trans-butene-2   (3)

this scheme a reversible addition step in the re- action of cis-butene-2 with a phosphine will be evidenced by the presence of trans-butene-2 in the reaction mixture.

cis-Butene-2 was allowed to react with phenyl- phosphine, dibutylphosphine and 2-cyanoethyl- phosphine at 70° using azobisisobutyronitrile as a free radical initiator. The results sum- marized in Table I give the percentage amount of butene-2 recovered, representing the butene-2 which was not converted to product by the ir- reversible displacement step, and the isomer con tent at various reaction times.

Isomerization of the cis to the trans isomer oc- curred in each case when the cis-butene-2, the phos- phine and the radical initiator were present, but no isomerization occurred when the phosphine or the radical initiator were separately present. The reversibility of the phosphinyl radical addition step is therefore demonstrated and the postulated reaction scheme 3 is established. Furthermore the extent of isomerization at low conversions to product (high percentages of butene-2 recovered) points up the fact that the rate constants for the reverse of the addition step (k_{-a1} and k_{-a2}) are large relative to k_d. In this vein the lower percentages of butene-2 recovered for 2-cyanoethylphosphine

TABLE I
RADICAL ADDITION OF PHOSPHINES TO cis-BUTENE-2 AT 70°

Time, hr.	Butene-2 recovd., %	% cis- butene-2 in recovd. materials	Time, hr.	Butene-2 recovd., %	% cis- butene-2 in recovd. materials
1.	Phenylphosphine[a]		3.	2-Cyanoethyl-	
2.5	100	58		phosphine[a]	
4.75	85	46	1	60	58
8	90	43	2	50	45
16.25	85	40	5	32	40
16.25[b]	100	100	16	15	34
16.25[c]	100	96			
2.	Di-n-butylphosphine[d]				
2	..	84			
8	88	64			
16	88	52			
16[c]	88	93			

[a] Initial reaction mixture contained: 2 ml. of cis-butene-2 (at 0°), 2 ml. of phosphine (at room temp.), 2 ml. of Nujol and 0.03 g. of AIBN (α,α'-azo-di-isobutyronitrile). [b] Phen- ylphosphine omitted. [c] AIBN omitted. [d] Initial re- action mixture contained 3.2 ml. of cis-butene-2 (at 0°); otherwise it was as in (a).

relative to those for phenylphosphine at equiva- lent extents of isomerization would indicate that the rate constant for the loss of $C_6H_5PH\cdot$ from C· is larger than that for the loss of the $CNCH_2CH_2PH\cdot$ since k_d for $C_6H_5PH_2$ is greater than that for CN- $CH_2CH_2PH_2$.[1] This conclusion is in accord with the concept of a greater stability for $C_6H_5\overset{\cdot}{P}H$ over $CNCH_2CH_2\overset{\cdot}{P}H$. It is felt that this work and that previously reported[1] establish a close analogy be- tween phosphines and thiols in free radical addi- tion to olefins and that this analogy is useful in understanding the detailed aspects of the phos- phine system in view of the detailed studies which have been carried out on the thiols.

The Effect of Polar Substituents on the Alkali-catalyzed Hydrolysis of Triorganosilanes[1]

BY OMAR W. STEWARD AND OGDEN R. PIERCE

The second-order rate constants for the alkali-catalyzed hydrolysis of twenty-four ω-cyanoalkyl-, ω-phenylalkyl-, fluoro- alkyl- and n-alkylsilanes have been determined using potassium hydroxide in 93.7 wt.-% ethanol at 0°. The second-order rate constants are correlated using the Taft equation. Steric effects and the two mechanisms which are consistent with the kinetic data are discussed in terms of the above correlations.

Introduction

The literature is almost completely void on the subject of polar effects of substituted alkyl groups on the reactivity of the silicon atom in organosili-

con compounds. In a previous paper[2] a study of the effect of substituent fluoroalkyl groups on the alkali-catalyzed hydrolysis of the silicon–hydrogen bond in triorganosilanes was reported. Recently

(1) Presented at the 138th Meeting of the American Chemical Society in New York, N. Y., September 11–16, 1960.

(2) O. W. Steward and O. R. Pierce, J. Am. Chem. Soc., 81, 1983 (1959).

