

OXIDATION OF SILANES

II*. THE REACTION OF OZONE WITH ARYLDIMETHYLSILANES**

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(Received August 18th, 1967)

INTRODUCTION

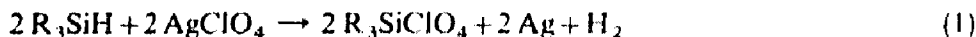
Nucleophilic substitution at a silicon atom is a characteristic reaction of organosilicon compounds and has been investigated extensively². The high reactivity of silicon derivatives as compared to their carbon analogs has been interpreted in terms of the ability of silicon to increase its coordination number above four by utilizing *d*-orbitals. The basic stereochemical features of displacement at silicon have been elucidated by Sommer³.

While interest in electrophilic displacement at a saturated carbon atom has been burgeoning recently, 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.

According to the Pauling electronegativities⁴, all atoms which might be conveniently attached to silicon for studies of their displacement by electrophiles are more electronegative than silicon. Indeed, this is one of the causative factors that can be invoked for the ready nucleophilic displacement of groups attached to silicon. The electronegativity of hydrogen is quite close to that of silicon. Therefore, from strictly electronegativity arguments, the silicon hydrogen bond appears to be the most likely center at which to observe electrophilic displacement.

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 perchlorate⁵, (b) the reaction of triethylsilane with mercuric acetate to yield triethylsilylacetate⁶ and (c) the reaction of triethylsilane with ozone to produce triethylsilanol⁷.

Eaborn⁵ studied the reaction of trisubstituted silanes and silver perchlorate in toluene in detail. The approximate material balance is represented by the general eqn. (1). However, deviations of as much as 20% in the yields of silver and hydrogen are



* For Part I see ref. 1.

** This research was supported in part by a Grant in Aid from the Ohio State University.

*** Goodyear Fellow 1965-66.

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.

Although the reaction of mercuric acetate with triethylsilane has been reported⁶, the generality of the 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 derivatives⁸. 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.

Recently the reaction of triethylsilane with ozone was reported⁷. Since the cleavage of silicon-carbon bonds is apparently slower than that of silicon-hydrogen bonds the reaction could be studied without complicating side reactions. Since ozone can behave as an electrophile, use of a non-nucleophilic solvent and the absence of any nucleophilic reagents in the reaction medium might allow the observation of electrophilic attack on silanes.

In order to examine the reaction of silicon-hydrogen bonds with electrophiles, the determination of the electrical factors controlling the process was selected as our first goal. While stereochemical studies might be of interest eventually, it is first necessary to determine whether there are any reactions which can be classed as electrophilic displacements. Accordingly, aryltrimethylsilanes were chosen as the substrates most likely to allow this determination to be made.

RESULTS AND DISCUSSION

Triethylsilane (neat) has been reported to react with ozone at room temperature in 2 hours to yield triethylsilanol. We have found that on our scale the reaction with aryltrimethylsilanes actually proceeds rapidly in dilute solution in methylene chloride at -78° in approximately 20 minutes. Since only a split stream of ozone at low gas concentration was used, the reaction time could be shortened by increasing flow rates and concentrations of ozone. While it is not possible to define a rate constant, it does appear that the reaction is significantly faster than implied by previous work⁷.

The course of the reaction can be monitored easily by VPC analysis and by IR and NMR spectra. After ceasing the flow of ozone, nitrogen was used to purge the system of ozone. The reaction solution was injected directly onto the VPC column and the disappearance of silane was monitored. Oxygenated products, silanols and siloxanes corresponding to the silane used, were formed. The exact distribution of silanol and siloxane was not determined in every case as it is dependent on the compound used, the reaction time and the time elapsed prior to analysis. Silanols are the primary products with condensation leading to siloxanes. The use of iodide solutions to eliminate ozone from the reaction solution was examined and analysis of the products by VPC indicated that no change had occurred by using the iodide workup.

