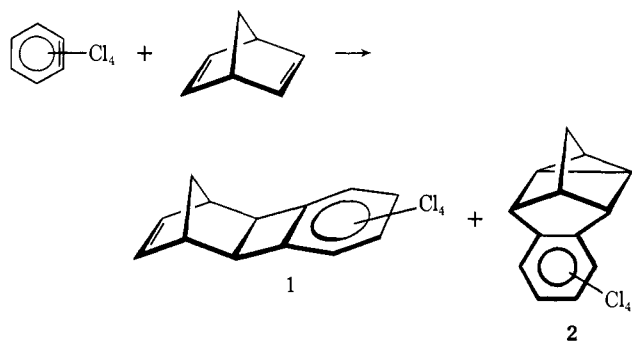


Figure 1. The effect of pressure on the ratio of cycloaddition products: (A)  $R = 1/2$ ; (B)  $R = 3/4$ .

dimerization of chloroprene and found that the [2 + 4] adducts become greatly favored at high pressure over the competing [2 + 2] products—presumably because the latter are formed by a pathway in which only one bond is developing in the main transition state.

It is also known<sup>2</sup> that the solvation of ionic sites causes large volume decreases (electrostriction), and it seemed to us that this effect might well mask the indication of a moderate activation volume for a stepwise cycloaddition; in fact, it seemed possible that pressure might favor this process over a concerted one if the intermediate is a full-blown zwitterion. In our search for examples, we have found that the cycloaddition of tetrachlorobenzene to norbornadiene, a reaction first studied by Heaney,<sup>6</sup> is a case in which solvation indeed compensates for a lag in bonding. The benzyne can be generated either by diazotation of tetrachloroanthranilic acid or by the reaction of butyllithium with hexachlorobenzene; the product ratio is virtually independent of the method of generation. Since the decomposition of pentachlorophenyllithium proceeds at a convenient rate at room temperature in ether, we employed this technique to generate the benzyne. The ratio 1/2 was

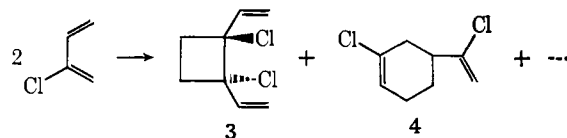


measured as a function of pressure by means of vpc; we showed that the several minor side products visible in the gas chromatograms derive from pentachlorophenyllithium alone, and that 1 and 2 are stable to our conditions. At high pressure these side reactions quickly become dominant, and it was not possible to

(6) H. Heaney, J. M. Jablonski, K. G. Mason, and J. M. Sketchley, *J. Chem. Soc. C*, 3129 (1971).

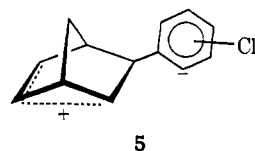
make measurements above 5 kbar. The results are shown in Figure 1.

For comparison we show Stewart's data for the ratio of 3/4 in the dimerization of chloroprene. It is clear



from this plot that the advantage bestowed upon the concerted cycloaddition by the application of pressure in Stewart's case is not present in ours; in fact, the [2 + 2] reaction is slightly favored. The  $\Delta\Delta V^\ddagger$  values are +8.4, and  $-0.7$  cm<sup>3</sup>/mol, respectively.

We ascribe the disappearance of this advantage to solvation of a zwitterionic intermediate, 5, and note



that this is in agreement with solvent effects on the product ratio noted by Heaney.<sup>7</sup> We conclude that inferences regarding the degree of concertedness drawn from the pressure effect in pericyclic reactions are safe only if definite information is available to judge the degree of diradical *vs.* zwitterionic character of any intermediates that might be intervening.<sup>8</sup>

**Acknowledgment.** Professor Heaney kindly sent us samples of his products for comparison. The National Science Foundation generously supported this work.

(7) H. Heaney and J. M. Jablonski, *Tetrahedron Lett.*, 2733 (1967).

(8) A similar problem has been encountered by Neuman<sup>2</sup> in the presumably concerted perester decomposition; electrostriction around the radicals due to partial charge development reduces the value of the activation volume in that case also.

