Organosilicon Compounds with Functional Groups Proximate to Silicon. I. Epoxidation and Infrared Studies of Vinylsilanes

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To investigate the behavior of organic functional groups adjacent to silicon, a series of vinylsilanes of the type, $R_3SiCH{=}CH_2$, was prepared, where R = ethyl, benzyl, phenyl, or a *p*-substituted phenyl group. Epoxidation of these vinylsilanes with peroxytrifluoroacetic acid generally afforded good yields of the corresponding epoxyethylsilanes, except when R was a labile group such as *p*-anisyl. The behavior of such epoxides, α,β to silicon, will be discussed in future papers. An infrared study of the CH_2 wag frequency of the preceding vinylsilanes revealed a correlation between the position of this frequency and the electron-withdrawing power of R, as measured by σ_p or σ^*. Although the CH_2 wag frequency for substituted vinylsilanes of the type, $Y_3SiCH{=}CH_2$, did increase as the σ^* value of Y increased, the trend deviated appreciably from a linear correlation. On the other hand, the use of σ_p values instead for the substituents Y revealed an excellent linear correlation of σ_p with the CH_2 wag frequency. The electronic implications of the foregoing observations are discussed in terms of the inductive and resonance effects of substituents attached to silicon.

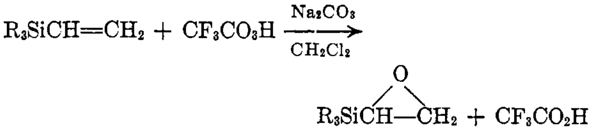
The organic chemistry of organosilicon compounds containing functional groups adjacent to the silicon atom often departs strikingly from that observed with the corresponding carbon compounds.[2] In order to learn more about the effect of silicon on the behavior of a proximate organic functional group, a systematic study of unexplored organosilicon compounds with functional carbon groups α or β with respect to the silicon atom has been undertaken. With this goal in mind, it became of interest to investigate the preparation and behavior of epoxyethylsilanes, since it is well known that the epoxide linkage exhibits a high order of reactivity toward a variety of reagents.[3] The present study describes the preparation of a series of vinylsilanes and their epoxidation to yield the corresponding epoxyethylsilanes. Further papers in this series will deal with the novel chemical behavior of these epoxides.[4] In addition, an infrared study of these silicon-substituted vinylsilanes has uncovered an illuminating correlation between the frequency of the vinyl CH_2 out-of-plane deformation (CH_2 wag) and the electronic nature of the substituent.

Preparation and Epoxidation of Vinylsilanes.—The requisite vinylsilanes were prepared by the interaction of an excess of the appropriate Grignard reagent with trichlorovinylsilane (equation 1). The use of tetrahydrofuran (THF) as the reaction medium generally resulted in considerably higher yields than those reported for analogous preparations conducted in ethyl ether.[5] The pertinent experimental conditions and the physical constants of the resulting vinylsilanes are summarized in Table I. The *para* substituents in the triarylvinylsilanes were chosen to embrace a breadth of electron availability; unfortunately, certain groups, such as nitro and carbalkoxyl, could not be employed in this series, since they are incompatible with the Grignard method of preparation.

$$Cl_3SiCH{=}CH_2 + 3RMgX \xrightarrow[THF]{} R_3SiCH{=}CH_2 + 3MgClX \quad (1)$$

Although several reports on the successful preparation of epoxyalkoxysilanes[6] and epoxyalkylsiloxanes[7] have appeared, previous work with epoxyalkylsilanes has been sparse. Aside from the synthesis of β,γ- and γ,δ-epoxyalkylsilanes, and other systems having the epoxide linkage further removed from silicon,[8] the first studies concerning the preparation of α,β-epoxyalkylsilanes appeared during the course of the present research.[7a,b,9] (However, up to the present, no reactions of α,β-epoxyalkylsilanes have been reported.) These workers epoxidized trialkylvinylsilanes in poor to moderate yields by the use of peracetic,[7a] monoperphthalic,[7b] and perbenzoic[9] acids. In the present study such epoxidizing agents were found to be extremely slow in their action and to give very poor yields of epoxyethyltrialkylsilanes. Furthermore, the small amounts of distilled epoxyethyltrimethylsilane and epoxyethyltriethylsilane, as obtained from just such published procedures,[7b,9] were contaminated with difficultly separable carbonyl impurities (*cf.* Experimental).

A superior epoxidation reagent for vinylsilanes was found to be a solution of peroxytrifluoroacetic acid in methylene chloride with suspended sodium carbonate as a trifluoroacetic acid scavenger[10] (equation 2). The pertinent data on the epoxides prepared by this method are summarized in Table II.



$$R_3SiCH{=}CH_2 + CF_3CO_3H \xrightarrow[CH_2Cl_2]{Na_2CO_3} R_3Si\overset{\overset{O}{\diagup\ \diagdown}}{CH{-}CH_2} + CF_3CO_2H \quad (2)$$

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[1] Raybestos-Manhattan Predoctoral Fellow, 1959–1962.

[2] *Cf.* C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, especially chap. 4 and 14, for a superb, comprehensive treatment of carbon-functional organosilicon compounds.

[3] (a) R. E. Parker, *Chem. Rev.*, **59**, 737 (1959), has presented a critical treatment of the mechanisms of epoxide reactions; (b) E. L. Eliel in M. S. Newman, ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 106–114.

[4] A typical example of the unusual behavior of this epoxide system is that its reduction with lithium aluminum hydride leads to the β-silylethanol, $R_3SiCH_2CH_2OH$, as the predominant product.

[5] R. Nagel and H. W. Post, *J. Org. Chem.*, **17**, 1379 (1952).

