Oxidation of Silanes. III. The Reaction of Aryldimethylsilanes with Mercuric Acetate and Thallium Triacetate[1,2]

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The reaction of aryldimethylsilanes with mercuric acetate and thallium triacetate in acetic acid at 25° has been studied by competitive techniques. The reactions are first order in the silane. Hammett correlations with σ of the ring substituents have been established with $\rho = -0.96$ and -1.15 for mercuric acetate and thallium triacetate, respectively. The reactions are postulated to involve electrophilic attack of the metal acetate on the silicon–hydrogen bond to produce an unstable silicon–metal bond which solvolytically decomposes to yield the observed products, aryldimethylsilyl acetates.

Nucleophilic substitution at a silicon atom is a characteristic reaction of organosilicon compounds and has been investigated extensively.[5] The high reactivity of silicon derivatives as compared to their carbon analogs has been interpreted in terms of the ability of silicon to increase its coordination number above four by utilizing d orbitals. The basic stereochemical features of displacement at silicon have been elucidated by Sommer.[6]

While interest in electrophilic displacement at a saturated carbon atom is receiving increased attention, little note has been made of the possibilities for similar reactions at a silicon atom. Considering the propensity for nucleophilic displacement at silicon it might be assumed that electrophilic attack would be even less likely to occur at silicon than at carbon. However, it is not clear whether the two modes of attack are directly comparable. Experimentally it might be difficult to observe electrophilic attack on silicon in the absence of competitive nucleophilic attack.

A search of the literature revealed several reactions which might proceed by attack of an electrophile at a silicon–hydrogen bond. These are (a) the formation of silyl perchlorates by treatment of silanes with silver perchlorate,[7] (b) the reaction of triethylsilane with mercuric acetate to yield triethylsilylacetate[8] and (c) the reaction of triethylsilane with ozone to produce triethylsilanol.[9]

Eaborn[7] studied the reaction of trisubstituted silanes and silver perchlorate in toluene in detail. The approximate material balance is represented by general eq 1.

$$2R_3SiH + 2AgClO_4 \longrightarrow 2R_3SiClO_4 + 2Ag + H_2 \qquad (1)$$

However, deviations of as much as 20% in the yields of silver and hydrogen are common. Eaborn postulated an electrophilic attack of silver ion on the hydrogen bound to silicon to yield silver hydride which then could decompose and initiate a chain process. The reaction exhibits a marked steric deceleration of rate and, therefore, a nucleophilic attack of perchlorate ion on silicon also was postulated. Therefore, the question of electrophilic substitution is still an open one.

The aryldimethylsilanes were shown to be ideal substrates for an examination of the electronic factors controlling the conversion into silanol by the action of ozone.[1] However, the difficulty of controlling the reaction variables for the low-temperature reaction involving a two-phase system limits the extension of studies of the ozone reaction.

Although the reaction of mercuric acetate with triethylsilane has been reported,[8] the generality of the

$$(C_2H_5)_3SiH + Hg(OAc)_2 \longrightarrow (C_2H_5)_3SiOAc + Hg + HOAc \qquad (2)$$

reaction has not been demonstrated. While mercuric acetate reacts as an electrophile with a variety of compounds having electron-rich centers, the effect of electronic and steric factors of its reaction with silanes are not known. Mercuric acetate is known to cleave aryl–silicon bonds in aryltrimethylsilanes to produce arylmercuric acetates and oxygenated silicon derivatives.[10] Therefore, a study of the reaction of mercuric acetate with the silicon–hydrogen bond of arylsilanes could entail experimental difficulties with a competing desilylation reaction. However, mercuric acetate can be handled with greater facility than ozone and is a well-known electrophile toward centers such as π bonds.[11] Our recent work with this reagent in the cleavage of cyclopropane bonds by mercuric acetate[12] has provided a point of reference for comparison of the reaction of silanes under identical reaction conditions. Furthermore the thallium triacetate[13] oxidative cleavage of cyclopropanes also has been studied and a quantitative comparison of the electrophilicities of the two metal acetates has been obtained. A study of the reaction of mercuric acetate and thallium triacetate with silanes should provide a criterion for the proposed electrophilic attack on silicon–hydrogen bonds.

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Results

The aryldimethylsilanes where the ring substituents are *p*-MeO, *p*-Me, *p*-Cl, *m*-Cl and *p*-CF_3 in addition to the parent unsubstituted compound all react almost instantaneously with mercuric acetate at 30° to quantitatively yield mercury. At 25° the aryl–silicon bond cleavage by mercuric acetate has a half-life of over 1 hr for phenyltrimethylsilane. Since the reaction of mercuric acetate with the silicon–hydrogen bond is much faster than the cleavage of the carbon–silicon bond, the latter reaction may be neglected.

