Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

CARBONIUM ION-SILANE HYDRIDE TRANSFER REACTIONS
IV. STRUCTURE AND REACTIVITY AT SILICON

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(Received February 7th, 1969; in revised form May 23rd, 1969)

SUMMARY

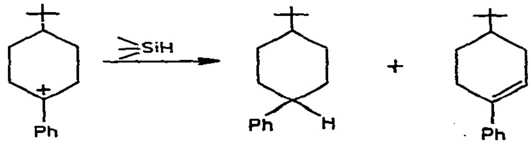
Rates of hydride transfer from substituted silanes to the tris(2,6-dimethoxyphenyl)methyl cation were measured spectrophotometrically in acetic acid. For a series of triarylsilanes the value of ρ was -1.84 and for aryldimethylsilanes ρ was -1.01. For both series a better correlation was obtained for σ than for σ^+.

The primary kinetic isotope effect k_H/k_D was measured for transfer from triphenylsilane and triphenyldeuteriosilane to the tris(2,6-dimethoxyphenyl)methyl cation, the 9-*p*-anisylxanthyl cation and the phenyl-*p*-tolyldeuteriomethyl cation and found to be between 1.51 and 1.89 for the three carbonium ions.

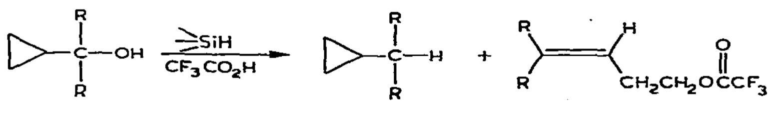
The results indicate that the transition state for hydride transfer from silicon involves a four center array (trigonal bipyramid at silicon) in which nucleophilic participation by solvent aids in displacement of hydride from silicon.

INTRODUCTION

In the course of studying hydride transfers from silicon to carbonium ions we have reported some qualitative observations about the relative reactivities of several silanes as hydride donors[1]. These observations were made by comparing the amounts of hydride transfer with elimination in the 4-tert-butyl-1-phenylcyclohexyl cation.



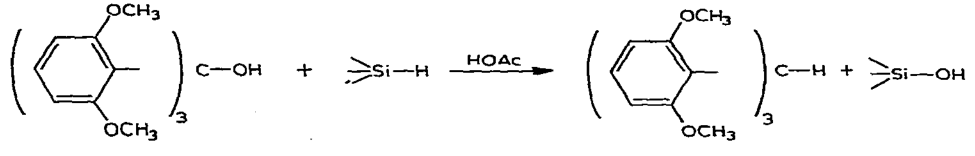
The results indicated that silane reactivity decreases in the order triethylsilane ~ diethylsilane > diphenylsilane > triphenylsilane > phenylsilane. Kursanov[2] has found the approximate order to be diphenylsilane > phenylsilane > triphenylsilane for similar reactions. We have also observed for hydride transfer to cyclopropylmethyl cations that much more ring-opening occurs with triphenylsilane as the carbonium ion trap than with triethylsilane[3].



In contrast to these results, triphenylsilane has been shown to be more reactive than triethylsilane for the hydrogen–halogen exchange between trityl chloride and silanes[4].

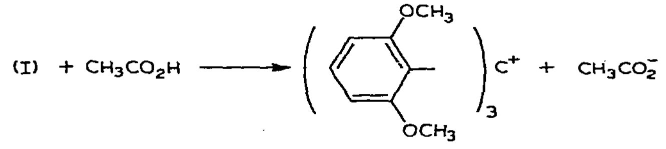
In order to obtain more quantitative data regarding the effectiveness of silanes as hydride donors we have studied the rates of hydride transfer to stable carbonium ions from a variety of silanes. We also felt that this study would give us an insight into the mechanism of the reaction and the amount of positive charge, if any, generated at silicon during the reaction.

Previously we found that tris(2,6-dimethoxyphenyl)methanol (I) was quantitatively converted to the corresponding triarylmethane (II) with silanes in acetic acid.



(I) (II)

This reaction was chosen for the kinetic study since it proceeded at a convenient rate to give a single product. The carbonium ion (III) (pK_a 6.5)[5] formed from (I) is very stable in acetic acid* and its UV spectrum is characterized by an intense long wavelength absorption at 522 mμ (log ε 4.5)[5]. Since the absorbance of 4.8×10^{-5} M solution of (I) in acetic acid is the same as that of a 4.8×10^{-5} M solution of (I) in 90% acetic acid/10% trifluoroacetic acid, it is likely that the conversion of (I) to (III) is complete in acetic acid. This conclusion is further supported by the fact that the extinction coefficient in acetic acid (1.93×10^4) is in good agreement with that reported for (III) in other media[5].