[6] (a) R. M. Martin, U. S. Patent 2,730,532 (January, 1956) (Shell Development Co.) [*Chem. Abstr.*, **50**, 12108 (1956)]; (b) K. A. Andrianov and V. G. Dubrovina, *Dokl. Akad. Nauk, SSSR*, **108**, 83 (1956) [*Chem. Abstr.*, **50**, 14517 (1956)].

[7] (a) E. P. Plueddemann and G. Fanger, *J. Am. Chem. Soc.*, **81**, 2632 (1959); (b) V. Bazant and V. Matousek, *Collection Czech. Chem. Commun.*, **24**, 3758 (1959) [*Chem. Abstr.*, **54**, 7607 (1960)]; (c) G. Gerber and L. Metzinger, *Makromol. Chem.*, **39**, 167 (1960).

[8] (a) S. Brynolf, *Acta Chem. Scand.*, **10**, 883 (1956); (b) S. I. Saykh-Zade, L. V. Nozdrina, and A. D. Petrov, *Dokl. Akad. Nauk, SSSR*, **118**, 723 (1958) [*Chem. Abstr.*, **52**, 11805 (1958)]; (c) L. L. Shchukovskaya and A. D. Petrov, *Izv. Akad. Nauk, SSSR, Otd. Khim. Nauk*, 1011 (1958) [*Chem. Abstr.*, **53**, 119 (1959)]; (d) R. Neville, *J. Org. Chem.*, **25**, 807, 1063 (1960); **26**, 3031 (1961).

[9] Tsin-LiChow, *Hua Hsueh Hsueh Pao*, **24**, 426 (1958) [*Chem. Abstr.*, **54**, 471 (1960)].

[10] W. D. Emmons and A. S. Pagano, *J. Am. Chem. Soc.*, **77**, 89 (1955).

TABLE I

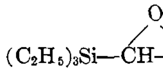
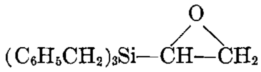
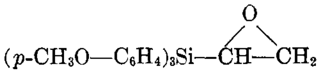
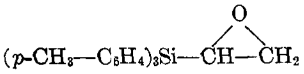
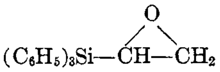
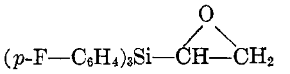
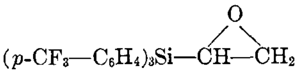
PREPARATION OF VINYLSILANES FROM TRICHLOROVINYLSILANE AND ORGANOMETALLIC REAGENTS

Compound	Yield, %	M.p., °C.	Organometallic reagent	Solvent	Time, hr.	Temp.	Calcd. C	Calcd. H	Found C	Found H	Ref.
$(C_2H_5)_3SiCH{=}CH_2$	76	145° (b.p.)	C_2H_5MgBr	Ethyl ether	72	Reflux	...	...	...	...	5
$(C_6H_5CH_2)_3SiCH{=}CH_2$	80	80	$C_6H_5CH_2MgCl$	Ethyl ether	18	Room temp.	...	...	...	...	5
$(C_6H_5)_3SiCH{=}CH_2$	91	72	C_6H_5MgBr	THF	40	Reflux	...	...	...	...	5
$(p\text{-}CH_3\text{-}C_6H_4)_3SiCH{=}CH_2$	83	84	$p\text{-}CH_3\text{-}C_6H_4MgBr$	THF	56	Reflux	8.55%	Si	8.54%	Si	
$(p\text{-}CH_3O\text{-}C_6H_4)_3SiCH{=}CH_2$	80	89	$p\text{-}CH_3O\text{-}C_6H_4MgBr$	THF	42	Reflux	73.37	6.42	73.36	6.45	
$(p\text{-}F\text{-}C_6H_4)_3SiCH{=}CH_2$	65	71	$p\text{-}F\text{-}C_6H_4MgBr$	THF	44	Reflux	70.56	4.44	70.39	4.37	
$(p\text{-}CF_3\text{-}C_6H_4)_3SiCH{=}CH_2$	49	100	$p\text{-}CF_3\text{-}C_6H_4MgBr$	Ethyl ether[a]	48	Room temp.	56.32	3.08	56.54	3.36	
$(C_6H_5)_2ClSiCH{=}CH_2$	42	125 0.5 mm. (b.p.)	C_6H_5Li	Ethyl ether	[b]	−45°	68.69	5.32	68.81	5.32	19

[a] With tetrahydrofuran a poor yield of the Grignard reagent was obtained. [b] Phenyllithium was added to trichlorovinylsilane at −45° and the system was allowed to warm to 0°.

TABLE II

PREPARATION OF EPOXYETHYLSILANES

Compound	Yield, %	M.p., °C.	Calcd. C	Calcd. H	Found C	Found H	Reaction time, hr.	Infrared epoxide absorption cm.⁻¹
	62	B.p. 184 (740 mm.)	60.70	11.46	60.89	11.24	0.33	890
	54[a]	65	80.18	7.02	80.13	6.96	5	880
	22[b]	94–95	70.38	6.16	70.39	6.16	20	877
	57	84–85	80.18	7.02	80.26	6.91	2	887
	84	85–86	79.43	5.99	79.28	6.02	4	875
	81	72–73	67.39	4.24	67.66	4.45	10	882
	80	98–99	54.55	2.99	54.78	3.28	10	875

[a] 0.2-mole sample of olefin with trifluoroacetic acid from 0.50 mole of hydrogen peroxide was used. [b] Monoperphthalic acid method.