The initial products of the reactions are the aryldimethylsilyl acetates as shown by an nmr analysis. The acetates are quite prone to hydrolysis and an aqueous work-up produces a mixture of silanols and siloxanes. When equimolar amounts of *p*-methoxyphenyldimethylsilane and mercuric acetate react in acetic acid in the absence of water, a 95% yield (nmr) of *p*-methoxyphenyldimethylsilyl acetate is obtained. Analysis by vpc indicated the absence of any other volatile products.

The initial concentrations of various mixtures of silanes and mercuric acetate were gravimetrically established. Since the reaction is quantitative, the remaining quantities of each silane in a competitive reaction can be mathematically determined without the use of an internal standard for vpc analysis of reactions in which equimolar quantities of mercuric acetate were not employed. The total amount of silane remaining at the conclusion of the reaction are related in eq 3 where [X] and [Y] represent the molar concentrations of individual silanes and $[X]_0$ and $[Y]_0$ are the initial concentrations. The molar ratio of the silanes remaining, [X]/[Y], is available from corrected integrated peak areas obtained from vpc analysis. The peak areas were corrected for molecular weights and differences in thermal conductivity. Using eq 3 and the ratio [X]/[Y] the individual concentrations of [X] and [Y] can be calculated. The kinetic order is first power with respect to the silane. The initial and final concentrations of the silanes are related by eq 4.

$$[X] + [Y] = [X]_0 + [Y]_0 - [HgOAc_2]_0 \qquad (3)$$

$$\log([X]/[X]_0) = k_X/k_Y \log([Y]/[Y]_0) \qquad (4)$$

The ratios of the rate constants given in Table I as calculated from eq 4 are identical within experimental error and confirm the kinetic order. The relative rates of the *p*-methoxy, *p*-methyl, *p*-chloro, *m*-chloro and *p*-trifluoromethyl derivatives relative to the phenyl compound are listed in Table II. From a plot (Figure 1) of $\log k_X/k_H$ *vs.* σ, $\rho = -0.96$ is obtained with a correlation coefficient $r = 0.995$.

Phenyldiisopropylsilane reacts 8.2 times slower than *m*-chlorophenyldimethylsilane. Therefore the calculated rate of phenyldiisopropylsilane relative to phenyldimethylsilane is 0.056.

Table I

Kinetic Order Determination

$[p\text{-}CH_3OC_6H_4Si(CH_3)_2H]_0$, *M*	$[p\text{-}ClC_6H_4Si(CH_3)_2H]_0$, *M*	$[HgOAc_2]_0$, *M*	$k_{p\text{-}CH_3O}/k_{p\text{-}Cl}$
0.0390	0.0417	0.0280	3.07
0.0404	0.0404	0.0400	3.15
0.0202	0.0202	0.0202	3.20
0.0605	0.0238	0.0400	3.04

Table II

Relative Reaction Rates of Aryldimethylsilanes with Mercuric Acetate and Thallium Triacetate

Substituent	k_X/k_H	
	$HgOAc_2$	$TlOAc_3$
p-Methoxyl	1.89 ± 0.07	2.07 ± 0.06
p-Methyl	1.61 ± 0.06	1.65 ± 0.05
p-Chloro	0.60 ± 0.02	0.57 ± 0.02
m-Chloro	0.46 ± 0.02	0.38 ± 0.01
p-Trifluoromethyl	0.36 ± 0.01	

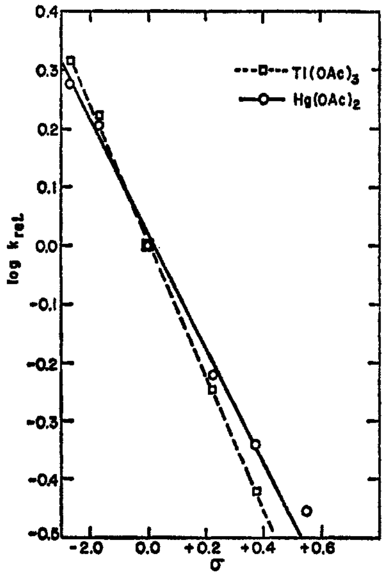
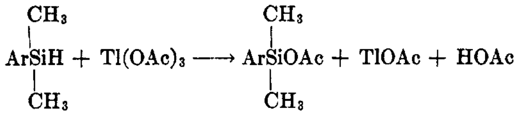


Figure 1.—Hammett correlation of rates of oxidation by mercuric acetate and thallium triacetate.