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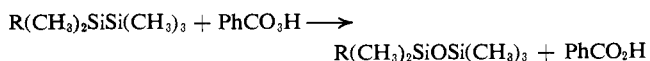
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### Charge-Transfer Spectra and Peracid Oxidation of 1,2-Disilacycloalkanes. A Rate-Charge-Transfer Relationship in the Electrophilic Reaction at $\sigma$ -Bonds

Sir:

In 1965 we reported an oxidation reaction of organo-disilanes with perbenzoic acid involving direct insertion of an oxygen atom into the silicon-silicon  $\sigma$ -bond.<sup>1</sup>






This reaction, with obvious indications by kinetic results,<sup>1</sup> can be considered as a typical example of electrophilic reactions taking place at the  $\sigma$ -bond.<sup>2</sup> Recently,

(1) H. Sakurai, T. Imoto, N. Hayashi, and M. Kumada, *J. Amer. Chem. Soc.*, **87**, 4001 (1965).

(2) M. Kira, Ph.D. Thesis, Tohoku University, Sendai, Japan, 1973.

Table I. Charge-Transfer Energies and Rate Parameters of Peracid Oxidation of Disilanes

Compound	$E_{CT}^a$		$10^3 k_2, \text{l. mol}^{-1} \text{sec}^{-1b}$			$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , eu
	cm <sup>-1</sup>	kcal mol <sup>-1</sup>	25.00°	35.00°	45.00°		
Me <sub>6</sub> Si-SiMe <sub>6</sub>	24,000 ± 75	68.6 ± 0.2	0.461 ± 0.023	0.966 ± 0.016	2.17 ± 0.02	14.0 ± 0.5	-26.8 ± 1.6
Me <sub>2</sub> Si-SiMe <sub>2</sub> 	23,500 ± 57	67.2 ± 0.2	4.13 ± 0.09	8.39 ± 0.10	16.3 ± 0.6	12.3 ± 0.1	-28.1 ± 0.1
Me <sub>2</sub> Si-SiMe <sub>2</sub> 	22,500 ± 48	64.3 ± 0.1	47.8 ± 1.4	97.2 ± 2.5	160 ± 6	10.7 ± 0.7	-28.5 ± 2.2
Me <sub>2</sub> Si-SiMe <sub>2</sub> 	21,600 ± 45	61.8 ± 0.1	982 ± 7	1590 ± 80	2650 ± 20	8.75 ± 0.22	-29.3 ± 0.7

<sup>a</sup> Frequencies of charge-transfer complexes with tetracyanoethylene in dichloromethane at room temperature. <sup>b</sup> The range of concentrations of disilanes and peracid used for the determination of the rate constants were 0.016–0.023 mol/l. and 0.014–0.021 mol/l., respectively. Benzene was used as a solvent. See also footnote 8.

Traven and West<sup>3</sup> and we<sup>4</sup> have observed charge-transfer complexing between permethylpolysilanes and tetracyanoethylene as evidenced by low energy charge-transfer absorptions<sup>3,4</sup> and photoinduced epr signals of the tetracyanoethylene anion radical.<sup>4</sup> These are the realization of the electron-donor ability of bonding electron pairs of the Si-Si  $\sigma$ -bond.<sup>5</sup> In this communication, we report the rate-charge-transfer relationship as determined by charge-transfer spectra and rates of peracid oxidation of 1,2-disilacycloalkanes.

In an analogous way to the previous paper,<sup>4</sup> the charge-transfer absorptions of 1,1,2,2-tetramethyl-1,2-

disilacycloalkanes, (CH<sub>3</sub>)<sub>2</sub>SiSi(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub> (*n* = 3, 4, 5),<sup>6</sup> were determined in dichloromethane at room temperature.