In general, the epoxides were obtained in good to excellent yields. Since this epoxidation proceeded more rapidly than with other peracids, the shorter reaction times usually allowed degradative side reactions to be minimized. The importance of temperature and time is seen in the fact that the attempted epoxidation of triethylvinylsilane over a prolonged period at the reflux temperature of methylene chloride (40°) gave no isolable epoxide. In addition, several attempts to epoxidize tri-*p*-anisylvinylsilane under the conditions so successful with the other vinylsilanes met with complete failure. The pronounced tendency of *p*-anisyl groups to be cleaved from silicon by acids may be the basis for this failure.[11] Alternatively, the recent finding that peroxytrifluoroacetic acid attacks anisole to form *o*- and *p*- hydroxyanisoles[12] suggests that the failure to isolate the desired epoxide may have been due to the predominance of hydroxyldesilylation of the silicon–*p*-anisyl linkage. Therefore, recourse to the monoperphthalic acid method was necessary to obtain even a 22% yield of tri-*p*-anisylepoxyethylsilane. In the cases of the solid epoxides, column chromatography of the crude products provided epoxyethylsilanes free of carbonyl-containing impurities. As a characteristic infrared absorption of the epoxide linkage the strong band between 875 and 890 cm.⁻¹ proved most helpful.

Infrared Studies of Vinylsilanes.—In a recent study of the out-of-plane hydrogen deformation frequencies in substituted ethylenes it was found that the frequency of the CH_2 deformation (CH_2 wag) in compounds of the type, $Y{-}CH{=}CH_2$, increases as the π-electron-attracting power of Y becomes greater.[13] Although the correlation was not linear, the observed trend was best

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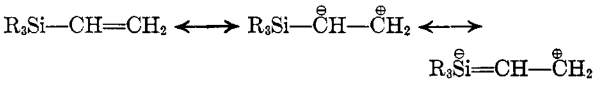
[11] C. Eaborn, *J. Chem. Soc.*, 4859 (1956), determined the following relative rates for the protodesilylation of a series of aryltrimethylsilanes with perchloric acid: *p*-anisyl, 1510; *p*-tolyl, 21; phenyl, 1.0; *p*-fluorophenyl, 0.75.

[12] J. D. McClure and P. H. Williams, *J. Org. Chem.*, **27**, 627 (1962).

[13] W. J. Potts and R. A. Nyquist, *Spectrochim. Acta*, **15**, 679 (1959).

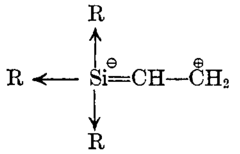
related to the quantity, $\sigma_p - \sigma'$, which measures the resonance polar effect of the substituent Y.[14] In the same study[13] several vinylsilanes were also examined and the abnormally high frequency of the CH_2 wag was noted. However, it was stated merely that an electropositive group, such as R_3Si (R = alkyl, phenyl, chloro), raises the frequency of this deformation.

A substantial body of evidence indicates that silicon may interact with an adjacent unsaturated system through overlap of the π-orbital with a d-orbital of silicon (I).[15] Therefore, spectral evidence was sought



$$R_3Si{-}CH{=}CH_2 \longleftrightarrow R_3Si{-}\overset{\ominus}{C}H{-}\overset{\oplus}{C}H_2 \longleftrightarrow R_3\overset{\ominus}{Si}{=}CH{-}\overset{\oplus}{C}H_2 \quad \text{(I)}$$

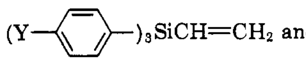
for such π-electron withdrawal by examining the infrared spectra of a number of vinylsilanes. With reference to previous findings with substituted ethylenes,[13] an electron-withdrawing group R in vinylsilanes would be expected to enhance the extent to which silicon permits delocalization of the π-electrons of an adjacent vinyl group (II). Such a π-electron withdrawal might



II

be reflected in a shift of the CH_2 wag to higher frequencies. Conversely, an electron-donating group R would be expected to lower the frequency of the CH_2 wag.

The infrared spectra of vinylsilanes of the types,

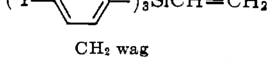


and $Y_3SiCH{=}CH_2$,

were considered in the present work. The calibrated frequencies of the vinyl CH_2 wag are compiled in Tables III and IV, respectively. Comparison with the CH_2 wag frequency of 3,3,3-triphenyl-1-propene (925 cm.$^{-1}$) and of 3,3-dimethyl-1-butene (910 cm.$^{-1}$), carbon analogs of triphenylvinylsilane and of trimethylvinylsilane, respectively, points up the influence of silicon in determining the position of this frequency.

TABLE III

CORRELATION OF THE CH_2 WAG OF *para*-SUBSTITUTED PHENYLVINYLSILANES



Y	CH_2 wag (cm.$^{-1}$)	σ_p[a] of Y	($\sigma_p - \sigma'$) of Y
CH_3O	957	−0.27	−0.50
CH_3	958	− .17	− .13
H	961 (960)[b]	0.00	0.00
F	963	+ .06	− .44
CF_3	966	+ .55	+ .14
$(C_6H_5)_3CCH{=}CH_2$	925[c]		
$(CH_3)_3CCH{=}CH_2$	910[d]		

[a] σ_p and ($\sigma_p - \sigma'$) values obtained from ref. 14. [b] M. C. Henry and J. G. Noltes, *J. Am. Chem. Soc.*, **82**, 555 (1960). [c] *Cf.* Experimental. [d] Ref. 13.