(III)

Since (I) is converted quantitatively to (III) in acetic acid and (III) is stable in this medium the efficiency of silanes toward hydride transfer can be found by measuring the rate of disappearance of (III) spectrophotometrically.

$$\text{(III)} + \text{R}_3\text{SiH} \xrightarrow{k} \text{(II)}$$

The rate

$$\frac{-\mathrm{d}[\text{(III)}]}{\mathrm{d}t} = k \cdot [\text{(III)}] \cdot [\text{R}_3\text{SiH}]$$

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* This carbonium ion is not stable in aqueous acid where it undergoes cyclization to a xanthyl cation[5].

For a second order reaction

$$k \cdot t = \frac{1}{a-b} \ln \frac{a-x}{b-x} + \frac{1}{a-b} \ln \frac{b}{a} \qquad (1)$$

where a and b are initial concentrations of carbonium ion and silane respectively and x is the concentration of (II). Also, when $a = b$,

$$\frac{1}{[(\text{III})]} = k \cdot t + \text{constant} \qquad (2)$$

When silane is in large excess, a pseudo first order reaction obtains,

$$\log A = k' \cdot t + \log A_0 \qquad (3)$$

where k' is the pseudo first order reaction rate constant. The second order rate constant

$$k = k'/[\text{R}_3\text{SiH}] .$$

RESULTS

The rate of hydride transfer to (III) from silanes was measured spectrophotometrically at 523 mμ in acetic acid. The reaction was shown to be first order in silane concentration using triethylsilane as the donor. These reactions were run under conditions where [Et_3SiH] was much greater than [(III)] and the data plotted as for a pseudo-first order reaction (Table 1 and Fig. 1). Good fits were obtained for eqn. (3) and the values of the second order rate constant k obtained were very similar. A test was made for possible catalysis by Et_3SiOH generated during the course of the reaction by adding Et_3SiOH to the reaction mixture. No catalysis was observed.

TABLE 1

EFFECT OF SILANE CONCENTRATION ON RATE OF HYDRIDE TRANSFER TO III

[(III)] (moles/l) × 10^5	[Et_3SiH] (moles/l) × 10^3	[Et_3SiOH] (moles/l) × 10^4	k ($l \cdot mole^{-1} \cdot min^{-1}$)
4.8	1.52	0	39.5
5.1	3.05	0	42.9
4.8	3.2	0	39.6
4.8	6.0	0	39.9
4.8	4.5	4.4	37.6

In one instance rates were measured under conditions where the concentration of silane (in this case, *p*-tolyldimethylsilane) and (III) were comparable and the data plotted according to eqn. (2) for a second order reaction (Fig. 2). An excellent fit was obtained as were also for intermediate ratios of concentrations for hydride transfer from *p*-tolyldimethylsilane to (III) when these data were plotted according to eqn. (1) (Fig. 3).

The relative reactivities of a series of substituted triarylsilanes and aryldimethylsilanes were determined by measuring the rates under pseudo first-order conditions and are summarized in Tables 2 and 3.

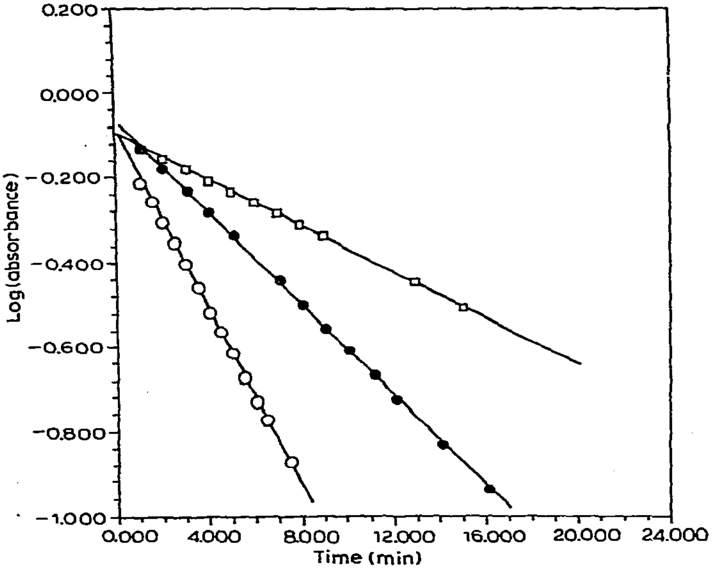


Fig. 1. Pseudo-first-order rate plot for hydride transfer from Et_3SiH to (III) in acetic acid: [Et_3SiH] in moles/l: □ 1.52×10^{-3}; ● 3.18×10^{-3}; ○ 6.0×10^{-3}.