TABLE I

RATE DATA FOR THE ALKALI-CATALYZED HYDROLYSIS OF THE TRIORGANOSILANES AT 0° IN 93.7 WT. % ETHANOL

No.	R	R'	R"	C_{silane}, mole l.$^{-1}$	C_{KOH}, mole l.$^{-1}$	k_1, min.$^{-1}$	k_2,^{a} l. mole^{-1} min.$^{-1}$	Relative rate	$\Sigma\sigma*$ ^{b}
1	CH_3	CH_3	CH_3	0.0612^c	0.460	0.128	0.0278	1.0	0.00
				$.0382^c$	.460	.130	.0283		
2	CH_3CH_2	CH_3	CH_3	.0607	.460	.00631	.0137	0.50	−0.10
				.0604	.460	.00652	.0142		
				.0629	1.875	.0145	.00773		
				.0582	1.875	.0142	.00757		
3	CH_3CH_2	CH_3CH_2	CH_3	.0500	1.875	.00649	.00346 (0.00629)^e	0.22	−0.20
				.0496	1.875	.00626	.00334 (.00607)		
4	CH_3CH_2	CH_3CH_2	CH_3CH_2	.0512	1.875	.00269	.00144 (.00262)^e	0.093	− .30
				.0508	1.875	.00266	.00142 (.00258)		
5^d	$CH_3CH_2CH_3$	CH_3	CH_3	.0259	0.478	.00564	.0118	0.43	− .115
				.0506	0.478	.00580	.0121		
6	$CH_3CH_2CH_2$	$CH_3CH_2CH_2$	CH_3	.0417	1.875	.00410	.00219 (.00398)^e	0.14	− .23
				.0456	1.875	.00417	.00222 (.00403)		
7	$C_6H_5CH_2$	CH_3	CH_3	.0516	0.460	.0150	.0326	1.1	.215
				.0471	.460	.0145	.0315		
8	$C_6H_5CH_2$	$C_6H_5CH_2$	CH_3	.0390	.460	.0219	.0476	1.7	.43
				.0422	.460	.0214	.0465	1.3	.08
9	$C_6H_5CH_2CH_2$	CH_3	CH_3	.0458	.460	.0172	.0374		
				.0393	.460	.0175	.0380	1.5	.16
10	$C_6H_5CH_2CH_2$	$C_6H_5CH_2CH_2$	CH_3	.0375	.460	.0190	.0413		
				.0411	.460	.0194	.0422		
11	$C_6H_5CH_2CH_2$	$C_6H_5CH_2CH_2$	$C_6H_5CH_2CH_2$	.0255	.460	.0200	.0435	1.5	.24
				.0253	.460	.0191	.0415		
12	$C_6H_5CH_2CH_2CH_2$	CH_3	CH_3	.0375	.460	.00927	.0202	0.72	.02
				.0375	.460	.00941	.0205		
13	$C_6H_5CH_2CH_2CH_2$	$C_6H_5CH_2CH_2CH_2$	CH_3	.0398	1.875	.00958	.00511 (.00928)^e	0.33	.04
				.0380	1.875	.00953	.00508 (.00923)		
14	$C_6H_5CH_2CH_2CH_2$	$C_6H_5CH_2CH_2CH_2$	$C_6H_5CH_2CH_2CH_2$	.0243	1.875	.00376	.00201 (.00365)^e	0.13	.06
				.0146	1.875	.00370	.00197 (.00358)		
15^d	$CF_3CH_2CH_2$	CH_3	CH_3	.00356	0.0389	.0385	.990	25	.32
				.0222	.478	.344	.719		
				.0217	.478	.339	.709		
				.0547	.478	.335	.703		
16^d	$CF_3CH_2CH_2$	$CF_3CH_2CH_2$	CH_3	.00339	.0389	1.40	35.9 (25.8)^f	920	.64
				.00377	.0389	1.40	35.9 (25.8)		
17^d	$CF_3CH_2CH_2CH_2$	CH_3	CH_3	.0293	.478	0.0479	0.100	3.6	.12
				.0333	.478	.0478	.100		
18	$CF_3CH_2CH_2CH_2$	$CF_3CH_2CH_2CH_2$	CH_3	.0359	.460	.156	.339	12	.24
				.0400	.460	.152	.330		
19	$CF_3CH_2CH_2CH_2$	$CF_3CH_2CH_2CH_2$	$CF_3CH_2CH_2CH_2$	.0386	.460	.553	1.20	44	.36
				.0357	.460	.578	1.26		
20	$CF_3CF_2CH_2CH_2$	CH_3	CH_3	.0359	.460	.456	0.991	36	
				.0367	.460	.474	1.03		
21	$CF_3CF_2CF_2CH_2CH_2$	CH_3	CH_3	.0364	.460	.474	1.03	36	
				.0389	.460	.454	0.987		
22	$N{\equiv}CCH_2CH_2$	CH_3	CH_3	.00327	.0389	.233	5.96 (4.27)^f	150	.46^h
				.00346	.0389	.229	5.89 (4.23)		
				.0460	.460	~2.17	~4.72^g		
23	$N{\equiv}CCH_2CH_2CH_2$	CH_3	CH_3	.0446	.460	0.0986	0.214	7.8	.17^h
				.0494	.460	.0970	.211		
24	$N{\equiv}CCH_2CH_2CH_2CH_2$	CH_3	CH_3	.0375	.460	.0269	.0585	2.1	.06^h
				.0460	.460	.0269	.0585		

^{a} The rate constants are thought to be accurate to ±3%. ^{b} Reference 5. ^{c} Calculated from the amount of hydrogen evolved. ^{d} Rate data has been previously reported; ref. 2. ^{e} Rate constants were calculated for 0.460 N potassium hydroxide assuming the same salt effect as observed for ethyldimethylsilane. ^{f} Rate constants were calculated for 0.478 N potassium hydroxide assuming the same salt effect as observed for 3,3,3-trifluoropropyldimethylsilane. ^{g} Rate was too fast to measure accurately. ^{h} The $\sigma*$-values for the ω-cyanoalkyl groups were calculated by dividing the $\sigma*$-value for the cyanomethyl group by the factor of 2.8 for each intervening methylene group; ref. 15.

