After the pentane solution had been dried over magnesium sulfate it was concentrated by distilling the pentane through a semimicro column (30 × 1 cm) packed with glass helices. After most of the pentane had been distilled, 2 ml of chlorobenzene was added to the distillation flask. The distillation was continued and the portion boiling from 70 to 120° was collected. This material was analyzed by vpc at 98° on a 20 ft × ⅜ in. column packed with 30% SE-30 on Chromosorb 60–80 mesh.

Isolation of 3-Nortricyclenecarboxylic Acid.—A 60-ml separatory funnel was attached at its stem to a piece of glass capillary tubing (i.d. 1.0 mm). A second 60-ml separatory funnel was attached to a piece of capillary tubing (i.d. 1.7 mm). The smaller capillary tubing was joined to the larger one and the larger tubing was cut off 2 cm below the junction. By trial and error, conditions were found under which equivalent amounts of sodium biphenyl (1 M) in glyme and a mixture of dehydronorbornyl chloride and nortricyclyl chloride (*ca.* 80:20) would pass through the capillary tubes and meet at the junction. The funnel attached to the larger capillary was charged with 60 ml of 1 M sodium biphenyl in glyme and in the other funnel was placed 2.5 g of the chloride mixture. A slight pressure of nitrogen was applied to the funnel containing the chloride mixture and the stopcocks on the two funnels were opened simultaneously. As the reaction mixture issued from the capillary tubing, it dropped into an excess of vigorously stirred crushed Dry Ice. After the reaction was complete, the Dry Ice was allowed to sublime. The yellow liquid residue was treated with 50 ml of water and extracted with one 100-ml and two 50-ml portions of ether. The aqueous solution was acidified with concentrated hydrochloric acid and extracted with three 40-ml portions of ether. The combined ether extracts were washed with 10 ml of saturated sodium chloride solution and then dried over magnesium sulfate. After removal of the magnesium sulfate by filtration and concentration of the ether in a rotary evaporator, there remained approximately 1.5 g of a viscous yellow oil. Thin layer chromatography on silica gel indicated the presence of at least five components. Chromatography of 0.75 g of the oil on a 1 × 45 cm column and elution with 2% ether in Skelly-B resulted in the isolation of 237 mg of a foul-smelling amber oil. Thick layer chromatography of this material on silica gel and developing with 5% methyl alcohol in ether resulted in the isolation of 103 mg of a yellow-brown oil. Trituration of this oil with pentane followed by evaporation of the solvent left 80 mg of amber oil. Vapor phase chromatography of this oil (on a 7 m × 0.25 in. stainless steel column packed with 20% QF-1-0065 on 70–80 mesh Anakrom ABS) indicated the presence of three components. A minor component had the same retention time as biphenyl and the major component (probably 80% of the mixture assuming equal detector response) had the same retention time as authentic 3-nortricyclenecarboxylic acid. By collecting the major component of a portion of the mixture by gas chromatography on a 20 ft × ⅜ in. column packed with 30% QF-1-0065 on Anakrom SD 70–80 mesh, 14 mg of 3-nortricyclenecarboxylic acid was obtained. After one recrystallization from pentane, it had mp 49.5–51.6° (lit.[9] mp 49–50°) and a mixture melting point with an authentic sample was not depressed. The ir spectra of the major component of the oil and of authentic 3-nortricyclenecarboxylic acid were identical. Whether or not 5-norbornene-2-carboxylic acid was present was not determined.

The Addition of Trichloromethyl Radicals to Alkenylsilanes[1]

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Dibenzoyl peroxide catalyzed addition of bromotrichloromethane to various types of vinyl- and ω-alkenylsilanes have been investigated. Six new addition compounds have been prepared and characterized. It has been found that the reactivity of the double bond in the series of $R(CH_3)_2SiCH=CH_2$, where R = Me, Et, *i*-Pr, and *t*-Bu, toward addition of the trichloromethyl radical is governed by the Taft steric factor, E_s, of R, while the reactivity in the series of $Cl_n(CH_3)_{3-n}SiCH=CH_2$ is approximately related to the inductive effect. In the series of $(CH_3)_3Si(CH_2)_nCH=CH_2$, where n = 0–4, the reactivity reaches a maximum when n = 1. Factors influencing the reactivity have been discussed.

The addition of reagents across the double bond of vinyl- and alkenylsilanes is one of the most useful reactions in preparing carbon-functional organosilicon compounds.[2] These reagents can involve electrophilic and nucleophilic ones, as well as free-radical, or carbene intermediates and the influence of the silicon atom upon the reactivities has been one of the fascinating problems in organosilicon chemistry.