TABLE IV

CORRELATION OF THE CH_2 WAG OF VINYLSILANES WITH SUBSTITUENT CONSTANTS[a]

$Y_3SiCH{=}CH_2$

Compound	CH_2 wag (cm.$^{-1}$)	σ^* of Y	σ_p of Y	($\sigma_p - \sigma'$) of Y
$Cl_3SiCH{=}CH_2$	976 (975)[b]	+2.94[c]	+0.23	−0.24
$(C_6H_5)_2ClSiCH{=}CH_2$	966	+1.38[d]	+ .08[d]	− .11[d]
$(C_6H_5)_3SiCH{=}CH_2$	961 (960)[e]	+0.60	+ .01	− .09
$(C_2H_5)_2(C_6H_5)SiCH{=}CH_2$	(954)[b]	+ .13[d]	− .11[d]	− .10[d]
$(CH_3)_3SiCH{=}CH_2$	948	.00	− .17	− .13
$(C_2H_5)_3SiCH{=}CH_2$	948	− .10	− .15[f]	− .10[g]
$(C_6H_5CH_2)_3SiCH{=}CH_2$	951	+ .22	[h]	[h]
$(C_6H_5)_3SiCH_2CH{=}CH_2$	895	. . .	[h]	[h]

[a] Unless otherwise noted, σ^*, σ_p, and ($\sigma_p - \sigma'$) values were obtained from ref. 14. [b] See ref. 13. [c] This value was calculated from the system Cl—CH_2— (14). [d] Weighted arithmetic mean for the two substituent values. [e] M. C. Henry and J. G. Noltes, *J. Am. Chem. Soc.*, **82**, 555 (1960). [f] H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953). [g] σ' for methyl was used in calculating this value. [h] Data not available.

As the position of the CH_2 wagging frequency for the vinylsilanes was shown to depend upon the nature of the substituents, attempts were made to correlate the trend in this frequency with well-known substituent parameters for Y.[16] However, in contrast to previous findings for other substituted ethylenes,[13] no correlation at all could be seen between the CH_2 wagging frequency of these vinylsilanes and the $\sigma_p - \sigma'$ values of their Y substituents (Tables III and IV). On the other hand, in both of the series of vinylsilanes studied, the frequency of the CH_2 wag was found to increase with increasing electron-attacting power of the substituents on silicon. For the series of triarylvinylsilanes (Table III) the CH_2 frequency rises as the net electron-attracting power of the YC_6H_4-substituent increases. In Fig. 1, the σ_p[16] of the Y in the YC_6H_4-group is used as a measure of the net electron-attacting power of the YC_6H_4-substituent. Although this trend appears to be real, it should be pointed out that the frequency spread for the entire series is only 9 cm.$^{-1}$ and that the experimental uncertainty is ±1 cm.$^{-1}$.

In the second series of vinylsilanes, given in Table IV, the observed trend in the CH_2 frequency was found to parallel the inductive character of the substituents Y bonded directly to silicon, as measured by Taft σ^*[17] values of these groups. This nonlinear correlation is plotted in Fig. 2. Thus in both series of vinylsilanes the increase in an already high CH_2 wagging frequency by electron-attracting substituents shows that silicon is behaving as an electron-attracting substituent on the vinyl group, rather than as an electron-donating one. Since electronic considerations based solely on the

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(14) *Cf.* R. W. Taft, Jr., in M. S. Newman, ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 594–597.

(15) (a) *Cf.* ref. 2, pp. 91–113; (b) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955).

(16) *Cf.* ref. 14, pp. 570–575.

(17) (a) *Cf.* ref. 14, pp. 587–597. Although there is a close parallel between the inductive parameters, σ' and σ^*, σ^* values were employed in this study, since a greater number of them can be obtained from more direct experimental data; (b) For previous studies of substituent effects on the frequency of the Si—H stretching vibration, *cf.* A. L. Smith and N. C. Angelotti, *Spectrochim. Acta*, **15**, 412 (1959) and H. W. Thompson, *ibid.*, **16**, 238 (1960). In the former study special, empirical parameters (E values) were obtained from R_3SiH types and applied to predicting the Si—H stretching frequency of mixed silicon hydrides, $R_1R_2R_3SiH$. The latter study pointed out that a more generalized correlation exists between the Si—H stretching frequency and Taft σ^* values of the substituents.

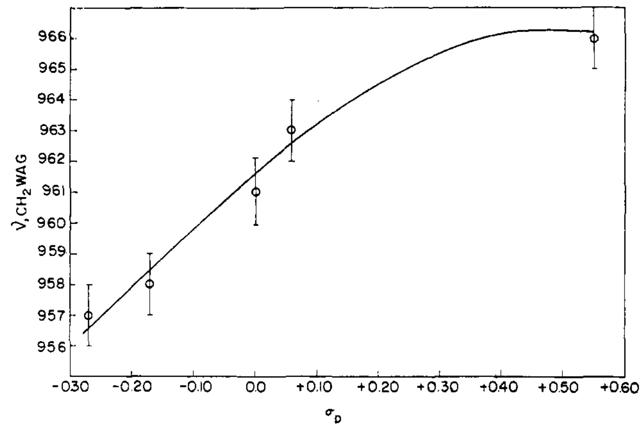


Fig. 1.—Variation of the vinyl CH_2 wag frequency of *para*-substituted phenylvinylsilanes with the σ_p value of the *para* substituent.

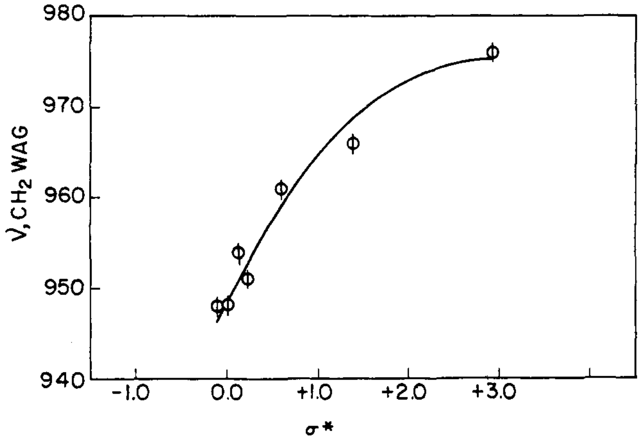


Fig. 2.—Variation of the vinyl CH_2 wag frequency of vinylsilanes of the type, $Y_3SiCH=CH_2$, with the σ^* value of Y.