Sommer, et al.,[3] studied the alkali-catalyzed hydrolysis of chloromethyl- and iodomethyldimethylsilane, and Pike, et al.,[4] have compared the relative rate of hydrolysis of β-trichlorosilylpropionitrile with methyltrichlorosilane.

In this paper the effect of ω-cyanoalkyl, ω-phenylalkyl, n-alkyl and some additional fluoroalkyl groups on the rate of the alkali-catalyzed hydrolysis of the silicon–hydrogen bond in triorganosilanes has been determined. A correlation of the data with the Taft equation[5] is presented and discussed.

Experimental

Starting Materials.—(3-Bromopropyl)-benzene, (2-bromoethyl)-benzene and benzyl chloride were obtained from the Eastman Kodak Co. 5-Bromo-1,1,1,2,2,3,3-heptafluoropentane was synthesized by the method of Pierce, et al.[6] 4-Bromo-1,1,1-trifluorobutane was prepared as described previously.[2]

(3) L. H. Sommer, W. P. Barie, Jr., and D. R. Weyenberg, J. Am. Chem. Soc., 81, 251 (1959).

(4) R. A. Pike, J. E. McMahon, V. B. Jex, W. T. Black and D. L. Bailey, J. Org. Chem., 24, 1939 (1959).

(5) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 556–675.

(6) O. R. Pierce, E. T. McBee and R. E. Cline, J. Am. Chem. Soc., 75, 5618 (1953).

TABLE II
TRIORGANOSILANES

No.[a]	Method	Yield, %	B.p. °C.	Mm.	$n^{25}D$	d^{25}_4	Mole % purity[b]	Silane hydrogen, % Calcd.	Found	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Fluorine or nitrogen, % Calcd.	Found
1[c]	1	85	10	754			>99								
2[d]	2[e]	55	42–43	743	1.3767	0.677	95.0	1.14	1.09	54.5	54.8	13.7	13.2		
3[f]	2	27	78	748	1.3953	0.700	98.9	0.985	0.95						
4[f,i]	2	54	108	740	1.4091		>99	.87	.87						
5[f,g]	2	46	74	750	1.3884	0.692		.99	.96						
6[f]	2	38	129	746	1.4105	.729	>99	.77	.75						
7	1	83	70	15	1.4990	.869	>99	.67	.67	71.9	72.1	9.4	9.8		
8	2	85	129	2	1.5633	.977	>99	.445	.45	79.6	80.1	8.0	8.2		
9	2	55	89	15	1.4923	.868	>99	.61	.605	73.1	73.5	9.8	9.9		
10	2	59	156	2	1.5438	.957	98.9	.40	.39	80.2	79.0	8.7	9.2		
11	2	62	208	0.6	1.5707	1.004	..	.29	.30	83.7	83.3	8.2	8.5		
12	2	68	105	15	1.4922	0.873	98.2	.565	.54	74.1	74.2	10.2	10.4		
13	2	80	162	1	1.5359	.946	98.4	.36	.35	80.9	79.8	9.3	9.4		
14	2	58	232	0.7	1.5569	.986	..	.26	.26	83.9	84.3	8.9	9.1		
15[g]		72	80	748	1.3485	.954		.64	.66						
16[g]		49	64	40	1.3500	1.078		.42	.43						
17[g]		52	105	756	1.3612	0.950		.59	.60						
18	2	60	88	30	1.3663	1.115	>99	.38	.37	40.6	40.1			42.8	43.0
19	2	46	116	10	1.3690	1.207	>99	.28	.28	39.8	39.8			47.2	47.2
20[g]		73	94	743	1.3387	1.078		.49	.49						
21	2	49	111	741	1.3344	1.176	>99	.39	.39	32.8	33.0			51.9	52.0
22	3	65	62	15	1.4246	0.829	>99	.89	.87	53.05	53.05	9.8	9.8	12.4	12.3
23	3	63	77	15	1.4280	.829	>99	.79	.80	56.7	56.8	10.3	10.2	11.0	11.0
24[h]	3	60	93	15	1.4322	.829	>99	.71	.71	59.5	59.8	10.7	10.7	9.1	9.3

[a] Table I. [b] Determined by vapor phase chromatography. [c] Reference 12. [d] H. Westermark, *Acta Chem. Scand.*, 9, 947 (1955). [e] The solvent was tetrahydrofuran. [f] Reference 13. [g] Reference 2. [h] Reference 14.