Bromotrichloromethane has been known to undergo the reaction resulting in the formation of a carbon-carbon bond *via* the free-radical mechanism.[3a] A useful tabular survey[3b] has been compiled by Walling and Huyser.

For vinylsilanes, some examples of addition products with bromotrichloromethane by the free-radical mechanism have been reported; thus, dibenzoyl peroxide catalyzed[4] and light-induced[5] addition to (trichloro)-vinylsilane, light-induced addition to (methyldichloro)-vinylsilane,[4] and dibenzoyl peroxide catalyzed addition to (triphenyl)vinylsilane[6] are known. However, no systematic study on the reactivity of vinyl- and alkenyl-substituted silanes toward free radicals has been undertaken.

During the course of studies on the structure and reactivity in the homolytic process, we have been interested in the reactivities of these compounds toward the trichloromethyl radical and have found an interesting effect of rate enhancement of trimethylsilyl-methyl group in the free-radical addition reaction of bromotrichloromethane to substituted ethylenes.

(1) Presented in part at the 7th Symposium on Free-Radical Reactions, Osaka, Japan, Nov 30, 1966; Preprint, p 17.

(2) (a) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, Chapter 14; (b) V. Bažant, V. Chvalovský, and J. Rathousky, "Organosilicon Compounds," Publishing House of the Czechoslovak Academy of Sciences, Prague, 1965, p 292.

(3) (a) M. S. Kharasch, W. Nudenberg, and E. Simon, *J. Org. Chem.*, **18**, 328 (1953); (b) C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 91 (1963).

(4) Midland Silicones Ltd., British Patent 769,499 (1957); *Chem. Abstr.*, **51**, 13903 (1957).

(5) A. M. Geyer, R. N. Haszeldine, K. Leedham, and R. J. Marklow, *J. Chem. Soc.*, 4472 (1957).

(6) R. K. Freidlina, G. T. Martirosyan, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **137**, 1129 (1961); *Chem. Abstr.* **55**, 19842 (1961).

TABLE I
#### BOILING POINTS AND CH_2 WAGGING FREQUENCIES OF VINYL- AND ALKENYLSILANES[a]

Compound	Bp, °C	CH_2 wag, cm^{-1}
$Me_3SiCH=CH_2$	55	950
$EtMe_2SiCH=CH_2$	88–89	950
$i\text{-}PrMe_2SiCH=CH_2$	110	951
$t\text{-}BuMe_2SiCH=CH_2$	127	951
$ClMe_2SiCH=CH_2$	82.5–83	962
$Cl_2MeSiCH=CH_2$	91	971
$Cl_3SiCH=CH_2$	90	979
$Me_3SiCH_2CH=CH_2$	85–86.5	893
$Me_3Si(CH_2)_2CH=CH_2$	113–115	903
$Me_3Si(CH_2)_3CH=CH_2$	127–128	912
$Me_3Si(CH_2)_4CH=CH_2$	155–156	910
$Me_3SiSiMe_2CH=CH_2$	131–132	944
$Me_3SiSiMe_2CH_2CH=CH_2$	154	893

[a] Source and other physical properties are described in the Experimental Section.

In this paper, we describe the preparation of some adducts of bromotrichloromethane to vinyl- and alkenylsilanes and discuss factors influential on the relative reactivities.

Results and Discussion

Vinylsilanes were prepared conveniently from vinyl-magnesium chloride with the corresponding chloro-silanes in tetrahydrofuran (THF) (eq 1). It seems

$$RMe_2SiCl + CH_2=CHMgCl \xrightarrow{\text{THF}} RMe_2SiCH=CH_2 \quad (1)$$
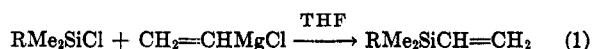
noteworthy that isopropyldimethylchlorosilane can be prepared more simply by the reaction of isopropyl-magnesium chloride with dimethyldichlorosilane in THF[7] than by the previous method[8] involving an intramolecular rearrangement of (α-chloroethyl)tri-methylsilane. However, isopropylmagnesium bromide gave less satisfactory results.

(ω-Alkenyl)trimethylsilanes were prepared according to the known procedures. Physical properties of these compounds agreed very closely with those reported. Table I lists boiling points and $=CH_2$ deformation frequencies of these compounds, other physical constants being described in the Experimental Section.

Since vinylsilanes have no or very little tendency to homopolymerize with free-radical initiators,[9] the formation of 1:1 adducts may be obtained almost quantitatively. However, because of the relatively unstable nature of the adducts, the final yields after purification are not necessarily high. Some of new addition compounds so prepared are shown in Table II.