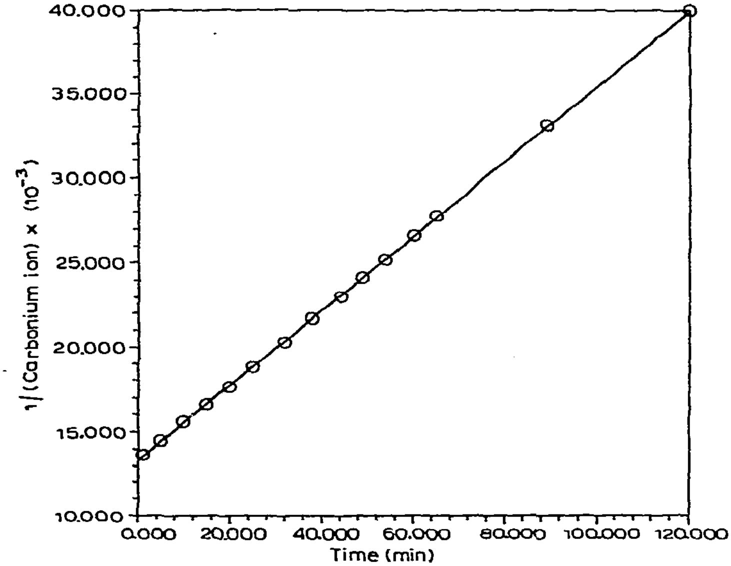


Fig. 2. Second order rate plot for hydride transfer from *p*-tolyldimethylsilane to (III): $[(III)]_0 = 7.3\times10^{-5}$ *M* and $[\equiv SiH]_0 = 7.2\times10^{-5}$ *M*.

Both the triarylsilanes and aryldimethylsilanes are similar in that electron-withdrawing substituents on the aromatic ring decrease the rate of hydride transfer while electron releasing substituents make the silane more reactive. The value of ρ for the series of five triarylsilanes was -1.84 ± 0.23 (correlation coefficient of 0.983) when plotted[6] against $\Sigma\sigma$ (Fig. 4). A poorer fit was obtained (correlation coefficient

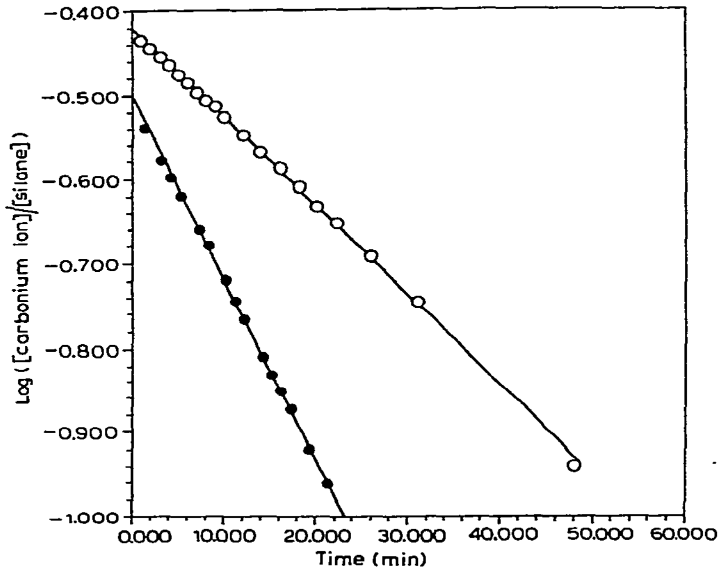


Fig. 3. Second order rate plot for hydride transfer from *p*-tolyldimethylsilane to (III). Concentrations in moles/l: ○ [(III)] 6.4×10^{-5}, [$\geqslant$SiH] 1.65×10^{-4}; ● [(III)] 9.6×10^{-5}, [$\geqslant$SiH] 3.07×10^{-4}.