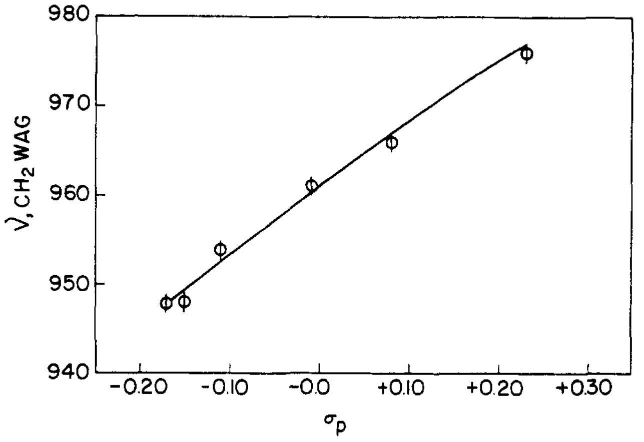
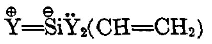


Fig. 3.—Variation of the vinyl CH_2 wag frequency of vinylsilanes of the type, $Y_3SiCH=CH_2$, with the σ_p value of Y.

greater electronegativity of carbon *vs.* silicon (2.5 *vs.* 1.8) would predict silicon to be an electron-donating center toward carbon, clearly additional electronic factors underlie these correlations.

Although there is some apparent correlation of the CH_2 frequency and the inductive electron-attracting power of Y in $Y_3SiCH=CH_2$, it appears from the rather marked curvature in the plot of frequency *vs.* σ^* (Fig. 2) that the inductive effect of the substituent is not the correct measure of net electron-attracting power for substituents on silicon.

In choosing a more suitable parameter to describe the net electron-attracting power of Y in $Y_3SiCH=CH_2$, it should be recalled that resonance interactions of the $d_\pi-p_\pi$ type[15] can occur when the substituent Y is unsaturated or possesses unshared electron pairs (III).


$\overset{\oplus}{Y}=\overset{\ominus}{Si}\ddot{Y}_2(CH=CH_2)$

III

Thus, any parameter which is to mirror more precisely the net electrical effects of the substituents Y on silicon must measure both resonance (III) and inductive (II) effects. Unfortunately, no data on the magnitude of the resonance interaction depicted in III are available. One might hypothesize that the inductive and resonance interaction of a substituent Y bonded directly to silicon will parallel approximately the net electronic interaction of the same substituent Y on the *para* position of a substituted benzoic acid (modifying the pK_a of the acid). In this case, then, the well known Hammett σ_p values, which measure the net electrical effect of substituents on such an unsaturated carbon system, would seem to be more appropriate parameters for this group of vinylsilanes. From the plot of the CH_2 frequency *vs.* σ_p for these vinylsilanes given in Fig. 3, an excellent linear correlation between the frequency and σ_p over a spread of 28 cm.$^{-1}$ was found. Surpassing that shown for σ^*, this correlation suggests that, in its substituent effects, a silicon atom behaves much more like an unsaturated carbon system (*e.g.*, a *para*-substitued phenyl group) than like a saturated carbon atom. Despite this gratifying correlation, further evidence will be needed to strengthen the novel assumption that an aromatic substituent constant, σ_p, may be used to describe the electronic nature of a substituent bonded directly to silicon.

A final point concerning the effect of silicon on the CH_2 wag frequency of an adjacent vinyl group is that the intervention of a methylene group, as in allyltriphenylsilane, should prevent the $d_\pi-p_\pi$ interaction shown in I. Hence the CH_2 wag should no longer fall at an abnormally high frequency. Indeed, its observed position at 895 cm.$^{-1}$ is somewhat lower than normal (905–912 cm.$^{-1}$).[13] This fact suggests that the silicon can now function only as an electron-releasing group by virtue of its electropositive nature relative to carbon (IV).

$$(C_6H_5)_3Si \rightarrow CH_2 \rightarrow CH=CH_2$$

IV

Experimental[18]

Starting Materials.—Trichlorovinylsilane (Practical grade from Anderson Chemical Co., Weston, Mich.) was carefully fractionated through a 25-cm., glass helices-filled column before use, b.p. 90°. The organic halides employed in the preparation of the organometallic reagents were reagent grade, commercially available chemicals which were dried with anhydrous calcium sulfate or phosphorus pentoxide and were freshly distilled before use. The *p*-bromobenzotrifluoride was obtained from the Peninsular Chemical Co., Gainesville, Fla. The trifluoroacetic acid necessary for the preparation of trifluoroacetic anhydride was Eastman White Label, b.p. 71–73°. The 90% hydrogen peroxide was obtained from the Becco Chemical Division of the Food, Machinery and Chemical Co., Buffalo, N. Y. The Florisil chromatographic

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[18] All melting points are uncorrected. Procedures involving the preparation and reaction of organometallic compounds were conducted under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran (THF) was purified by storage over pellet potassium hydroxide and by subsequent refluxing over metallic sodium. Successive distillations from metallic sodium and lithium aluminum hydride were performed just prior to use.

adsorbent (magnesium silicate, 60–110 mesh) was obtained from the Floridin Co., Tallahassee, Fla. All reaction and chromatography solvents were dry, reagent grade chemicals.