As shown in Table I, the charge-transfer energies decreased from 68.6 kcal/mol of hexamethyldisilane to 61.8 kcal/mol of disilacyclopentane systematically with decreasing ring size. For charge-transfer complexes of various donors with the same acceptor, the charge-transfer energy should be related to the ionization potential, hence to the levels of the highest occupied molecular orbitals for the donor.<sup>7</sup> It is then clear that the highest occupied molecular orbital, *i.e.*, the level of the Si-Si bond of a small ring compound, is raised, at least in part, by the ring strain.

Oxidation of these disilanes with *m*-chloroperbenzoic acid in benzene gave single disiloxanes, and second-order kinetics were observed strictly for all compounds.<sup>8</sup> Table I also contains second-order rate constants to-

(3) V. F. Traven and R. West, *J. Amer. Chem. Soc.*, **95**, 6824 (1973).

(4) H. Sakurai, M. Kira, and T. Uchida, *J. Amer. Chem. Soc.*, **95**, 6826 (1973).

(5) For intramolecular  $\sigma(\text{SiSi})-\pi$  interactions, see H. Sakurai and M. Kira, *J. Amer. Chem. Soc.*, **96**, 791 (1974), and references cited therein.

(6) M. Kumada, K. Tamao, T. Takubo, and M. Ishikawa, *J. Organometal. Chem.*, **9**, 43 (1967).

(7) R. S. Mulliken and W. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969.

(8) The oxidation reaction was followed iodometrically in the range of 0–60% completion and was found to obey the second-order kinetics in the wide range of concentrations of both disilane and peracid. No acid catalysis was found with trichloroacetic acid. No significant solvent effect was observed on rates and activation parameters in benzene, hexane, carbon tetrachloride, chloroform, and dichloromethane for the oxidation reaction, although solvents such as *tert*-butyl alcohol, ether, and dioxane, which may disrupt the intramolecular hydrogen bonding of the peracid, reduced the rate considerably. For a convenience, benzene was used as a solvent of the kinetic study. Detailed kinetic investigations were done on various disilane derivatives and will be published later.<sup>2</sup>

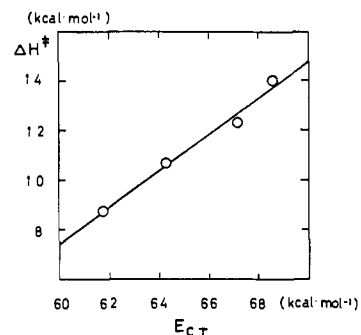


Figure 1. Plot of charge-transfer energies ( $E_{CT}$ ) for tetracyanoethylene-disilane complexes against the enthalpy of activation ( $\Delta H^\ddagger$ ) in the oxidation reaction of disilanes with *m*-chloroperbenzoic acid.

gether with enthalpies and entropies of activation of the reaction.

The most strained disilacyclopentane was oxidized more than 1000 times faster than open-chain hexamethyldisilane. The entropies of activation of the reaction remained nearly constant, so that the reaction is controlled by enthalpy changes. Significantly, a good linear relationship between  $\Delta H^\ddagger$  and  $E_{CT}$ ,  $\Delta H^\ddagger$  (kcal/mol) = 0.737 $E_{CT}$  (kcal/mol) - 36.8 (correlation coefficient = 0.991), was obtained as shown in Figure 1. This linear relationship, which means about 74% of the differences in the levels of the highest occupied molecular orbitals of substrates to be reflected in the differences of the activation enthalpies, certainly implies that an electron donor-acceptor interaction between the substrate and peracid (electrophile)<sup>9</sup> is important in the transition state of the reaction.

The general concept of the electrophilic reaction at a  $\sigma$ -bond has been greatly advanced since the work of Olah and his colleagues on the reactions of saturated hydrocarbons in superacid has appeared.<sup>10</sup> However, much yet remains to be done in this area, especially on the quantitative study of the reactivity of  $\sigma$ -bonds. The result in this communication is an example of the

(9) The acceptor property of peracids with low-lying vacant orbitals has been indicated, as a result of extended Hückel calculations, by T. Yonezawa, H. Kato, and O. Yamamoto, *Bull. Chem. Soc. Jap.*, **40**, 307 (1967).