TABLE 2

RELATIVE RATES OF HYDRIDE TRANSFER TO (III) FROM $(XC_6H_4)_3SiH$ IN ACETIC ACID AT 24°

X	σ	[(III)] (moles/l) × 10^5	[$\geqslant$SiH] (moles/l) × 10^2	k (l/mole^{-1}·min^{-1})	k_{rel}
p-CH_3O	−0.268	5.20	0.62	18.1	16.9
		5.20	0.62	16.4	
H	0.000	5.20	4.63	1.05	1.00
		5.20	6.53	0.99	
p-F	0.062	3.75	32.6	0.0929	0.088
		4.25	41.0	0.0899	
p-Cl	0.226	12.8	8.24	0.0267	0.0258
		8.22	7.45	0.0259	
m-CF_3	0.415	7.20	66.0	0.00367	0.00345
		12.8	56.6	0.00335	

0.933) when plotted against σ^+. The situation was similar for the six aryldimethylsilanes in that a better correlation (0.975) was obtained for σ than for σ^+ (correlation coefficient 0.966). The aryldimethylsilanes were less sensitive to substituent effects than the triarylsilanes, ρ being -1.01 ± 0.052 (Fig. 5).

It should also be noted that the aryldimethylsilanes were always more reactive than the corresponding triarylsilanes, in fact, the least reactive aryldimethylsilane, [*m*-(trifluoromethyl)phenyl]dimethylsilane, was over 4 times as reactive as the most reactive triarylsilane, tris(*p*-methoxyphenyl)silane. The effect was magnified with the least reactive member of each group, [*m*-(trifluoromethyl)phenyl]dimethylsilane.

TABLE 3

RELATIVE RATES OF HYDRIDE TRANSFER TO (III) FROM $(XC_6H_4)Si(CH_3)_2H$ IN ACETIC ACID AT 24°

X	σ	[(III)] (moles/l) × 10^5	$[\equiv\text{SiH}]$ (moles/l) × 10^3	k ($l \cdot mole^{-1} \cdot min^{-1}$)	k_{rel}
p-CH_3O	−0.268	4.9	1.65	356	2.10
			2.19	318	
p-CH_3	−0.170	4.8	0.83	237	1.46
		4.8	0.84	251	
		6.4	0.18	236	
		9.6	0.31	231	
		7.3	0.072	222	
H	0.00	4.9	1.56	160	1.00
		4.9	2.31	161	
p-F	0.062	4.9	5.98	110	0.68
		4.9	4.65	107	
p-Cl	0.226	4.9	6.84	96	0.59
		4.9	7.94	94	
m-CF_3	0.415	4.9	12.7	70	0.43
		4.9	9.4	67	

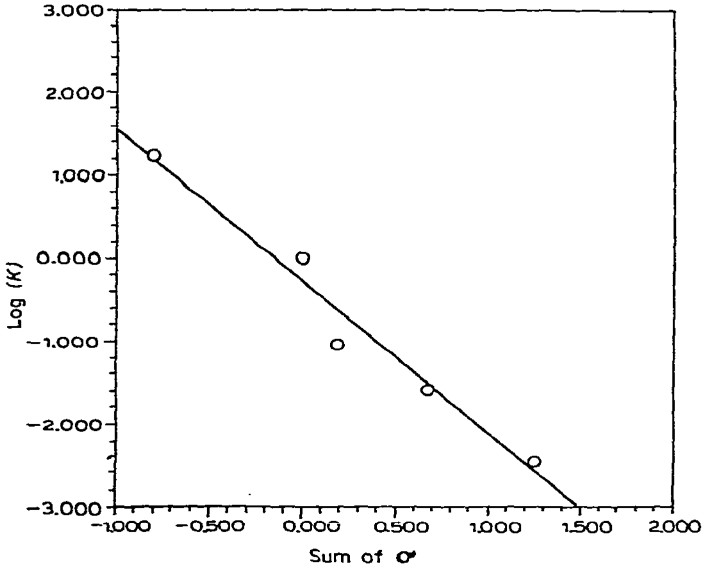


Fig. 4. Plot of log (k/k_0) vs. $\Sigma\sigma$ for hydride transfer from $(XC_6H_4)_3SiH$ to (III).