Preparation of the Vinylsilanes.—The requisite vinylsilanes were prepared by the interaction of trichlorovinylsilane with the appropriate Grignard reagent.[5] The use of tetrahydrofuran as the reaction solvent and purification of crude solid products by column chromatography afforded high yields of the vinylsilanes in most cases. The experimental conditions and results of these preparations are summarized in Table I. The following detailed procedure for the preparation of tri-*p*-anisylvinylsilane may be regarded as typical.

A solution of 19.3 g. (0.12 mole) of trichlorovinylsilane in 250 ml. of anhydrous tetrahydrofuran was added with stirring to 0.50 mole of *p*-anisylmagnesium bromide in 525 ml. of tetrahydrofuran over a period of 5 min. [The Grignard reagent was prepared from 93.7 g. (0.50 mole) of *p*-bromoanisole and 18.2 g. (0.75 g.-atom) of magnesium turnings in 500 ml. of anhydrous tetrahydrofuran. The yield of Grignard reagent, as determined by titration of a hydrolyzed aliquot with standard acid, was 100%.] After the reaction mixture had been stirred at the reflux temperature for 40 hr., it was cooled and then hydrolyzed with aqueous ammonium chloride. The separated organic layer was dried over anhydrous magnesium sulfate and the solvent thereupon evaporated. The resulting crude product was chromatographed on a column of Florisil with petroleum ether (b.p. 30–60°) and eluted with ethyl ether to yield 36.3 g. of colorless solid. Recrystallization from absolute ethanol provided 36.0 g. of pure tri-*p*-anisylvinylsilane (80%), m.p. 89.5–90.5°.

Chlorodiphenylvinylsilane.[19]—A solution of 126 g. (0.78 mole) of trichlorovinylsilane in 250 ml. of anhydrous ether, cooled to −45° by a Dry Ice–methylene chloride bath, was treated with 1.57 moles of phenyllithium in 1 l. of ether over a period of 90 min. When the addition was complete, the reaction was warmed to 0° and filtered under dry nitrogen. The filtrate was concentrated to a volume of 300 ml. and thereupon 500 ml. of dry benzene were added. The precipitated salts were filtered off and the filtrate was freed of volatile solvent. The residue was distilled under reduced pressure to provide a distillate boiling up to 200° at 0.5 mm. Careful fractionation of the foregoing distillate through a 90-cm. column packed with glass helices afforded 76.9 g. (42%) of product, b.p. 132–134° (1.0 mm.).

3,3,3-Triphenyl-1-propene.—This compound was prepared from 3,3,3-triphenyl-1-propanol by following published procedures.[20,21] The starting alcohol was prepared *via* a useful procedue for procuring trityllithium.[22] Thus a mixture of 0.42 g. (0.061 g.-atom) of lithium metal pieces and 7.70 g. (0.050 mole) of biphenyl was stirred in 75 ml. of anhydrous tetrahydrofuran until a complete, dark green solution was attained. Thereupon a solution of 11.5 g. (0.048 mole) of triphenylmethane in 60 ml. of tetrahydrofuran was introduced. After a 14-hr. stirring period at room temperature and 2 hr. at the reflux temperature the resulting red solution was treated with gaseous ethylene oxide until the color no longer faded. The solution was hydrolyzed and extracted with ether. Drying of the ether extract, evaporation of the solvent and reduced pressure distillation of the residue afforded a fraction, b.p. 175–190° (0.4 mm.), amounting to 12.5 g. (91%) of crude alcohol. Recrystallization from petroleum ether (b.p. 90–100°) yielded colorless crystals, m.p. 107–108°.

Epoxidation Studies with Vinylsilanes. (a). Perbenzoic and Monoperphthalic Acids.—Duplication of the directions of Bazant and Matousek[7b] for the epoxidation of trimethylvinylsilane with monoperphthalic acid gave a small yield of product having properties in agreement with those reported for epoxyethyltrimethylsilane. However, the infrared spectrum of the distilled product displayed a definite absorption at 1740 cm.$^{-1}$, indicative of a carbonyl impurity.

Attempted epoxidations of triethylvinylsilane with perbenzoic acid[9] in benzene, carbon tetrachloride, and chloroform, or with monoperphthalic acid in ether[7b] yielded only modest amounts of distilled epoxyethyltriethylsilane (10–20%), b.p. 70° (10 mm.), $n^{23}\text{D}$ 1.4427. In all cases the infrared spectra of these products displayed moderate to strong carbonyl absorptions at 1730 cm.$^{-1}$, besides the characteristic epoxide band at 890 cm.$^{-1}$.

Neither of the previous reports on the epoxidation of trialkylvinylsilanes[7b,9] cited any infrared support for the purity of their epoxyethylsilanes.

Tri-*p*-anisylepoxyethylsilane.—Since this compound could not be obtained by the peroxytrifluoroacetic acid method (*cf. infra*), the low yield obtained with monoperphthalic acid had to suffice, in order to procure this desired epoxide. Thus a solution of 35.0 g. (0.093 mole) of tri-*p*-anisylvinylsilane and 0.21 mole of monoperphthalic acid in 500 ml. of ether was distilled to remove 400 ml. of the ether. The resulting system was heated at 50° for 20 hr. After being cooled to room temperature the suspension was filtered to remove the precipitated phthalic acid. The filtrate was washed several times with dilute sodium carbonate solution and finally with water. Evaporation of the solvent from the dried organic layer gave a residue which subsequently was dissolved in cyclohexane and chromatographed on a Florisil column. After recovery of 15.6 g. of olefin by elution with 10% (by volume) ethyl ether in cyclohexane, the epoxide (4.3 g., 22% based on unrecovered olefin) was obtained by elution with ethyl ether. Recrystallization from an ethyl ether–cyclohexane pair afforded an analytically pure sample, m.p. 94–95°.