Addition products from allyltrimethylsilane and allylpentamethyldisilane could not be isolated. It has been established that (β-bromoalkyl)trialkylsilanes are extremely unstable with respect to β eliminations; consequently, from both allylsilanes, 4,4,4-trichloro-butene-1 and the corresponding bromosilanes were obtained (eq 2 and 3). Alternatively, it seemed also possible that the intermediate radical itself would decompose into the silyl radicals and the olefin. This
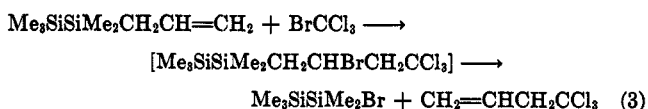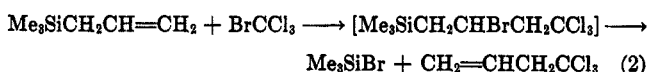
(7) H. Sakurai, N. Hayashi, and M. Kumada, unpublished materials.
(8) L. H. Sommer, D. L. Bailey, J. R. Gould, and F. C. Whitmore, *J. Amer. Chem. Soc.*, **76**, 801 (1954).
(9) H. Sakurai, K. Tominaga, and M. Kumada, *Bull. Chem. Soc. Jap.*, **39**, 1279 (1966).

TABLE II
PROPERTIES OF ADDITION PRODUCTS FROM VINYL- AND ALKENYL-SUBSTITUTED SILANES WITH BROMOTRICHLOROMETHANE

Compound	Registry no.	Yield, %	Bp, °C (mm)	$n^{20}D$	d^{20}_4	MR, deg Calcd	MR, deg Found	Anal., % C Calcd	C Found	H Calcd	H Found
$Me_3SiCHBrCH_2CCl_3$	19185-53-6	88.5	121–122 (27)	1.5024	1.4339	61.70	61.48	24.14	24.67	4.05	4.09
$EtMe_2SiCHBrCH_2CCl_3$	19185-54-7	88.8	140–143 (25)	1.5081	1.4119	66.35	66.00	26.90	26.99	4.52	4.62
$i\text{-}PrMe_2SiCHBrCH_2CCl_3$	19185-55-8	65.5	137–139 (19)	1.5069	1.3725	71.00	70.80	29.42	29.72	4.94	4.96
$t\text{-}BuMe_2SiCHBrCH_2CCl_3$	19185-56-9	64.7	145–146 (20)	1.5093	1.3490	75.65	75.43	31.74	32.04	5.33	5.51
$Me_3SiMe_2SiCHBrCH_2CCl_3$	19185-57-0	80.2	120–122 (2)	1.5139	1.3026	82.69	82.42	26.94	27.12	5.09	5.24
$Me_3(SiCH_2)_2CHBrCH_2CCl_3$	19185-58-1	49.1	137–142 (20)	1.4940	1.3409	71.00	70.90	29.42	29.81	4.94	5.03

$$Me_3SiCH_2CH=CH_2 + BrCCl_3 \longrightarrow [Me_3SiCH_2CHBrCH_2CCl_3] \longrightarrow$$

$$Me_3SiBr + CH_2=CHCH_2CCl_3 \quad (2)$$

$$Me_3SiSiMe_2CH_2CH=CH_2 + BrCCl_3 \longrightarrow$$

$$[Me_3SiSiMe_2CH_2CHBrCH_2CCl_3] \longrightarrow$$

$$Me_3SiSiMe_2Br + CH_2=CHCH_2CCl_3 \quad (3)$$

may be regarded as the reverse process of the free-radical addition of the silyl radical to olefin (eq 4).

$$Me_3SiCH_2\dot{C}HCH_2CCl_3 \longrightarrow Me_3Si\cdot + CH_2=CHCH_2CCl_3 \quad (4)$$

However, the following facts may exclude this possibility. Thus, Topchiev, *et al.*,[10] have reported that dibenzoyl peroxide catalyzed reaction of trichlorosilane and methyl(diphenyl)allylsilane effected smooth addition (eq 5).