Preparation of the ω-Cyanoalkyldimethylchlorosilanes.— The general procedure used is described by Sommer, *et al.*,[7] for the addition of methyldichlorosilane to allyl cyanide. Addition of dimethylchlorosilane to 4-pentenenitrile gave δ-dimethylchlorosilylvaleronitrile,[8] b.p. 119° (11 mm.), $n^{25}D$ 1.4468, d^{25}_4 0.974, a 63% yield. Using a 5% platinum-on-charcoal catalyst, dimethylchlorosilane was added to allyl cyanide to yield γ-dimethylchlorosilylbutyronitrile,[9] b.p. 109° (15 mm.), $n^{25}D$ 1.4444, d^{25}_4 0.989, a 35% yield. β-Dimethylchlorosilylpropionitrile,[10] b.p. 93° (15 mm.), $n^{25}D$ 1.4427, d^{25}_4 1.004, was available in small quantities.

Preparation of the Triorganosilanes.— The triorganosilanes were prepared by the three general methods given below. The compounds prepared by each method are designated in Table II.

(a) **Method 1.—** The procedure used for the reduction of the triorganochlorosilanes with lithium aluminum hydride is described by West.[11] A variation of the above procedure was used to prepare trimethylsilane because of its low boiling point. Lithium aluminum hydride (13.3 g., 0.35 mole) and 1,2-dimethoxyethane (250 ml.), distilled from calcium hydride, were placed in a flask equipped with a stirrer, condenser and dropping funnel. The system was vented to the atmosphere *via* a Dry Ice trap and drying tube. The system was purged with nitrogen, and trimethylchlorosilane (108.6 g., 1.0 mole), dissolved in 1,2-dimethoxyethane (100 ml.), was added over a period of 2 hours. The trimethylsilane formed was collected in the Dry Ice trap. The reaction mixture was slowly heated to reflux (86°) to ensure removal of all of the trimethylsilane from the reaction mixture. Fractional distillation of the material in the trap gave trimethylsilane,[12] b.p. 10° (754 mm.), an 85% yield.

(7) L. H. Sommer, F. P. MacKay, O. W. Steward and P. G. Campbell, *J. Am. Chem. Soc.*, **79**, 2764 (1957).

(8) O. W. Steward, Ph.D. Thesis, The Pennsylvania State University, 1957, pp. 88–90; *Dissertation Abstr.*, **17**, 2827 (1957).

(9) P. G. Campbell, Ph.D. Thesis, The Pennsylvania State University, 1957, pp. 80–81; *Dissertation Abstr.*, **17**, 2808 (1957).

(10) G. D. Cooper and M. Prober, *J. Org. Chem.*, **25**, 240 (1960).

(11) R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

(12) I. Tannenbaum, S. Kaye and G. F. Lewenz, *ibid.*, **75**, 3753 (1953).

(b) **Method 2.—** This method consists of adding the appropriate chlorosilane to the Grignard reagents according to the procedure reported by Price.[13] The chlorosilanes used were trichlorosilane, methyldichlorosilane and dimethylchlorosilane. In every reaction one equivalent of the Grignard reagent was added per silicon–chlorine bond. The reaction mixtures were refluxed 8 hours or longer.

(c) **Method 3.—** The procedure for the reduction of the ω-cyanoalkyldimethylchlorosilane with lithium aluminum hydride dissolved in ether to the corresponding ω-cyano-alkyldimethylsilanes is described by Steward.[14]

Kinetic Procedure.— The method of measuring the rate constants has been previously reported.[2]

Results

The rate data for the alkali-catalyzed hydrolysis of the triorganosilanes are reported in Table I. The physical properties, analytical data and yields of the triorganosilanes are reported in Table II.

All of the rate constants were determined at 0° in 93.7 wt.-% ethanol. The concentration of potassium hydroxide was 0.460 N or 0.478 N except where higher or lower concentrations were necessary to obtain measurable rates. In these cases it was necessary to correct the rate constants for a salt effect in order that the data could be compared on the same basis. This was accomplished by measuring the rate of a triorganosilane having intermediate reactivity at the two base concentrations employed and applying a proportionate correction factor to calculate the desired rate constant.

The rate data were correlated using the Taft equation[5]

$$\log (k/k_0) = (\Sigma\sigma^*)\rho^*$$

(13) F. P. Price, *ibid.*, **69**, 2600 (1947).