Iodide workup was employed during this investigation in order to eliminate experimental hazards. In order to use the kinetic analytical method described below it is necessary to show that there is no alternate route leading to the disappearance of silane. Desilylation or oxidation of the aromatic ring appear to be the only likely possibility. These two possible competitive reactions were shown not to be important by allowing (*p*-methoxyphenyl)dimethylsilane to react with excess ozone. The only product obtained was (*p*-methoxyphenyl)dimethylsiloxane and this corresponded to essentially a quantitative yield. In the case of (*p*-chlorophenyl)dimethylsilane a run which had proceeded to 46% reaction was analyzed by NMR in order to determine if any side reaction had occurred. By the use of an internal standard, 96% of the substances were identified. In addition to the starting silane, the related silanol and siloxane were present in a 2:1 ratio. Therefore, no significant side reactions occur to destroy the silane.

Aryldimethylsilanes were examined in competitive studies with ozone in order to determine the mechanism of the reaction. The kinetic order has been established to be first power with respect to silane. Our mathematical procedure involves the time independent eqn. 3. The symbols *X* and *Y* refer to the concentrations of the two

$$\frac{dX}{dY} = \frac{k_x}{k_y} \cdot \left(\frac{X}{Y}\right)^n \quad (3)$$

silanes and *n* is the order of the reaction with respect to silane. The symbols *k* with subscripts are the rate constants for the reaction of the designated substrates. Since ozone is present and available to both substrates, its dependence cancels from the quotient of the usual time dependent rate expressions. Integration of eqn. 3 when *n* = 1 and substitution of the appropriate limits leads to eqn. 4. The terms with subscript

$$\log(X/X_0) = (k_x/k_y) \cdot \log(Y/Y_0) \quad (4)$$

zero refer to the initial concentrations of the designated silane which were gravimetrically determined. The quantities *X* and *Y*, representing the amount of each silane remaining after partial reaction with ozone, were determined by VPC analysis. Either *p*-bromotoluene or 2,4-dimethylacetophenone was used as the internal standard. The choice of standards was dictated by the retention times of the pairs of silanes being studied. Correction factors for the differences in thermal conductivities of the silanes and references were used.

The total initial concentration of silanes was maintained at approximately 0.2 *M* in this study. The concentrations of individual silanes were varied according to their relative reactivities. The rate ratios *k_x/k_y* were determined using convenient pairs of compounds to facilitate VPC analysis.

In determining the kinetic order of the reaction with respect to silane, (*p*-chlorophenyl)dimethylsilane and (*p*-methoxyphenyl)dimethylsilane were used. A mixture which was 0.158 *M* in the methoxy compound and 0.046 *M* in the chloro compound was allowed to react to the extent of 72% of the total silane present. Under these conditions *k_{MeO}/k_{Cl}* = 5.16. When a mixture which was initially 0.098 *M* in methoxy compound and 0.101 *M* in chloro compound was allowed to react to 28% of the total silane present, a rate ratio of 5.09 was observed. Thus by simultaneously changing the molar ratio of the substrates by a factor of three and the percent reaction

from high conversion to low conversion a constant rate ratio is obtained. The reaction is first order with respect to silane.

In Table I are listed the rate ratios relative to phenyldimethylsilane. The compound actually used in competition is indicated in the second column. Proper conversion of the rate ratios for various pairs of compounds yields the rate ratios relative to a single reference, phenyldimethylsilane. The maximum percent reaction of total silane present also is given in Table I.

TABLE I

RELATIVE RATE RATIOS FOR OZONIZATION

Substrate	Reference	k_p/k_H	Conversion ^a
<i>p</i> -Methoxy	<i>p</i> -Chloro	2.5	72
<i>p</i> -Methyl	<i>m</i> -Chloro	1.8	70
Hydrogen	<i>p</i> -Methyl	1.0	59
<i>p</i> -Chloro	<i>p</i> -Methyl	0.48	70
<i>m</i> -Chloro	<i>p</i> -Methyl	0.31	75
<i>p</i> -Trifluoromethyl	<i>m</i> -Chloro	0.20	66

^a Maximum percent reaction of total silane present.