$$HSiCl_3 + CH_2=CHCH_2SiMePh_2 \xrightarrow{\text{(PhCOO)}_2}$$

$$Cl_3SiCH_2CH_2CH_2SiMePh_2 \quad (5)$$
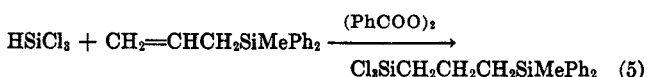
We have also observed that thiophenol added to trimethylallylsilane with peroxide to give (3-phenylthiopropyl)trimethylsilane in good yield (eq 6). These

$$PhSH + CH_2=CHCH_2SiMe_3 \xrightarrow{\text{(PhCOO)}_2} PhSCH_2CH_2CH_2SiMe_3$$

$$(6)$$
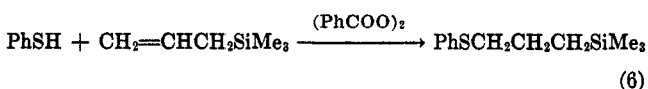
facts support that the intermediate free radicals from allylsilanes are stable enough not to decompose. Even if the intermediate free radicals decompose partly, still addition of the trichloromethyl radicals should be rate controlling, since the trichloromethyl radicals may be regenerated very rapidly from bromotrichloromethane by bromine abstraction with silyl radicals.

In Table III are listed the data of relative reactivities for alkenyltrimethylsilanes toward the addition of trichloromethyl radical measured by the disappearance of the olefin in competitive reaction conditions. Vinyltrimethylsilane was taken as the reference standard.

The addition of the trichloromethyl radical to carbon–carbon double bond is an example of well-

Figure 1.—Correlation of $1 + \log (k/k_0)$ and E_s of R for the addition of the trichloromethyl radical to $R(CH_3)_2SiCH=CH_2$ at 80.0°.

analyzed free-radical reactions.[11] For aliphatic 1 olefins (reaction 7), the excellent linear correlation of the rate data by the Hammett–Taft equation[12] has been observed.

$$X(CH_2)_nCH=CH_2 + CCl_3\cdot \longrightarrow X(CH_2)_n\dot{C}HCH_2CCl_3 \quad (7)$$

Since steric effects are considered to be constant for the compounds studied by Martin and Gleicher, the rate constant of the reaction 7 would be governed only by the inductive polar effects of the substituent.

In a series of vinylsilanes of the $R_3SiCH=CH_2$ type, Eisch and Trainor[13] have pointed out that there exists a good correlation between the position of the CH_2 deformation frequency (CH_2 wag) and the electronic effect of R as measured by σ_{para}. In the series of vinylsilanes, $RMe_2SiCH=CH_2$, where R = Me, Et, *i*-Pr, and *t*-Bu, CH_2 wag frequencies are in the same position as seen in Table I, indicative of virtually constant electronic effect of silyl groups, RMe_2Si-, toward the carbon–carbon double bond regardless of the nature of an alkyl group. Therefore, the governing factor in the rates of the series of $R(CH_3)_2SiCH=CH_2$ seems to be only steric effects, where the relative rates are correlated with Taft steric factors,[12] E_s, of R as shown in Figure 1 above.

TABLE III
RELATIVE REACTIVITIES OF ALKENYLSILANES TOWARD TRICHLOROMETHYL RADICAL AT 80.0° IN CHLOROBENZENE

Compound	Relative rate, $k/k_0{}^a$
$RMe_2SiCH=CH_2$	
$Me_3SiCH=CH_2{}^b$	1.00
$EtMe_2SiCH=CH_2$	0.945 ± 0.005
i-$PrMe_2SiCH=CH_2$	0.867 ± 0.005
t-$BuMe_2SiCH=CH_2$	0.694 ± 0.000
$Cl_nMe_{3-n}SiCH=CH_2$	
$Me_3SiCH=CH_2{}^b$	1.00
$ClMe_2SiCH=CH_2$	0.851 ± 0.05
$Cl_2MeSiCH=CH_2$	0.753 ± 0.002
$Cl_3SiCH=CH_2$	0.476 ± 0.068
$Me_3Si(CH_2)_nCH=CH_2$	
$Me_3SiCH=CH_2{}^b$	1.00
$Me_3SiCH_2CH=CH_2$	8.34 ± 0.84
$Me_3Si(CH_2)_2CH=CH_2$	1.60 ± 0.40
$Me_3Si(CH_2)_3CH=CH_2$	1.09 ± 0.00
$Me_3Si(CH_2)_4CH=CH_2$	0.94
1-Heptene	1.05 ± 0.01

^{a} Deviations listed for two runs. ^{b} Vinyltrimethylsilane was taken as the reference standard.

Figure 2.—Correlation of $1 + \log (k/k_0)$ and the number of the chlorine atom in $Cl_n(CH_3)_{3-n}SiCH=CH_2$ for the addition of the trichloromethyl radical at 80.0°.