being 1.95×10^4 times as reactive as tris[m-(trifluoromethyl)phenyl]silane. This suggests that alkyl substituents activate silanes toward hydride transfer relative to aryl substituents. By measuring the rate of hydride transfer to (III) from triethylsilane it was found that k was 40.5. Diethylsilane is more reactive than triethylsilane, k being 166. It should be noted here, however, that since the carbonium ion being examined is sterically hindered, it is difficult to ascertain how much of this is due to

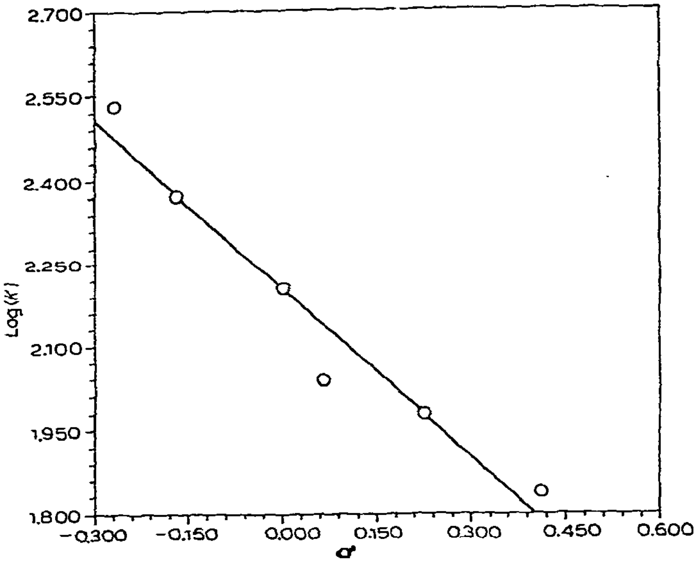
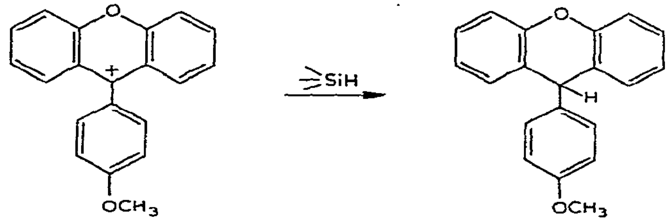


Fig. 5. Plot of log (k/k_0) *vs.* σ for hydride transfer from $(XC_5H_4)Me_2SiH$ to (III).

electronic effects and how much is due to steric effects.

In order to gain further information about the reaction we have measured the rate of transfer of deuterium to (III) from Ph_3SiD. Such measurements performed under conditions identical with transfer of protium from Ph_3SiH gave a value for the primary kinetic isotope effect $k_H/k_D = 1.89$. Since (III) is so stable, we thought it might be useful to examine hydride transfer to some less stable carbonium ions.

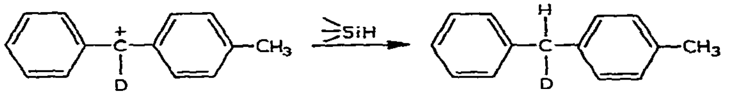
For the 9-(*p*-methoxyphenyl)xanthyl cation (IV) [pK(R^+) +1.55] the rate of transfer from Ph_3SiH and Ph_3SiD was measured spectrophotometrically in methylene chloride/trifluoroacetic acid and found to be 1.89, the same as for (III).



(IV) (V)

To check this result k_H/k_D was measured by an independent method in which Ph_3SiH and Ph_3SiD were allowed to compete for a deficiency of (IV). By isolating the 9-(*p*-methoxyphenyl)xanthene (V) by chromatography on alumina and integrating the NMR signals of the *p*-methoxy protons and the hydrogen at the 9-position the relative amounts of hydrogen and deuterium at C-9 could be calculated. The value for k_H/k_D obtained in this manner was 1.72 ± 0.11 in reasonable agreement with the value obtained spectrophotometrically.

The competition technique was also used to measure the primary kinetic isotope effect for hydride transfer to the phenyl-*p*-tolyldeuteriomethyl cation (VI).



(VI) (VII)

The reason for using the α-deuterium compound was a practical one, namely, to increase the accuracy possible in measurement of the peak areas in the NMR. The p$K(R^+)$ of cation (VII) was not measured but is estimated to be about −12.