(14) O. W. Steward, Ph.D. Thesis, The Pennsylvania State University, 1957, pp. 132–134; *Dissertation Abstr.*, **17**, 2827 (1957).
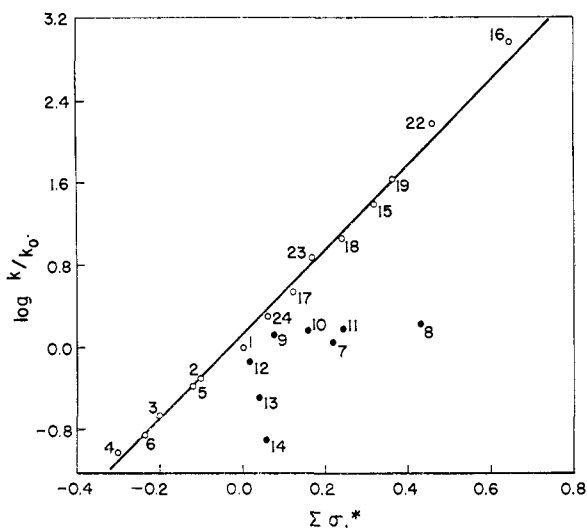
Fig. 1.—Straight line correlation of the second-order rate constants for the alkali-catalyzed hydrolysis of the triorganosilanes in 93.7 wt.-% ethanol at 0°, KOH concn. 0.460–0.478 N. The numbers refer to the compounds listed in Table I. The solid circles represent the ω-phenylalkylsilanes.
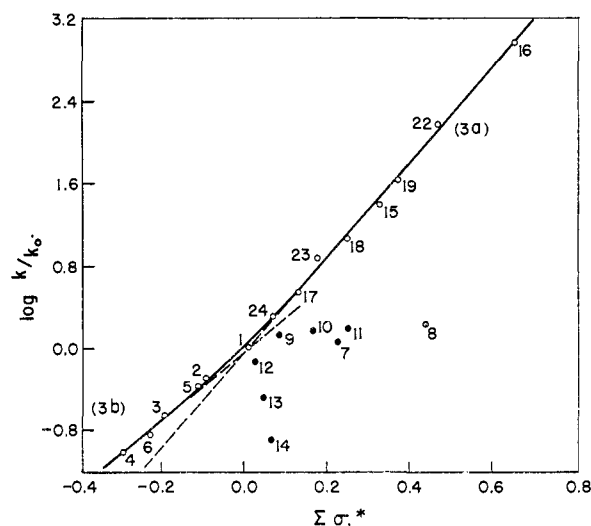

Fig. 2.—Curved line correlation of the second-order rate constants for the alkali-catalyzed hydrolysis of the triorganosilanes in 93.7 wt.-% ethanol at 0°, KOH concn. 0.460–0.478 N. The numbers refer to the compounds listed in Table I. The solid circles represent the ω-phenylalkylsilanes.

Plots of log (k/k_0) vs. $\Sigma\sigma^*$ are shown in Figs. 1 and 2.

Three different correlations of the rate data were obtained by the method of least squares omitting the points representing the triorganosilanes with ω-phenylalkyl groups: (1) the best straight line (Fig. 1), (2) the best straight line through the origin, and (3) the best pair of straight lines representing a concave-upward curve (Fig. 2). The results are given in Table III.

TABLE III

CORRELATION DATA

Correlation	ρ^*	$s_0{}^a (\rho^*)$	a^b	$s_e(a)$	s_e (log k/k_0)	r^c
1	4.27	0.08	0.123	0.022	0.08	0.998
2	4.42	.14			.15	.992
3a	4.60	.09	.013	.017	.05	.998
3b	3.55	.15	.024	.015	.03	.996

^{a} Standard error. ^{b} Intercept. ^{c} Correlation coefficient.

The straight line correlation (1) and the concave-upward curve correlated by two straight lines (3) appear to represent equally well the data. However, the straight line does not pass through the origin as required by the Taft equation, while the pair of straight lines come very close to the origin (one line passes through the origin within the standard error and the other within two standard errors). If the straight line is forced through the origin (2), the two straight lines (3) represent a better correlation.

The above calculations are based on the assumption that the errors in the log k/k_0 terms are considerably greater than the errors in the σ^*-values. The precision of the σ^*-values is not well known, and the errors are additive. Therefore, a decision on the best correlation cannot be obtained with the above data.

The fourteen points included in the correlations represent only triorganosilanes with primary organic groups and cover a total spread of approxi-

mately four powers of ten in the rate constant. Experimental limitations prevent the data from being extended in either direction to aid in the decision on the best correlation.

The eight triorganosilanes with ω-phenylalkyl groups do not appear to be correlated by the Taft equation. The deviation from the equation toward slower rates is successively larger as methyl groups are replaced with ω-phenylalkyl groups. This type of behavior is what would be expected if steric effects were involved.

The σ^*-values for the ω-cyanoalkyl groups used in the above correlations were calculated by dividing the reported σ^*-value for the cyanomethyl group (1.30) by the factor 2.8 for each intervening methylene group.[15] Stevenson and Williamson[16] have reported larger values for the ω-cyanoalkyl groups based on the base strengths of the ω-cyanoalkyldiethylamines. The observed rate constants for the alkali-catalyzed hydrolysis of the ω-cyanoalkyldimethylsilanes are not correlated by these values.