(10) A. V. Topchiev, N. S. Nametkin, T. I. Chernysheva, and S. G. Drgaryan, *Dokl. Akad. Nauk SSSR*, **110**, 97 (1956); *Chem. Abstr.*, **51**, 4979 (1957).
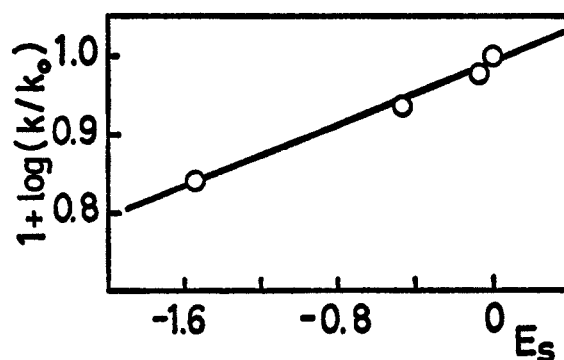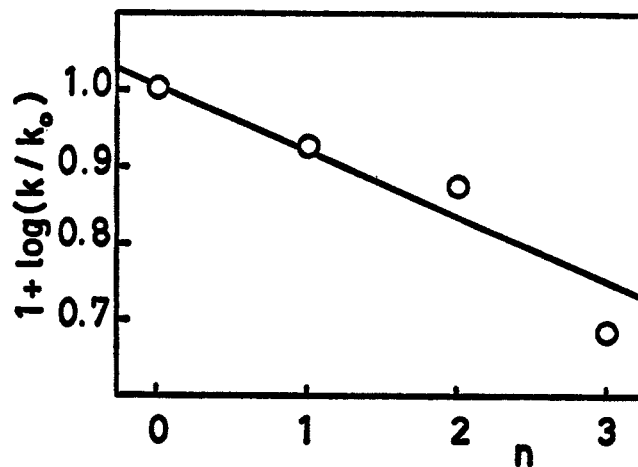
(11) M. M. Martin and G. J. Gleicher, *J. Amer. Chem. Soc.*, **86**, 233, 238, 242 (1964), and references cited therein.

(12) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 13.

(13) J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 487 (1963).

In the series of vinylsilanes of the $(CH_3)_nCl_{3-n}SiCH=CH_2$ type, situations are more complicated than those of peralkylvinylsilanes, since, when the silicon atom binds electronegative atoms or groups capable of the $(p \rightarrow d)_\pi$ interactions between them, the orignal $(p \rightarrow d)_\pi$ bond between silicon and vinyl group may be influenced in a way.[14] Therefore, a simple summation of electron-releasing and -withdrawing inductive effect of methyl and chloro group, respectively, does not account fully for the reactivity; however, as shown in Figure 2, a general trend may be explained in this way.

The most striking feature seen in Table III is an enhancement of rate in allyltrimethylsilane compared with that in other ω-alkenyltrimethylsilanes.

The relative reactivities of silyl-substituted olefins toward carbethoxycarbene[15] and dichlorocarbene[16,17] have also been found to show enhanced reactivities of allylsilanes compared with those of vinylsilanes. For example, Culdín and Chvalovský[16b] have recorded the relative rates of the following olefins to addition of the dichlorocarbene as generated by the reaction of chloroform with potassium *t*-butoxide at $-30°$: Me_3SiCH_2-$CH=CH_2$ (4.97) > $Me_3SiCH_2CH_2CH=CH_2$ (1.20) > 1-heptene (1.00, standard) $\gg Me_3SiCH=CH_2$ (0.0474).

Since these carbenes as well as the trichloromethyl radical are electron seeking in nature, the relative reactivities toward these species decrease with decreasing nucleophilic character of the olefin. The marked inertness of vinylsilanes toward the dichlorocarbene has been ascribed to a decrease in the nucleophilicity of the carbon–carbon double bond in the vinylsilane due to the overlap of olefinic π bond with vacant d_π orbitals of silicon atom.[14,16,18] However very recently, Seyferth and Dertouzos have pointed out the importance of steric hindrance to attack of the dichlorocarbene in addition to the still important $(p \rightarrow d)_\pi$ bonding effect.[17] Such steric factors seem quite relevant in view of the somewhat crowded structures in the transition state proposed for carbene addition.[19] On the other hand, the relatively high reactivity of allyltrimethylsilane was rationalized in terms of an electron-releasing inductive effect of the trimethylsilyl group.[17] In this case, the trimethylsilyl group is separated from the carbon–carbon double bond by a methylene group; therefore, no decreasing effect on the nucleophilicity of the double bond by $(p \rightarrow d)_\pi$ bonding nor steric hindrance can be operated.