(10) (a) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972); (b) G. A. Olah, R. Renner, P. Schilling, and Y. K. Mo, *ibid.*, **95**, 7686 (1973), and previous papers of the series.

quantitative description on the reactivity of a  $\sigma$ -bond toward an electrophile. The related work is actively in progress and will be reported soon.

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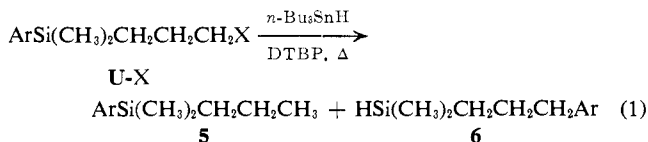
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### Halogen Leaving Group Effect in the Reductive Rearrangement of $\gamma$ -Silyl Halides with Tri-*n*-butyltin Hydride

Sir:

Although considerable information exists on the reduction of alkyl halides by organotin hydrides,<sup>1</sup> including the use of the reaction to study free radical rearrangements,<sup>2</sup> we have uncovered an unexpected and heretofore unreported aspect of the reaction. During a study of aryl group migration from silicon to carbon as reported<sup>3</sup> for the chlorides in eq 1, it was found that



chlorides gave more rearranged product than did bromides. This halogen effect was more pronounced at higher reactant concentrations and appeared to level off with decreasing concentration. Some data are given in Table I.<sup>4</sup>

Table I. Effect of Halogen on Rearrangement<sup>a</sup>

U-X, Ar	U-X $\xrightarrow[\text{DTBP, } \Delta]{n\text{-Bu}_3\text{SnH}}$ 5 + 6					
	Percentage rearranged product 6 <sup>b</sup>					
	10 <sup>-1</sup> M <sub>init</sub>		10 <sup>-2</sup> M <sub>init</sub>		10 <sup>-3</sup> M <sub>init</sub>	
	Cl	Br	Cl	Br	Cl	Br
<i>p</i> -Anisyl, 1	12	<i>c</i>	26	<i>c</i>	41	<i>c</i>
<i>p</i> -Tolyl, 2	5.5	2.5	19	6.0	31	30
<i>p</i> -Fluorophenyl, 3	5.0	2.0	16	5.0	28	21
Phenyl, 4 <sup>d</sup>	4.5	tr	15	4.0	Not studied	

<sup>a</sup> U-X:*n*-Bu<sub>3</sub>SnH:DTBP = 30:10:3 in purified benzene at 140 ± 5° for 20 hr. Yields of 5 + 6 were 60–80%. <sup>b</sup> Determined by glpc. The values are percentage compositions rounded to the nearest 0.5%. The values are the average of several determinations with a precision of ±5%. <sup>c</sup> This bromide proved to be a sensitive substance. Only modest yields of 35–38% of unrearranged 5 were obtained, along with several unidentified compounds. <sup>d</sup> Data from ref 3.

#### The rearranged product from either halide of both 2

(1) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968), and references therein.

(2) J. W. Wilt, "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 8.

(3) J. W. Wilt and C. F. Dockus, *J. Amer. Chem. Soc.*, **92**, 5813 (1970).

(4) Most of our studies have centered on the  $\gamma$ -silyl halides U-X. However, the effect noted in the table occurs also with *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>X, a  $\delta$ -silyl halide. The extents of rearrangement here with 10<sup>-1</sup>, 10<sup>-2</sup>, and 10<sup>-3</sup> M halide were, respectively, 7, 25, and 33% for X = Cl, and a trace, 3%, and 27% for X = Br.

and 3 still retained the para-oriented substituent, so the migration path is Ar<sub>1</sub>-5 in nature, as earlier postulated.<sup>3</sup>

Normally, simple alkyl chlorides undergo reduction by tin hydrides about 10<sup>4</sup> times more slowly than do bromides.<sup>5</sup> Surprisingly, however, a 10<sup>-2</sup> M mixture of 1:1 3-Cl and 3-Br in benzene underwent competitive reduction with limited *n*-Bu<sub>3</sub>SnH to give a reduced product containing 13% 6. Reduction of 5 × 10<sup>-3</sup> M 3-Cl under the same conditions gave 25% 6, whereas the same treatment of 3-Br gave 9% 6. Clearly, these two halides have comparable reactivities toward reduction (within threefold). Suitable control experiments indicated that no thermal or Lewis acid catalyzed rearrangement of either the reactants or products occurred in any of these reductions.