(b). **Peroxytrifluoroacetic Acid.**—The procedure of Emmons and Pagano[10] was found to be most satisfactory for the synthesis of epoxyethylsilanes in good yield, except in the case of tri-*p*-anisylvinylsilane (*cf. supra*).

The trifluoroacetic anhydride was prepared by the repeated fractional distillation of a mixture of trifluoroacetic acid and phosphorus pentoxide until a constancy of boiling point (38–39°) was attained. The anhydrous, granular sodium carbonate was dried in a vacuum oven at 100° for 24 hr. Noteworthy is the report[12] that suspensions of 90% hydrogen peroxide in methylene chloride have been shown to detonate by a modification of the drop weight test method. The following expoxidation procedures may be regarded as typical for the epoxides listed in Table II.

Epoxyethyltriethylsilane (Short Reaction Time).—To a stirred suspension of 4.5 ml. (0.17 mole) of 90% hydrogen peroxide in 50 ml. of methylene chloride cooled to 0° were added dropwise 40.7g. (0.19 mole) of trifluoroacetic anhydride. The reaction mixture was allowed to stir at 0° for another 15 min. Over a period of 75 min. the foregoing solution was introduced into a well stirred mixture of 52 g. (0.49 mole) of anhydrous, granular sodium carbonate, 7.10 g. (0.050 mole) of triethylvinylsilane, and 100 ml. of methylene chloride. Spontaneous reflux accompanied the addition of the peroxytrifluoroacetic acid. The resulting reaction mixture was stirred at the reflux temperature for 20 min. and thereupon cooled and filtered. The filtrate was washed with sodium carbonate solution and with water. After drying with anhydrous magnesium sulfate, the solution was fractionally distilled to remove solvent. The residual liquid was distilled through a short Vigreux column to provide 4.89 g. (62%), b.p. 179–183°, $n^{25}\text{D}$ 1.4420, of epoxyethyltriethylsilane. This product was shown to be free of triethylvinylsilane by vapor phase chromatography on a 10% silicone oil–firebrick column. Its infrared spectrum showed no bands indicative of hydroxyl or carbonyl impurities; a sharp, intense absorption at 890 cm.$^{-1}$ was characteristic of the epoxide linkage.

Epoxyethyltriethylsilane (Long Reaction Time).—To a stirred suspension of 17.6 ml. (0.64 mole) of 90% hydrogen peroxide cooled to 0° were added dropwise 163 g. (0.77 mole) of trifluoroacetic anhydride. After the addition was complete, the system was allowed to stir at 0° for 30 min. The above solution was introduced into a well stirred mixture of 204 g. (1.93 moles) of anhydrous, granular sodium carbonate, 32.0 g. (0.25 mole) of triethylvinylsilane, and 500 ml. of methylene chloride over a period of 40 min. After the reaction mixture was stirred for 5 hr. at the reflux temperature and for 3 hr. at room temperature, it was cooled and the salts filtered off. After removal of the solvent from the filtrate the liquid residue was distilled through a 60 cm., glass helices-filled column to yield two fractions: (1) 133–175° (7 mm.), 11.6 g. and (2) 90–200° (17 mm.), 15.3 g. The infrared spectra showed no typical epoxide band at 890 cm.$^{-1}$, but both fractions displayed intense carbonyl absorptions. Fraction 1 showed characteristic bands at 3200–3400 (broad; O—H), 1720–1800 (broad; C═O), and 1050–1100 cm.$^{-1}$ (broad; Si—O—C). Fraction 2 possessed significant bands at 3200 (O—H), 1790 (C═O), 1730 (C═O), and 1080 (Si—O—C) cm.$^{-1}$. Treatment of fraction 1 with aqueous sodium hydroxide, work-up by ether extraction, and distillation gave a product, b.p. 140–160° (740

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[19] *Cf.* J. W. Curry, *J. Am. Chem. Soc.*, **78**, 1686 (1956), who prepared this compound in 47% yield from dichlorophenylvinylsilane and phenylmagnesium chloride. However, trichlorovinylsilane is a much more accessible starting material.

[20] W. D. McPhee and E. G. Lindstrom, *ibid.*, **65**, 2177 (1943).

[21] F. J. Piehl and W. G. Brown, *ibid.*, **75**, 5023 (1953).

[22] J. Eisch and W. Kaska, *Chem. Ind.* (London), 470 (1961).

mm.), whose infrared spectrum had intense bands at 3400 (O—H) 1795 (C═O, intense), 1730 (C═O, weak), 1070 (Si—O—C), and 830 (Si–O—H) cm.$^{-1}$. From these data it appears that a mixture of triethylsilanol, triethylsilyl trifluoroacetate, and the trifluoroacetate ester of triethylsilylethylene glycol may be present. Examination of fraction 2 from the original distillation by careful fractional distillation and vapor phase chromatography revealed the presence of at least nine components. The infrared spectra of the resulting fractions were free of hydroxyl absorptions, but all possessed bands of varying intensities at 1795 (C═O), 1740 (C═O), 1390 and 1070 (Si—O—C) cm.$^{-1}$.

Epoxyethyltriphenylsilane.—To a stirred suspension of 13.2 ml. (0.50 mole) of 90% hydrogen peroxide in 250 ml. of methylene chloride cooled to 0° were added dropwise 121 g. (0.57 mole) of trifluoroacetic anhydride. The solution was then stirred at 0° for 15 min. The foregoing solution of peroxytrifluoroacetic acid was added dropwise to a well stirred mixture of 170 g. (1.60 moles) of anhydrous, granular sodium carbonate, 28.6 g. (0.10 mole) of triphenylvinylsilane, and 1500 ml. of methylene chloride. After being stirred for 4 hr. at room temperature, the system was filtered and the filtrate was freed of solvent. The crude epoxide was introduced onto a Florisil column with petroleum ether (b.p. 30–60°) and elution with ethyl ether yielded the epoxide, m.p. 82–85°, 25.3 g. (84%). Successive recrystallizations from methanol and cyclohexane provided an analytical sample, m.p. 85–86°. This product was shown to contain no triphenylvinylsilane by vapor phase chromatography on a 5% silicone gum rubber on firebrick column. Its infrared spectrum displayed the characteristic epoxide peak at 875 cm.$^{-1}$ but showed no hydroxyl or carbonyl absorptions.