The relative reactivities toward the trichloromethyl radical in the present study show that vinyltrimethylsilane is no more unreactive than 1-heptene. Therefore, addition of the radical may lead to less crowded transition state; yet bulkiness of alkyl groups on silicon can be the controlling factor as evidenced in Figure 1. Obviously, the electron-releasing inductive effect of trimethylsilyl group should be responsible for the en-
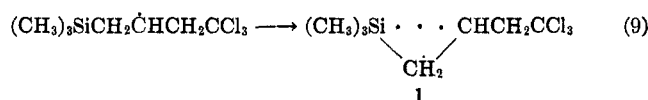
hanced reactivity of allyltrimethylsilane. If inductive effect is the sole factor, however, the relative rate of allyltrimethylsilane to 3-butenyltrimethylsilane may be estimated on the following basis. Since the ρ^* value of the reaction 7 has been known to be -0.42 with σ^* values of $X(CH_2)_n$ groups, where $n = 1, 2,$ and 3,[11] the relative rate of allytrimethylsilane to (3-butenyl)trimethylsilane can be calculated approximately as 1.2 from the reported σ^* value for trimethylsilylmethyl group.[20] Therefore, rate enhancement in allyltrimethylsilane appears too great to be expected if other factors would be equal. Since the extra steric effect of trimethylsilylmethyl group, if any, should decrease the reactivity, the enhancement in the reactivity of allyltrimethylsilane must arise from an extra resonance effect in the intermediate free radical.

Recent investigations of homolytic arylation to substituted benzene by Simamura and coworkers[21] have elegantly shown that the influence of a substituent can be divided into resonance and inductive effects. For *meta* substitution, only the latter term was predominant, while, for *para* substitution, partial rate factors were expressed as eq 8 where τ_{para} is the term of additional

$$\log (k/k_0) = \rho\sigma_{para} + \tau_{para} \qquad (8)$$

stabilization correlated with the difference of the extra resonance energy between the substrate and the substituted cyclohexadienyl radical.

Therefore, an enhanced reactivity observed for allyltrimethylsilane in the present case would also be ascribed to an extra resonance effect in the intermediate radical. We propose the homoconjugation shown in eq 9 of an odd electron with the 3d orbitals of silicon as a sort of an extra resonance effect.

$$(CH_3)_3SiCH_2\dot{C}HCH_2CCl_3 \longrightarrow (CH_3)_3Si \cdot \cdot \cdot CHCH_2CCl_3 \qquad (9)$$
$$\diagdown \diagup$$
$$CH_2$$
$$\mathbf{1}$$

Price and Yukuta[22] have currently reported a greater reactivity of allylsilanes $(Q \simeq 0.06)$ compared with that of vinylsilanes $(Q \simeq 0.03)$ in the free-radical colpolymerization and suggested that such enhanced reactivity of allylsilanes could arise either from the homoconjugation like **1** or hyperconjugation such as **2** (eq 10). The latter conjugation involves the carbon–

$$\sim\dot{C}H-CH_2-SiR_3 \longleftrightarrow \sim CH=CH_2 \cdot SiR_3 \qquad (10)$$
$$\mathbf{2}$$
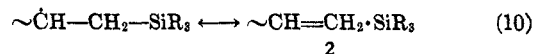
silicon-bonding electrons, and, hence, may resemble to the concept of $\sigma-\pi$ conjugation proposed by Russian workers[23] to explain the high reactivity of allylsilanes compared with that of vinylsilanes toward rhodanation. However, the fact that e value for allytrimethylsilane

(14) For pertinent review of this problem, see V. Chvalovský, *Pure Appl. Chem.*, **13**, 231 (1966).

(15) I. A. Dyakonov, G. V. Golodnikov, and I. B. Repinskaya, *Zh. Obshch. Khim.*, **35**, 2181 (1965); *Chem. Abstr.*, **64**, 11238 (1966).

(16) (a) J. Culdín and Chvalovský, *Collection Czech. Chem. Commun.*, **27**, 1658 (1962); (b) *ibid.*, **28**, 3088 (1963).

(17) D. Seyferth and H. Dertouzos, *J. Organometal. Chem.*, **11**, 263 (1968).

(18) For pertinent reviews of such π bonding in vinylsilanes, see D. Seyferth, *Progr. Inorg. Chem.*, **3**, 129 (1962); see also ref 1b and 13.

(19) (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, pp 163–172; (b) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964, pp 42–44.

(20) Only σ^* for trimethylsilylmethyl group is known to be -0.26,[11] but it has been established that the interposition of a methylene group decreases σ^* values by a factor of 2.3 to 3.3. For pertinent reviews of this topic, see (a) S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964); (b) C. D. Ritchie and W. F. Sager, *ibid.*, **2**, 323 (1964).