The σ^*-values have not been reported for the 3,3,4,4,4-pentafluorobutyl and 3,3,4,4,5,5,5-heptafluoropentyl groups. Using $\rho^* = 4.60$ in the Taft equation, $\sigma^* = 0.34$ for both groups. This value is very close to that reported by Taft[5] for the 3,3,3-trifluoropropyl group ($\sigma^* = 0.32$).

Discussion

Steric Effects.—Significant differences in steric effects are not observed for the triorganosilanes studied except for the ω-phenylalkylsilanes. Steric effects may be involved, but remain constant for the triorganosilanes as long as there is no branching in the substituent groups.

The triorganosilanes ($R_1R_2R_3SiH$) should be compared with the corresponding trialkylcarbinyl

(15) R. W. Taft, Jr., ref. 5, p. 592.

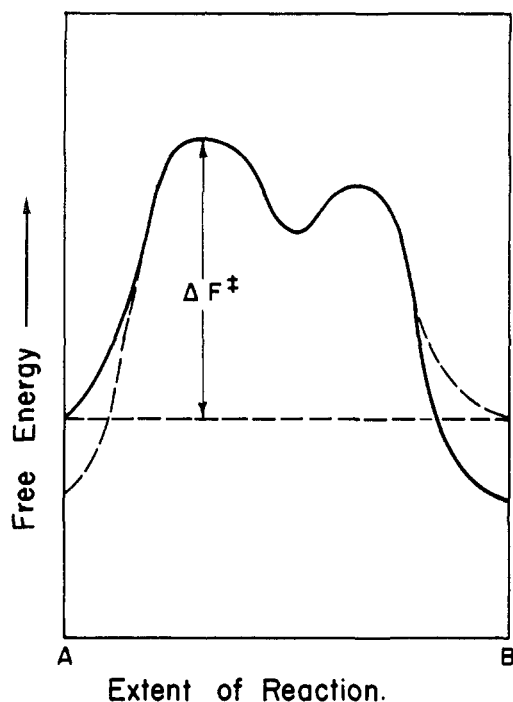(16) G. W. Stevenson and D. Williamson, J. Am. Chem. Soc., 80, 5943 (1958).

Fig. 3.—Qualitative free energy diagram of the reaction path: proceeding from A to B *via* the solid curve represents mechanism 1; proceeding from B to A *via* the dashed curve represents mechanism 2b.

halides ($R_1R_2R_3CX$) under S_N2 conditions for steric effects. Other than the effect of the greater size of the silicon atom on reducing steric effects, the steric requirements should be quite similar. However, these data are not available.

The alkali-catalyzed hydrolysis of triorganosilanes is quite susceptible to steric effects resulting from branching of the alkyl groups. Baines and Eaborn have shown that branching at the β-carbon atom in triisobutylsilane greatly reduced the rate of hydrolysis.[17] The steric effect of a *t*-butyl group on the alkali-catalyzed hydrolysis of *t*-butyldimethylsilane has been reported by Sommer and Barie.[18]
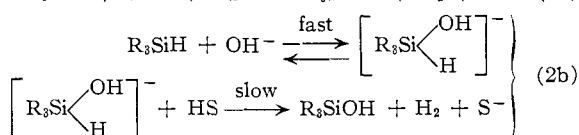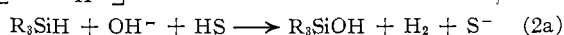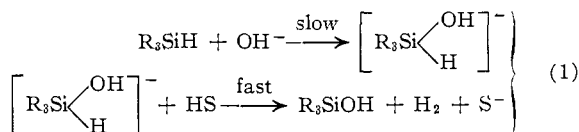
The ω-phenylalkylsilanes, which may be considered as triorganosilanes with branched alkyl groups, react at a slower rate than predicted by the Taft equation. The deviations from the predicted values are successively larger as methyl groups are replaced with ω-phenylalkyl groups indicating that considerable steric effects are probably involved. The deviations are approximately linear within each series. Linear steric effects with trialkylsilanes have been reported.[19] As expected, the benzylmethylsilanes show the largest deviations. However, it is not clear why the β-phenylethyl- and γ-phenylpropylsilanes show approximately the same deviations.