Again Ph_3SiH and Ph_3SiD were allowed to compete for a deficiency of the carbonium ion and the product isolated by chromatography on alumina and further purified by evaporative distillation. Integration of the *p*-methyl signal and the signal due to protium at the benzylic position gave $k_H/k_D = 1.51 \pm 0.07$.

DISCUSSION

Under the reaction conditions studied here the transfer of hydride from silicon to a carbonium ion involves a molecule of silane or other species the concentration of which is proportional to silane in the rate determining step. This is evidenced by the observed first order dependence of rate on silane concentration and the presence of a primary kinetic isotope effect for the hydride (deuteride) being transferred.

Hydride transfer reactions between carbons are postulated to proceed by way of linear transition states and lead to the destruction of one carbonium ion and the formation of another[7]:

$$R_3C^+ + R'_3CH \rightleftarrows R_3CH + R'_3C^+$$

Of immediate concern in the reaction studied here is the question of the intermediacy of siliconium ions:

$$R_3C^+ + R'_3SiH \rightarrow R'_3CH + R'_3Si^+$$

Such a reaction where R and R′ are methyl has been calculated to be exothermic by 8 kcal/mole in the gas phase from thermochemical data[8]. The first order rate dependence on silane and the presence of a primary kinetic isotope effect are consistent with, but do not require, such a rate-determining step in solution.

From the dependency of silane reactivity on substituents in triarylsilanes and aryldimethylsilanes it does not seem reasonable that a siliconium ion is involved as an intermediate in these reactions, however*. The values of ρ, −1.87 for triarylsilanes and −1.01 for aryldimethylsilanes are not of such magnitude as to be consistent with formation of a trivalent siliconium ion in the rate-determining step.

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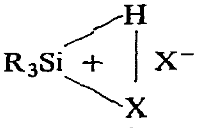
* For a review and excellent discussion regarding structure and reactivity in organosilicon chemistry see ref. 9.

By way of comparison, ρ for the insertion of dichlorocarbene into aryldimethylsilanes[10] is -0.63 while ρ for ozonolysis of aryldimethylsilanes has been reported[11] as -1.43. For bromination and chlorination of trialkylsilanes[12,13], a reaction which probably involves proton transfer by way of (VIII) (intermediate or transition state), ρ is -4.2.

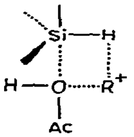


X = Br or Cl

(VIII)

West has suggested that hydride–halide exchange between Ph_3SiH and Ph_3CCl in ionizing solvents proceeds through a four-center transition state in which nucleophilic attack by the chloride of the ion-pair on silicon occurs while hydride is being transferred[4]. Such an explanation has received support from the observation that hydride transfer to Ph_3CCl by (+)-1-naphthylphenylmethylsilane occurs with complete retention of configuration of silicon[14].

A four-center arrangement involving a trigonal bi-pyramid at silicon is also consistent with all the data reported here.



R^+ = (III)

The fact that ρ is negative for both triarylsilanes and aryldimethylsilanes indicates that Si–H bond-breaking precedes Si–O bondmaking for hydride transfer to (III) under these conditions. We should probably point out that there could exist a continuum of transition state geometries for these reactions which depend on solvent, carbonium ion stability, steric effects in R^+ and R_3SiH and nucleophilicity of the counter ion and/or solvent.

The data for the primary kinetic isotope effects are also interesting and worth discussing. While the primary kinetic isotope effect for proton transfers is rather well understood in terms of loss of an X–H stretching vibration in the transition state[15,16] and appears to be a maximum value for a symmetrical transition state[17] the case for hydride transfers is less clear. Generally the primary kinetic isotope effect for hydride transfers is small (k_H/k_D between 1.0 and 2.5)[18] and is but a fraction of the value calculated for a transition state in which the vibration which is lost is the X–H stretching mode. Two reasonable explanations have been offered for this anomaly for the case of the base-catalyzed hydrolysis of Ph_3SiH:

(1). The transition state involves strong bonding between the hydride being removed and the proton of the solvent and, therefore, an H–H stretching vibration is gained in the transition state[19].

(2). The transition state involves attack by the electrophile on the Si–H bond through a triangular array of atoms rather than a linear array and the vibration which is lost is not the Si–H stretching mode but rather one which resembles Si–H bending[20,21]. Since bending modes are of much lower frequency than stretching modes, the difference in zero-point energy will be much less and the observed isotope effect will be small.