Thallium triacetate reacts with aryldimethylsilanes in acetate acid at 30° quite rapidly. However, in order to ensure completion of the reaction, it was necessary to allow sufficient time for all of the $Tl(TlOAc_4)$ formed to dissociate (eq 6) and react.[13]



$$Ar\overset{CH_3}{\underset{CH_3}{SiH}} + Tl(OAc)_3 \longrightarrow Ar\overset{CH_3}{\underset{CH_3}{SiOAc}} + TlOAc + HOAc \qquad (5)$$

$$Tl(OAc)_3 + TlOAc \rightleftarrows TlTl(OAc)_4 \qquad (6)$$

Analysis by nmr confirmed that the silicon-containing products of the thallium triacetate oxidation are identical with those of the mercuric acetate oxidation reaction.

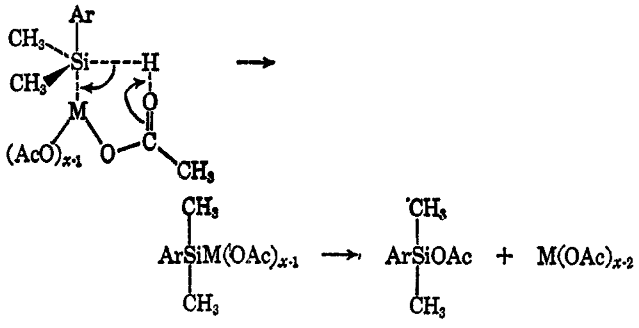
After 1 hr the reactions were analyzed in the same manner as for the reaction with mercuric acetate. The relative rate constants for the thallium triacetate reaction are given in Table II. From a plot (Figure 1) of $\log k_X/k_H$ *vs.* σ, $\rho = -1.15$ is obtained with a correlation coefficient $r = 0.993$.

Discussion

The negative ρ values for both the reactions of mercuric acetate and of thallium triacetate with aryldimethylsilanes indicate that some positive charge is generated on silicon in progressing to the transition state. Attack of electrophilic reagents such as mercuric acetate and thallium triacetate might be expected to lead to a σ^+ correlation. These reagents give rise to $\rho^+ = -3.3$ and -4.2 for the cleavage of arylcyclopropane by mercuric acetate[12] and thallium triacetate,[13] respectively. However, the data for the oxidation of silanes clearly eliminate any contribution of σ^+ of the substituent. Since both the σ and σ^+ scales are based on carbon centers, it is not obvious what function these values serve in organosilicon compounds. A positive charge on silicon in a pentacovalent siliconium ion intermediate might be tolerable without substantial resonance contribution of ring substituents.

The difference in magnitudes of the ρ values for the oxidation of silanes is consistent with the difference observed previously in the oxidative cleavage of cyclopropanes which involves electrophilic attack on the ring electrons. However, the level of response of the rate of reaction to changes in ring substituent is substantially lower. The reaction appears to involve an electrophilic substitution in which the positive charge generated at silicon is less than that generated at carbon in the cyclopropane cleavage reaction.

The reaction of the silicon-hydrogen bond may involve a concerted mechanism in which the metal acetate, $M(OAc)_x$, becomes attached to silicon.[14]



Rapid solvolysis of the intermediate compound containing the silicon-metal bond to yield the silyl acetate and a reduced metal species finds analogy in the solvolysis of alkylmercuric acetates.[15]

The decrease in the rate of oxidation when the two methyl groups are replaced by two isopropyl groups is not inconsistent with an SE2 mechanism. In a bipyramidal transition state the isopropyl and phenyl groups would have to be oriented at 90° to each other. Steric hindrance in proceeding to the transition state would be expected on the basis of the necessary alteration in bond angles.

Experimental Section

Aryldimethylsilanes.—The preparation of substituted phenyldimethylsilanes has been described previously.[1]

Phenyldiisopropylsilane.—The method of Harvey, Nebergal and Peake[16] was used in the preparation of the title compound.

Competition Reaction with Mercuric Acetate.—The procedure for the determination of relative rates of aryldimethylsilanes reacting with mercuric acetate is described for *p*-chlorophenyldimethylsilane and *p*-methoxydimethylsilane. A standard solution of mercuric acetate in acetic acid was prepared from 100 ml of acetic acid and 1.2744 g (4.000×10^{-3} mol) of mercuric acetate. The stoppered flask containing this solution was then placed in a 30.0° constant-temperature bath. A mixture of 0.1635 g (9.86×10^{-4} mol) of *p*-methoxyphenyldimethylsilane and 0.168 g (9.90×10^{-4} mol) of *p*-chlorophenyldimethylsilane contained in a 50-ml round-bottomed flask was also placed in this bath. After sufficient time had elapsed for achieving temperature equilibrium, 25 ml of the mercuric acetate solution was transferred by pipet to the silane mixture. Immediate precipitation of mercury occurred. After remaining in the bath for 15 min, the reaction mixture was filtered and the filtrate diluted with 70 ml of ether. This solution was then washed several times with both water and saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate and stripped of low-boiling solvent by means of a rotary evaporator. A control experiment was run, in which the same procedure as above was followed, except that pure acetic acid rather than mercuric acetate solution was used. Vpc analysis of the residue indicated no change in weight ratio of silanes took place during work-up. An Aerograph Model A-90 vpc was used to analyze the reaction mixture employing a 25% DC silicon oil 300 on Chromosorb 30/60 column at 90° column temperature. The relative peak areas of the two silanes was determined with a planimeter. All peak areas were corrected for variations in peak intensity due to variance in the thermal conductivities of the silanes.