(21) R. Itô, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

(22) C. C. Price and T. Yukuta, International Symposium on Macromolecular Chemistry, Tokyo and Kyoto, Sept 28–Oct 4 (1966), Abstracts I-17.

(23) (a) A. A. Bugorkova-Zelenetskaya, V. F. Mironov, and A. D. Petrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 474 (1960); *Chem. Abstr.*, **54**, 22328 (1960); (b) E. A. Chernyshev, N. G. Tolstikova, A. A. Ivashenko, A. A. Zelenetskaya, and L. A. Leites, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 660 (1963); *Chem. Abstr.*, **59**, 7552 (1963).

($e = 0.01$) is more positive than that of vinyltrimethylsilane ($e = -0.14$) could be the evidence in favor of the homoconjugation process at least in the free-radical intermediates, since the positive e value suggests that the silyl group is accepting electrons.[22]

This sort of a silyl-bridged radical has also been suggested as a possible intermediate for *trans* addition of trichlorosilane to 1-methylcyclohexene[24] in an analogous way to bromine-bridged[25] radicals.

Now these supporting evidences indicate such a homoconjugation to be a likely process and therefore it is concluded that an enhanced reactivity of allyltrimethylsilane toward the trichloromethyl radical is due to the homoconjugation effect as well as to the inductive effect.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen. Trimethylchlorosilane, dimethyldichlorosilane, (methyldichloro)vinylsilane, and vinyltrichlorosilane were commercial samples. Bromotrichloromethane, solvents, and other reagents were of reagent grade, and used after distillation through a 35-cm column packed with glass helicoils.

Vinylsilanes.—Trimethylvinylsilane was prepared by methylation of vinyltrichlorosilane with methylmagnesium chloride in dibutyl ether. The following were prepared according to known procedures: (ethyldimethyl)vinylsilane, bp 88–89°, n^{20}D 1.4097, d^{20}_4 0.7243 [lit.[26] bp 88° (737 mm), n^{20}D 1.4089, d^{20}_4 0.7242], MR 39.07 (calcd 39.01); (isopropyldimethyl)vinylsilane,[8] bp 110–110.5°, n^{20}D 1.4198, d^{20}_4 0.7412, MR 43.78 (calcd 43.66); (*t*-butyldimethyl)vinylsilane,[8] bp 127°, n^{20}D 1.4277, d^{20}_4 0.7497, MR 48.80 (calcd 48.31); and (dimethylchloro)vinylsilane, bp 82.5° (lit.[27] bp 82–82.5°). Vinylpentamethyldisilane[9] and allylpentamethyldisilane[23b] were also prepared by the published procedure.

Allyltrimethylsilane.—From allylmagnesium chloride and trimethylchlorosilane was prepared allyltrimethylsilane, bp 85–86.5°, n^{20}D 1.4072, d^{20}_4 0.7150 [lit.[28] bp 84.9° (737 mm), n^{20}D 1.4074, d^{20}_4 0.7193], MR 39.36 (calcd 39.01).

(**3-Butenyl**)**trimethylsilane.**[29]—This compound was prepared from trimethylsilylmethylmagnesium chloride and allyl chloride: bp 113–115°, n^{20}D 1.4141, d^{20}_4 0.7425 [lit.[30] bp 110.5° (752 mm), n^{20}D 1.4149, d^{20}_4 0.7372], MR 43.19 (calcd 43.46).

(**4-Pentenyl**)**trimethylsilane.**—4-Penten-1-ol was prepared from tetrahydrofurfuryl chloride with sodium in ether and was converted into 5-bromopentene-1 with phosphorus tribromide in pyridine. A Grignard reagent from 5-bromopentene-1 in ether was allowed to react with trimethylchlorosilane; after work-up, a mixture consisting of (4-pentenyl)trimethylsilane and other isomers (not identified) was obtained. (4-Pentenyl)-trimethylsilane was then separated from the mixture by preparative glpc on a 3-m silicone DC 550 column: bp 127–128° (as a mixture), n^{20}D 1.4232, d^{20}_4 0.7449 [lit.[31] 31–32° (14 mm), n^{20}D 1.4208, d^{20}_4 0.754], MR 48.67 (calcd 48.31).

(**5-Hexenyl**)**trimethylsilane.**[29]—From a Grignard reagent of 3-(trimethylsilyl)propyl bromide and allyl chloride was prepared (5-hexenyl)trimethylsilane, bp 155–156°, n^{20}D 1.4268, d^{20}_4 0.7673 [lit.[32] bp 158–159° (750 mm), n^{20}D 1.4246, d^{20}_4 0.7566], MR 52.29 (calcd 52.65).