Infrared Spectral Measurements.—Spectra of vinylsilanes and epoxyethylsilanes for characterization purposes were recorded on liquid film samples, where possible. Spectra of solids were obtained as mulls in Nujol oil.

For the comparative study of the infrared spectra of the vinylsilanes reported in Tables III and IV, the samples were recorded uniformly in solutions of reagent carbon disulfide (0.050 mole of vinylsilane in 100 ml. of solvent). By use of matched cells with sodium chloride optics, solvent-compensated spectra were obtained. Each recorded spectrum was calibrated by means of a polystyrene film, the known polystyrene band at 906 cm.$^{-1}$ in the region of interest serving as a standard. The instrument was linear with the frequency and the positions of the absorption bands were reproducible to within ±1 cm.$^{-1}$.

All the reported infrared spectra were measured on a Perkin–Elmer infrared spectrophotometer, Model 21 with a 927 slit program.

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Hydrogen Fluoride as a Condensing Agent. VI. Reactions of Fluoroölefins with Formaldehyde in Hydrogen Fluoride[1]

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Tetrafluoroethylene condenses with formaldehyde in liquid hydrogen fluoride to form 2,2,3,3,3-pentafluoro-1-propanol and fluoromethyl-2,2,3,3,3-pentafluoropropyl ether. 2,2,3,3-Tetrafluorooxetane, methyl-2,2,3,3,3-pentafluoropropyl ether, bis(2,2,3,3,3-pentafluoropropoxy)methane, and bis[(2,2,3,3,3-pentafluoropropoxy)-methyl] ether are formed as minor by-products. 2,3,3,3-Tetrafluoro-2-trifluoromethyl-1-propanol is obtained from hexafluoropropylene. 1,1-Difluoroethylene and fluoroethylene condense to give, respectively, bis(3,3,3-trifluoropropyl) ether and bis(3,3-difluoropropyl) ether. The formation of bis(fluoromethyl) ether from formaldehyde and hydrogen fluoride is postulated.

Hydrocarbons containing the ethylene linkage react with formaldehyde in the presence of acidic catalysts to form 1,3-glycols and formals.[2] Halogenated olefins react in much the same manner except that hydrolysis may occur in the presence of water leading to halohydracrylic acids.[3] Thus tetrafluoroethylene condenses with formaldehyde in sulfuric acid to give α,α-difluorohydracrylic acid.[4] Quite different results are obtained when fluoroölefins react with solutions of formaldehyde in hydrogen fluoride.

The reaction of aromatic compounds with formaldehyde in hydrogen fluoride, leading to diarylmethanes, has been reported[5] and has led these authors to postulate the initial formation of fluoromethanol, FCH_2OH. Our nuclear magnetic resonance investigation of a solution of paraformaldehyde in hydrogen fluoride confirmed the existence of the FCH_2— group. We have further determined that paraformaldehyde dissolves in hydrogen fluoride with the formation of water. Based on this analysis it is likely that we are dealing with a solution in which an equilibrium exists of fluoromethanol (about 25–30%) and bis(fluoromethyl) ether FCH_2OCH_2F (about 70–75%). The formation of the products obtained when fluoroölefins react with a solution of paraformaldehyde in hydrogen fluoride can be visualized as involving reaction with this hypothetical bis(fluoromethyl) ether.

One mole of tetrafluoroethylene reacts with one mole of bis(fluoromethyl) ether to give fluoromethyl-2,2,3,3,3-pentafluoropropyl ether, $CF_3CF_2CH_2OCH_2F$, b.p. 60°. 2,2,3,3,3-Pentafluoro-1-propanol, b.p. 81°, is formed simultaneously due to hydrolysis from the water formed in the formation of the bis(fluoromethyl) ether. At a low reaction temperature (20°) the fluoromethyl 2,2,3,3,3-pentafluoropropyl ether is the predominant product; at a higher reaction temperature (50–100°) the 2,2,3,3,3-pentafluoro-1-propanol forms the principal product. Small quantities of 2,2,3,3,3-tetrafluorooxetane, $\underline{CF_2CF_2CH_2O}$, b.p. 28°, methyl-2,2,3,3,3-pentafluoropropyl ether, $CF_3CF_2CH_2OCH_3$, b.p. 46°, bis-(2,2,3,3,3-pentafluoropropoxy)methane, $(CF_3CF_2CH_2O)_2CH_2$, b.p. 125° and bis[(2,2,3,3,3-pentafluoropropoxy)methyl] ether $(CF_3CF_2CH_2OCH_2)_2O$, b.p. 69°/15 mm., are also formed.

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(1) For paper V see V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955).

(2) J. F. Walker, American Chemical Society Monograph, "Formaldehyde," 2nd ed., pp. 326–335.

(3) H. J. Prins, *Rec. trav. chim.*, **51**, 469 (1932).

(4) D. D. Coffman, M. S. Raasch, G. W. Rigby, P. L. Barrick, and W. E. Hanford, *J. Org. Chem.*, **14**, 747 (1949).

(5) G. Olah and A. Palath, *Acta Chim. Acad. Sci. Hung.*, **3**, 425 (1953); *Chem. Abstr.*, **49**, 2384 (1956).