Competition Reaction with Thallium Triacetate.—The reactions were carried out using the same general procedure as described for the reactions with mercuric acetate. The sole difference was that 1 hr was allowed for the reaction.

***p*-Methoxyphenyldimethylsilyl Acetate.**—To a stirred solution of 0.50 g (3×10^{-3} mol) of *p*-methoxyphenyldimethylphenylsilane in 15 ml of carbon tetrachloride was added 48 g (0.003 mol) of bromine in 15 ml of carbon tetrachloride. A nitrogen atmosphere was maintained in the system throughout the reaction. After the solution had lost all bromine color, 0.42 g (7×10^{-3} mol) of acetic acid in 5 ml of carbon tetrachloride was added to it. The reaction mixture was stirred for 12 hr during which a slow stream of nitrogen was bubbled through the solution. At the end of this process most of the solvent had been driven off and the residue was then analyzed by vpc on a 25% D.C. silicon oil 300 on Chromosorb 30/60 at 140° and by nmr. Vpc analysis indicated one main product in addition to excess acetic acid while nmr analysis (six-proton singlet at τ 9.87, three-proton singlet at 8.28, three-proton singlet at 6.59 and four-proton multiplet at 3.42) confirmed the presence of the desired silyl acetate.

Product Analysis.—*p*-Methoxyphenyldimethylsilane was allowed to react with mercuric acetate in acetic acid in the same manner described for the relative rate determinations with the important exception that the reaction flask was kept under a nitrogen atmosphere and no work-up was attempted due to the inevitable hydrolysis of silyl acetate to silanol and siloxane. Vpc analysis of the reaction mixture under the same conditions as described above for *p*-methoxyphenyldimethylsilyl acetate showed a trace amount of remaining silane, acetic acid and a major peak at the same retention time as the silyl acetate.

In a separate experiment the nmr spectrum of the product in acetic acid was obtained. The six-proton singlet of *p*-methoxyphenyldimethylsilyl acetate was observed in addition to a very low-intensity doublet corresponding to the parent silane. The one-proton septuplet at τ 5.65 of the parent silane could not be detected. The yield of the silyl acetate was determined to be approximately 95% by the use of *t*-butylbenzene as an internal standard.

The yield of mercury in the case of the reaction of *p*-methoxyphenyldimethylsilane was determined as 98%. The analytical method involved dissolution of the mercury in nitric acid followed by a standard thiocyanate-silver ion back-titration.[17]

The products of the reaction of compounds other than *p*-methoxyphenyldimethylsilane were examined only by nmr. The disappearance of the one-proton septuplet at *ca.* τ 5.6 coupled with the appearance of a six-proton singlet at *ca.* τ 9.9 was regarded as sufficient to ensure that the same reaction was occurring for all compounds.

The product analysis procedure for the thallium triacetate reaction was identical with that for mercuric acetate. The yield of *p*-methoxyphenyldimethylsilyl acetate is essentially quantitative (>95% by nmr).

Registry No.—Mercuric acetate, 1600-27-7; thallium triacetate, 2570-63-0; aryldimethylsilane (aryl = *p*-CH_3O), 1432-38-8; aryldimethylsilane (aryl = *p*-CH_3), 1432-39-9; aryldimethylsilane (aryl = *p*-Cl), 1432-31-1; aryldimethylsilane (aryl = *m*-Cl), 2083-13-8; aryldimethylsilane (aryl = *p*-CF_3), 19254-78-5.

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(14) A referee suggests that a concerted reaction involving an electrophilic attack of the metal on the hydrogen atom of the silicon-hydrogen bond and nucleophilic attack of the acetate group on silicon also should be considered. Such a process could be consistent with the observed ρ. At the present time there is no physical probe extant which would provide a distinction between these mechanisms. Chemical support of our mechanism must await the isolation of suitable organometallic derivatives of the type proposed herein.

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