Dibenzoyl Peroxide Catalyzed Addition of Bromotrichloromethane to Trimethylvinylsilane.—The next procedure may serve as a typical example for preparation of the adducts. In a glass tube, 14.87 g (0.075 mol) of bromotrichloromethane, 6.12 g (0.061 mol) of trimethylvinylsilane, and 0.10 g of benzoyl peroxide were placed. After repeated freezing and melting under vacuum, the tube was sealed and immersed in a constant-temperature bath kept at 80° for 10 hr. The reaction mixture was then fractionated; after recovering a small amount of the starting materials, 3,3,3-trichloro-1-bromopropyltrimethylsilane was obtained. Physical constants and yields together with those of other adducts are listed in Table II.

Reaction of Allyltrimethylsilane with Bromotrichloromethane.—From 4.22 g (0.037 mol) of allyltrimethylsilane, 7.32 g (0.037 mol) of bromotrichloromethane, and 30 mg of dibenzoyl peroxide, 3.76 g (0.025 mol, 66.7% yield) of trimethylbromosilane, bp 78°, and 3.02 g (0.019 mol, 51.5% yield) of 4,4,4-trichlorobutene-1, bp 120–125°, n^{20}D 1.4693, d^{20}_4 1.2852, MR 34.57 (calcd 34.67) (lit.[33] bp 128–129°, n^{20}D 1.4678) were obtained. The nmr spectrum (CCl₄) of this compound exhibited a typical allylic pattern; two methylene protons occurred as a doublet ($J = 7$ cps) with further splitting into a doublet ($J = ca.$ 1 cps) at τ 6.64, two terminal vinylic protons as a pair of doublets with further complicated splittings at 4.66 and 4.73, and an olefinic proton as a diffused multiplet at 3.7–4.4.

Dibenzoyl Peroxide Catalyzed Addition of Thiophenol to Allyltrimethylsilane.—By essentially the same procedure as addition of bromotrichloromethane to vinyltrimethylsilane, 5.10 g (0.045 mol) of allyltrimethylsilane, 10.94 g (0.099 mol) of thiophenol, and 0.128 g (0.53 mmol) of dibenzoyl peroxide were subjected to reaction and, after fractional distillation through a 35-cm column packed with glass helices, 6.0 g (0.027 mol, 60.5 % yield) of pure 3-trimethylsilylpropyl phenyl sulfide was obtained: bp 140° (14 mm), n^{20}D 1.5287, d^{20}_4 0.9559, MR 72.38 (calcd 71.81). The nmr (CDCl₃) spectrum exhibited a sharp singlet at τ 9.97 (9 H, trimethylsilyl group), a multiplet at 9.15–9.5 (2 H, α-methylene to silicon), a multiplet at 7.95–8.6 (2 H, central methylene), a triplet ($J = 7.5$ cps) at 7.02, and an aromatic multiplet at 2.7.

Anal. Calcd for $C_{12}H_{20}SSi$: C, 64.22; H, 8.98. Found: C, 64.29; H, 9.21.

Procedure for Kinetic Runs.—Samples of olefin (A), trimethylvinylsilane (B, standard olefin), and carbon tetrachloride (internal standard) were accurately weighed into a flask, to which 5 ml of bromotrichloromethane and 10 ml of chlorobenzene containing dibenzoyl peroxide were added. A reactant ratio of bromotrichloromethane/trimethylvinylsilane/olefin/carbon tetrachloride/dibenzoyl peroxide of 4:1:1:0.75:0.012 was employed. In a glass tube the reaction mixture was then placed and degassed by repeated freezing and melting under vacuum. The tube was then sealed under vacuum and immersed in a constant-temperature bath kept at 80° for 0.5–1 hr. The extent of total olefin consumption varied from 30 to 60%. The mixtures were analyzed by glpc on a column packed with polyethylene glycol 20M or Apiezon L using helium as a carrier gas. In each run, the amount of chloroform was negligibly small, mostly not detectable, indicative of the absence of hydrogen abstraction by the trichloromethyl radical as a side reaction. The ratio of rate constants for addition was calculated by the usual expression shown in eq 11.

$$(k_A/k_B) = \frac{\log \text{(initial moles of A/final moles of A)}}{\log \text{(initial moles of B/final moles of B)}} \quad (11)$$

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(29) The authors are indebted to Mr. Isao Nakajima for the preparation of this compound.

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