Mechanism.—The alkali-catalyzed hydrolysis of the silicon–hydrogen bond in 95% ethanol has been found to be first order in silane and first order in hydroxide ion.[13] Two mechanisms have been formulated which are consistent with the kinetic data.[20] Mechanism 1 involves the rate-determin-

$$R_3SiH + OH^- \xrightarrow{slow} \left[R_3Si{<}^{OH}_{H} \right]^- \Bigg\}$$

$$\left[R_3Si{<}^{OH}_{H} \right]^- + HS \xrightarrow{fast} R_3SiOH + H_2 + S^- \Bigg\} \quad (1)$$

$$R_3SiH + OH^- + HS \longrightarrow R_3SiOH + H_2 + S^- \quad (2a)$$

$$R_3SiH + OH^- \underset{}{\overset{fast}{\rightleftarrows}} \left[R_3Si{<}^{OH}_{H} \right]^- \Bigg\}$$

$$\left[R_3Si{<}^{OH}_{H} \right]^- + HS \xrightarrow{slow} R_3SiOH + H_2 + S^- \Bigg\} \quad (2b)$$

ing attack of hydroxide ion on the silane to form a pentacovalent silicon intermediate which reacts rapidly with the solvent to yield the products. There are two possible variations of mechanism 2: (a) simultaneous attack by hydroxide ion and a solvent molecule to yield the products; (b) a rapid, reversible equilibrium of hydroxide ion with the silane to form a pentacovalent silicon intermediate which reacts in the rate-determining step with a solvent molecule to yield the products. The representation of the mechanisms above is not absolutely correct because the percentages of reaction due to hydroxide ion and ethoxide ion are not known as a result of the equilibrium

$$OH^- + C_2H_5OH \rightleftarrows C_2H_5O^- + H_2O$$
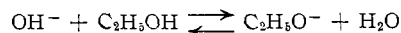
Price[13] presented data which indicated the reaction was probably first order in water and concluded the reaction proceeded *via* mechanism 2a. Kaplan and Wilzbach[20] gave evidence in support of mechanism 2 by studying isotope effects. Sommer, *et al.*,[21] have shown that rearward attack by the base is not necessary for the alkali-catalyzed hydrolysis of 1-silabicyclo[2.2.1]heptane[21a,b,c,d] and 1-silabicyclo[2.2.2]octane[21d,e] and presented evidence that a pentacovalent silicon intermediate is involved in the alkali-catalyzed hydrolysis of chloromethyldimethylsilane and iodomethyldimethylsilane.[21f] They also have shown that the base-catalyzed hydrolysis of 1-methyl-1-silacyclobutane cannot proceed by mechanisms 2a and 2b and probably proceeds by mechanism 1.[21g,h] It was pointed out that the conclusions of Price[13] and Kaplan and Wilzbach[20] which support mechanism 2 are questionable.[21g,h]

(17) J. E. Baines and C. Eaborn, *J. Chem. Soc.*, 4023 (1955). The following relative rates were reported using 1.120 *N* sodium hydroxide in 94.5% ethanol at 34.9°: triethylsilane, 100; tri-*n*-propylsilane, 40; tri-*n*-butylsilane, 27; triisobutylsilane, 4.1; triisopropylsilane, 2.2.

(18) L. H. Sommer and W. P. Barie, Jr., "Abstracts of Papers," 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 21 M.

(19) R. W. Taft, Jr., ref. 5, p. 647.

(20) L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, 77, 1297 (1955).

(21) (a) L. H. Sommer and O. F. Bennett, *ibid.*, 79, 1008 (1957); (b) L. H. Sommer, O. F. Bennett and P. G. Campbell, "Abstracts of Papers," 132th Meeting of the American Chemical Society, New York, N. Y., Sept., 1957, p. 56P; (c) L. H. Sommer, O. F. Bennett, P. G. Campbell and D. R. Weyenberg, *J. Am. Chem. Soc.*, 79, 3295 (1957); (d) L. H. Sommer, O. F. Bennett and P. G. Campbell, "Abstracts of Papers," 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 22M; (e) L. H. Sommer and O. F. Bennett, *J. Am. Chem. Soc.*, 81, 251 (1959); (f) L. H. Sommer, W. P. Barie, Jr., and D. R. Weyenberg, *ibid.*, 81, 251 (1959); (g) L. H. Sommer, D. R. Weyenberg and P. G. Campbell, "Abstracts of Papers," 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 23M; (h) D. R. Weyenberg, Ph.D. Thesis, The Pennsylvania State University, 1958; *Dissertation Abstr.*, 19, 2776 (1959).

Concave-upward curves have been observed for the Hammett equation for the reactions of alkyl and acyl halides with nucleophilic reagents.[22] This type of relationship can best be explained by postulating a change in mechanism or a gradual change in the importance of the bond-making and bond-breaking steps in the transition state of a concerted type mechanism.[22]
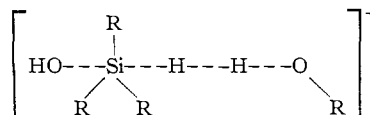
The significance of the concave-upward curve obtained from the Taft equation (Fig. 2) cannot readily be determined since the precision of the σ^*-values is not well known. However, if the concave-upward curve is significant, it could represent a gradual change from mechanism 1 to 2a or from mechanism 2b to 2a in the case of the base-catalyzed hydrolysis of the silicon–hydrogen bond. This can be demonstrated by using a qualitative free energy diagram (Fig. 3). Proceeding from A to B via the solid curve represents mechanism 1 and proceeding from B to A via the dashed curve represents mechanism 2b. As the groups attached to silicon are changed from electron-withdrawing groups to electron-releasing groups, the pentacovalent silicon intermediate which possesses a negative charge on the silicon would be expected to become less stable. When the free energy minimum of the pentacovalent silicon intermediate disappears, both mechanisms 1 and 2b would become identical to 2a.

