 mmol) of phenyl(bromodichloromethyl)mercury, 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*-$CF_3C_6H_4SiMe_2CCl_2H$, 31.9%, and $C_6H_5SiMe_2CCl_2H$, 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 equation[9]

$$k_{rel} = \frac{k_{X_1}}{k_{X_2}} = \frac{P_I I_{II}}{P_{II} I_I}$$

where P_I and P_{II} are the number of mmoles of product derived from silanes I and II, respectively, and I_I and I_{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 CCl_4) in which the absence of ν_{Si-H} at 2100 cm^{-1} and the presence of ν_{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 $PhHgCCl_2Br$ and 1.66 g (14.2 mmol) of Et_3SiD in 20 ml of benzene at reflux for 4 hr gave phenylmercuric bromide in 95% yield and Et_3SiCCl_2D in about 85% yield. Pure samples ($n^{25}D$ 1.4662) were collected by glpc (3.5 ft × 10 mm i.d. glass column packed with Dow Corning 710 silicone oil on Chromosorb P, 140°, 15 psi of helium).

Anal. Calcd for $C_7H_{15}DCl_2Si$: 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 Et_3SiCCl_2D (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 CCl_4) showed only a complex pattern from 0.5 to 1.2 ppm, which was identical with the C_2H_5 resonance observed in the nmr spectrum of Et_3SiCCl_2H, and no resonance due to CCl_2H 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 ($Et_3Si^+ \equiv 100$)): 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 ($(C_2H_5)_3Si^{28}CCl^{35}Cl^{35}D$, *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° 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_3SiCCl_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.

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