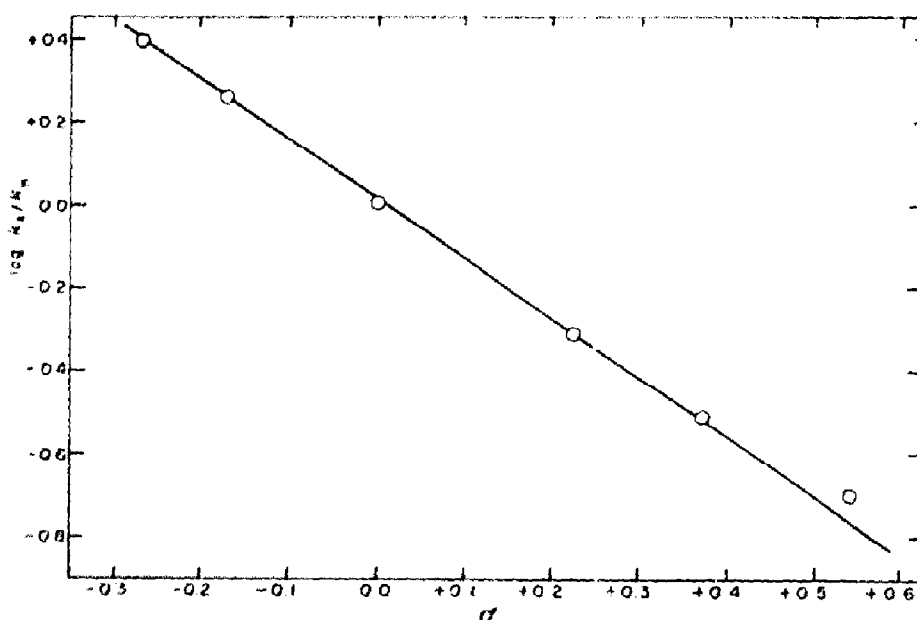


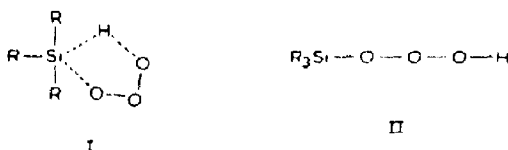
Fig. 1. Correlation of rates of ozone reaction with aryldimethylsilanes.

A plot of $\log k_p/k_H$ versus σ is given in Fig. 1. A $\rho = -1.43$ is calculated from the data excluding the results from the *p*-trifluoromethyl derivative as its σ value is not well established⁹. However, the correlation line falls well within the limits of uncertainty. Inclusion of the datum for trifluoromethyl leads to a correlation coefficient of 0.999.

The observed negative slope in the Hammett plot suggests that some positive charge is generated on silicon in going to the transition state. Attack of an electrophilic

species such as ozone might be expected to lead to a σ^+ correlation. However, the data clearly eliminates 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. Silicon is more electronegative than carbon and has available *d*-orbitals. Pentacovalent intermediates could be invoked in the transition state for reactions involving electrophilic attack on silicon. A substantial positive charge on silicon in a pentacovalent siliconium ion might be tolerable without substantial resonance contribution of ring substituents.

The available experimental facts do not allow a detailed postulate of the transition state. Considering the low polarity and ion stabilizing power of methylene chloride and the correlation with σ , the most likely process is a concerted one leading to a pentacovalent transition state (I) with some positive charge located on the silicon atom. The question of whether electrophilic substitution actually is involved is probably a moot point and depends on a definition of the sequence of bond formation and cleavage. After hydrogen transfer to oxygen a highly unstable intermediate (II)



containing three oxygen atoms could be formed. This peroxidic material could eject either singlet or triplet oxygen depending on the mode of bond cleavage and yield the silanol.