These distant aryl migrations are not very favorable. Concentrations of *n*-Bu<sub>3</sub>SnH larger than *ca.* 0.3 M gave no 6 in any case. Such rearrangements are therefore less facile than cyclizations or 1,2-aryl shifts<sup>6</sup> (carbon to carbon<sup>9</sup>).

A sample reduction is described. The appropriate halide U-X<sup>11,12</sup> was weighed into a volumetric flask, mixed with the proper volumes of stock solutions of redistilled tri-*n*-butyltin hydride and redistilled di-*tert*-butyl peroxide (DTBP), and diluted with purified, thiophene-free benzene to the mark. The final solution was made to contain U-X:*n*-Bu<sub>3</sub>SnH:DTBP in the ratios 30:10:3, with the initial concentration of U-X either 10<sup>-1</sup>, 10<sup>-2</sup>, or 10<sup>-3</sup> M. The reactant solution was then transferred to a 25-ml ampoule and put through three freeze-degas cycles on a vacuum line. The sealed ampoule was then heated in a wax bath at 140 ± 5° for 20 hr. The ampoule was cooled and opened and most of the benzene was removed by careful distillation. The remaining contents were then analyzed by glpc on a silicone gum rubber (SE 30) column. Products, yields, and composition data were all obtained by use of calibration mixtures of authentic samples.<sup>11,14</sup>

To our knowledge, no other report exists of such a halogen effect in organotin hydride reductions. In fact,

(5) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968). For chlorides, chlorine abstraction is usually the slow step of the reduction. For bromides, hydrogen transfer from the tin hydride is normally rate determining.

(6) Cyclization of 5-hexen-1-yl radical<sup>7</sup> has a calculated rate constant<sup>8</sup> of *ca.* 10<sup>8</sup> sec<sup>-1</sup> at 40°, and the 1,2-phenyl shift that rearranges the 2,2,2-triphenylethyl radical<sup>8</sup> has a calculated rate constant<sup>8</sup> of 5 × 10<sup>7</sup> sec<sup>-1</sup> at 100°. Both of these processes have rate constants comparable to that for hydrogen transfer from tin hydrides<sup>5</sup> (*ca.* 10<sup>4</sup>–10<sup>6</sup> sec<sup>-1</sup> at 10<sup>-2</sup> M hydride). The present rearrangements are much slower. Very approximate calculations indicate a rate constant of *ca.* 10<sup>3</sup> sec<sup>-1</sup> at 140°.

(7) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Amer. Chem. Soc.*, **88**, 5361 (1966).

(8) L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

(9) Radical 1,2-aryl shifts from silicon to carbon remain unknown.<sup>10</sup>

(10) Reference 2, p 354.

(11) All new compounds gave C, H analyses within 0.3% of theory. The ir and nmr spectra were in agreement with the structures proposed.

(12) U-Cl compounds were prepared by coupling reactions between Cl<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl and the appropriate Grignard reagents. U-Br compounds were similarly prepared from Cl<sub>3</sub>SiCH<sub>2</sub>CH=CH<sub>2</sub>. The allyl silanes so obtained were then converted to U-Br either by hydroboration-bromination<sup>13</sup> or by hydroboration-oxidation to the corresponding alcohol, tosylation, and displacement with lithium bromide in acetone.

(13) H. C. Brown and C. F. Lane, *J. Amer. Chem. Soc.*, **92**, 6660 (1970).

(14) Compounds 5 were prepared by coupling reactions between (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> and the appropriate Grignard reagents. Compounds 6 were similarly prepared using 1 mol of the appropriate Grignard reagent followed by reduction of the chlorosilane intermediate with lithium aluminum hydride.