In the light of the above discussion, the mechanism observed would depend on the structure of

(22) H. H. Jaffé, Chem. Revs., 53, 237 (1953).

the silane. If it can be assumed that silanes having strained rings and strongly electron-withdrawing groups proceed via mechanism 1 by analogy with the alkali-catalyzed hydrolysis of 1-methyl-1-silacyclobutane and from the large positive ρ^*-value, the curve obtained would represent a gradual change from mechanism 1 to 2a as electron-withdrawing groups are replaced by electron-releasing groups in the triorganosilanes.

Changing from mechanism 1 to 2a would be expected to reduce the ρ^*-value since a solvent molecule becomes involved in the transition state of the rate-determining step. The presence of a solvent molecule in the transition state would reduce the negative charge on the silicon by partially accepting the departing hydride ion. The transition state for mechanism 2a may be represented as[23]

$$\left[\begin{array}{c} R \\ | \\ HO\text{-}\text{-}\text{-}Si\text{-}\text{-}\text{-}H\text{-}\text{-}\text{-}H\text{-}\text{-}\text{-}O \\ \diagup \diagdown \qquad\qquad \diagdown \\ R \quad R \qquad\qquad\qquad R \end{array} \right]^-$$

(23) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, p. 200.

Preparation and Characterization of Octaphenylcyclotetrasilane

BY A. W. P. JARVIE, H. J. S. WINKLER, D. J. PETERSON AND H. GILMAN
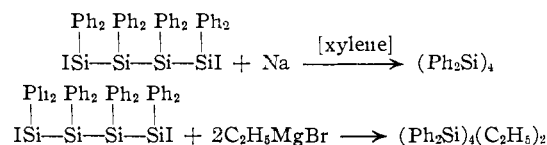
An improved method of preparation of Kipping's Compound (A) has been devised. The structure of this compound has been shown to be octaphenylcyclotetrasilane by the preparation of 1,4-dimethyloctaphenyltetrasilane from it. This latter compound was prepared by an independent route from methyldiphenylsilyllithium and sym-dichlorotetraphenyldisilane. In addition, 1,4-dichloroöctaphenyltetrasilane, which was prepared by the direct ring opening of octaphenylcyclotetrasilane, gave on reaction with phenyllithium the previously described decaphenyltetrasilane.

It was reported in a preliminary communication[1a] that the compound designated Compound (A) by Kipping,[1b] isolated from the reaction of dichlorodiphenylsilane with sodium, was octaphenylcyclotetrasilane. The structure assigned to Compound (A) by Kipping contained two "tervalent silicon atoms": –SiPh₂·SiPh₂·SiPh₂·SiPh₂–.[1b,2] This structure provided a reasonable explanation for the high reactivity of the compound in free radical-type reactions. For example, Compound (A) reacted with one mole equivalent of iodine to give 1,4-di-iodoöctaphenyltetrasilane,[1b] with atmospheric oxygen or nitrobenzene to give siloxanes,[2a]

(1) (a) H. Gilman, D. J. Peterson, A. W. Jarvie and H. J. S. Winkler, J. Am. Chem. Soc., 82, 2076 (1960); (b) F. S. Kipping and J. E. Sands, J. Chem. Soc., 119, 830 and 848 (1921).

(2) (a) F. S. Kipping, ibid., 123, 2590 and 2598 (1923); (b) F. S. Kipping, ibid., 119, 848 (1921); (c) F. S. Kipping, ibid., 125, 2291 (1924); (d) F. S. Kipping, ibid., 2978 (1927); (e) F. S. Kipping, "Bakerian Lecture," Proc. Roy. Soc. (London), 159A, 139 (1937).

and with certain halogenated solvents to give 1,4-dihalo-octaphenyltetrasilanes. The analytical results showed that the compound was composed of diphenylsilylene units and molecular weight determinations indicated that four such units were present. Two reactions of the di-iodo compound confirmed the presence of four diphenylsilylene units:

Ph₂ Ph₂ Ph₂ Ph₂
 | | | |
ISi—Si—Si—SiI + Na $\xrightarrow{\text{[xylene]}}$ (Ph₂Si)₄

Ph₂ Ph₂ Ph₂ Ph₂
 | | | |
ISi—Si—Si—SiI + 2C₂H₅MgBr $\longrightarrow$ (Ph₂Si)₄(C₂H₅)₂

Analytical data and molecular weight determinations agreed with the structures shown for the 1,4-di-iodo- and the 1,4-diethyloctaphenyltetrasilane.

Paramagnetic resonance measurements on the solid Compound (A) as well as on its solution in tol-