The isotope effects observed in our study are small and of the same order as those reported for several other reactions involving hydride transfer and do not serve to resolve the questions posed. The proposed four-center transition state does seem more easily reconciled with loss of the hydrogen bending mode, however. What is significant about the observed isotope effects is that their magnitude is relatively independent of carbonium ion (acceptor) stability. The three carbonium ions, (III), (VI) and (VIII) differ in stability by *ca.* 19 p$K(R^+)$ units (10^{19} in equilibrium constant) and yet exhibit isotope effect of 1.89, 1.89 and 1.51, respectively. Swain has proposed that isotope effects for proton transfers should be sensitive to substituent effects but that substituents should not influence the isotope effects for hydride transfer[22]. The independence of k_H/k_D on carbonium ion stability observed here provides experimental verification of Swain's proposal.

EXPERIMENTAL

Materials

The triarylsilanes were prepared by reacting the appropriate Grignard reagent with trichlorosilane in ether[23]. The m.p. of tris(*p*-methoxyphenyl)silane, tris(*p*-chlorophenyl)silane and tris(*p*-fluorophenyl)silane agreed with the reported values[23,24]. Tris[*m*-(trifluoromethyl)phenyl]silane prepared by this method was a liquid (b.p. 134–136° at 0.17 mm, n_D^{23} 1.4965). The value reported in the literature[25] for the b.p. of this compound (b.p. 147–150° at 0.05 mm) does not agree well but the reported n_D^{20} 1.4948 is satisfactory. The NMR and mass spectra were both consistent with the supposed structure. All of these triarylsilanes showed the signal for the Si–H resonance at δ 5.40–5.60 ppm*.

The aryldimethylsilanes were prepared by a similar procedure in which the Grignard reagent was allowed to react with dimethylchlorosilane (Pierce). The physical properties (b.p., refractive index, and NMR) corresponded with those reported by Damrauer[26]. (*p*-Methoxyphenyl)dimethylsilane had b.p. 91–93° (15–20 mm) and n_D^{23} 1.5120 (reported[27] b.p. 99–100° at 17 mm and n_D^{20} 1.5131). All the aryldimethylsilanes were homogeneous to gas chromatography.

Triphenylsilane-*d*, m.p. 43–44.5°, was obtained from the reaction of triphenylchlorosilane with lithium aluminum deuteride (Alfa Inorganics). Assay by NMR could detect no Ph_3SiH.

Triethylsilane, diethylsilane, triphenylsilane and diphenylsilane were purchased from the Pierce Chemical Company, Rockford, Illinois. The triphenylsilane was purified by recrystallization from hexane.

Tris(2,6-dimethoxyphenyl)methanol[5] and 9-*p*-anisylxanthydrol[28] were prepared as described in the literature. *p*-Methylbenzophenone (Aldrich) was converted to *p*-methylbenzhydrol-α-*d* with $LiAlD_4$ in ether. NMR analysis showed no α-protium.

Methylene chloride was stored over molecular sieves. The acetic acid was Analytical Reagent grade and the trifluoroacetic acid was Eastman White Label grade.

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* Measured in deuteriochloroform on a Varian A-60 NMR spectrometer.

Kinetic method

The rate of disappearance of the tris(2,6-dimethoxyphenyl)methyl cation was monitored by measuring the absorbance at 523 mμ using a Hitachi-Coleman GTS-3T Ultraviolet-Visible Recording Spectrophotometer. Since this instrument was not equipped with a thermostatted sample cell, rigorous temperature control was not possible, and the uncertainty in the temperature at which the measurements were taken is on the order of $\pm 1°$ at 24°. All kinetic runs were run at least in duplicate and the values of k reported in the Tables are the arithmetic mean of the measurements while the uncertainties represent the average error of the measurements.

The reactions were slow enough so that large excesses of silanes were employed to give reasonable rates. Therefore, the kinetics were treated as pseudo-first-order reactions in most cases. In a few instances the silanes were sufficiently reactive to allow the kinetics to be studied under conditions of similar alcohol/silane concentrations.

Rate constants were calculated from the integrated rate expression by a least-squares procedure using a Burroughs B-5500 digital computer. The Hammett plots were also obtained by a least squares computation on the B-5500.

A typical kinetic experiment was performed as follows.

Rate of hydride transfer to the tris(2,6-*dimethoxyphenyl*)*methyl cation by triphenylsilane.* One ml of a 0.139 M solution of triphenylsilane in acetic acid was added to a 1 cm cell containing 2 ml of 7.71×10^{-5} M tris(2,6-dimethoxyphenyl)methanol in acetic acid. The absorbance was measured between 517–527 mμ every minute and the absorbance at the "infinity point" measured after about 12 half-lives. A plot of log $(A - A_\infty)$ *vs.* time (min) was linear with slope/$[Ph_3SiH] = 1.05$.

Determination of the primary kinetic isotope effect in hydride (*deuteride*) *transfer from triphenylsilane* (*triphenyldeuteriosilane*) *to the* 9-(*p-methoxyphenyl*)*xanthyl cation*

A. By competition. To a solution containing 1.30 g (5 mmol) Ph_3SiH and 1.31 g (5 mmol) Ph_3SiD and 0.15 g (0.5 mmol) 9-*p*-anisylxanthydrol in 20 ml methylene chloride was added 15 drops trifluoroacetic acid. A deep red color formed instantly. After standing overnight the now colorless solution was evaporated and the residue chromatographed on neutral alumina. Elution with pentane removed the Ph_3SiH/Ph_3SiD mixture. A blend of benzene/pentane (1/2) was then used to elute the 9-*p*-anisylxanthene (91.6 mg; m.p. 111–113°).

The isotope effect was determined by NMR in the following manner. Repetitive integration of the signals for the methoxy protons in the *p*-anisyl ring (sharp singlet at δ 3.68) and the C-9 proton (singlet at δ 5.18) gave a ratio $OCH_3/CH = 4.87$. Since $CH/OCH_3 + CD/OCH_3 = 1/3$, the percent ^1H transfer can be calculated to be 61.6% and the isotope effect $k_H/k_D = 1.60$.

A repetition of this experiment gave a ratio $OCH_3/CH = 4.62$ corresponding to 64.9% ^1H transfer and $k_H/k_D = 1.83$.

B. By rate measurement. To a 1 cm cell containing 0.4 ml of 1.5×10^{-4} M 9-*p*-anisylxanthydrol in methylene chloride and 1.1 ml of 2.98×10^{-3} M trifluoroacetic acid in methylene chloride was added 1.5 ml of a 0.349 M solution of Ph_3SiH in methylene chloride and the solutions mixed thoroughly. The absorbance was measured between 365–375 mμ every minute with the "infinity point" being taken 2 h after the reaction was 90% completed. A plot of log $(A - A_\infty)$ *vs.* time was linear with slope/$[Ph_3SiH] = 0.233$. For a duplicate run k was determined to be 0.217.

Similarly, *k* for Ph_3SiD was determined in two separate experiments to be 0.119 and 0.120.

The primary kinetic isotope effect k_H/k_D is, therefore, 1.89 by this method.

Determination of the primary kinetic isotope effect in hydride (deuteride) transfer from triphenylsilane (triphenyldeuteriosilane) to the phenyl-p-totyldeuteriomethyl cation

Trifluoroacetic acid (30 drops) was added to a solution of 0.198 g (1 mmol) *p*-methylbenzhydrol-*α*-*d*, 1.30 g (5 mmol) Ph_3SiH and 1.305 g (5 mmol) Ph_3SiD in 20 ml methylene chloride. After 3 h 20 ml of a saturated solution of potassium hydroxide in 95% ethanol was added and the reaction mixture stirred overnight ($\geq$Si–H + KOH$\rightarrow$SiOK + H_2). The solution was poured into 150 ml of water and extracted with 50 ml pentane. The pentane layer was washed with water, dried over sodium sulfate and the pentane carefully evaporated. The residue was then purified by evaporative distillation in a Kugelrohr apparatus to give pure 4-methyldiphenylmethane. Repetitive integration of the signals for the methyl protons of $CH_3C_6H_4$ (sharp singlet at δ 2.30) and the CDH protons (broad signal due to geminal coupling to D at δ 3.90) gave a ratio $CH_3/CDH = 4.89$. Since $CHD/CH_3 + CD_2/OCH_3 = 1/3$, the percent ^1H transfer can be calculated to be 61.3% and $k_H/k_D = 1.58$.

A repetition of this experiment gave a ratio $CH_3/CHD = 5.08$ corresponding to 59.1% ^1H transfer and $k_H/k_D = 1.44$.

ACKNOWLEDGEMENT

Acknowledgement is made to the donors of the Petroleum Research Fund, aministered by the American Chemical Society for support of this work.

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