EXPERIMENTAL

Preparation of aryldimethylsilanes

The substituted phenyldimethylsilanes were prepared by the procedure described for the parent compound, phenyldimethylsilane.

Phenylmagnesium bromide was prepared from 47.1 g (0.3 mole) of bromobenzene and 7.3 g (0.3 mole) of magnesium turnings in 200 ml of anhydrous ether. The Grignard solution was filtered under a nitrogen atmosphere and added dropwise to a stirred solution of 30 g (0.3 mole) dimethoxydimethylsilane in 150 ml of anhydrous ether. The reaction mixture was stirred under reflux for 48 h and then rapidly filtered to remove inorganic salts. The filtrate was gradually added to a stirred suspension of

TABLE 2

PREPARATIVE DATA FOR ARYLDIMETHYLSILANES

Substituent	Yield (%)	B.p. [$^{\circ}$ C(mm)]	Reported b.p. [$^{\circ}$ C(mm)]
Hydrogen	35	52-55 (17-20)	158 (760) ¹⁰
<i>p</i> -Methoxy	41	88-99 (12)	105-105.5 (25) ¹¹
<i>p</i> -Methyl	48	51-52 (13)	181-182 (760) ¹²
<i>p</i> -Chloro	74	80-81 (15)	199.5 (760) ¹²
<i>m</i> -Chloro	56	81-82 (16)	140 (154) ¹³
<i>p</i> -Trifluoromethyl	48	52-53 (4)	

3.6 g (0.1 mole) of lithium aluminum hydride in 150 ml of anhydrous ether and the resulting reaction mixture was then stirred under reflux for 48 h. Following hydrolysis with water, the organic portion was separated, washed with water and saturated sodium chloride and dried over anhydrous magnesium sulfate. After removal of low boiling material by means of a rotary evaporator, the organic residue was fractionally distilled under reduced pressure. The boiling points and yields of the aryldimethylsilanes are given in Table 2.

Relative rate determination

As a general procedure, a mixture of two aryldimethylsilanes were reacted with a deficient quantity of ozone. The amounts of unreacted silanes were determined by VPC analysis. The procedure is described for a mixture of phenyldimethylsilane and (*p*-methylphenyl)dimethylsilane.

A solution of 0.1375 g (1.017 mmoles) phenyldimethylsilane, 0.1582 g (1.055 mmoles) (*p*-methylphenyl)dimethylsilane and 0.1284 g (0.808 mmole) 2,4-dimethylacetophenone in 10 ml of methylene chloride was placed in a 25 ml 3-neck round-bottom flask. The flask was fitted with a gas outlet stopcock and a gas inlet which was inserted so as to extend below the surface of the liquid. The apparatus was cooled in a dry ice/isopropyl alcohol bath for 5 min prior to the initiation of ozone generation. A Welsbach model T-408 ozonator was used as the source of ozone, employing an oxygen pressure of 8 lbs/in.², an ozone flow rate of 0.05 standard l/min and an 80 V electrical output. After 20 min reaction time, nitrogen was passed through the reaction solution for 30 min. After warming to room temperature the reaction solution was washed once with 50 ml of 2% potassium iodide solution and dried over anhydrous magnesium sulfate. The dry reaction solution was analyzed for unreacted silanes by means of an Aerograph model A-90-S VPC employing an 8' 25% DC silicone oil 30 on chromosorb 30/60 column at 90°. Relative peak areas of the silanes were determined by use of a planimeter. The peak areas were corrected for differences in the thermal conductivities of both the silanes and internal standards. The correction factors were determined by VPC analysis of known mixtures of the two silanes and internal standards. The corrected peak areas were converted to molar quantities and used in calculating the relative rate ratios by means of eqn. 4.

SUMMARY

A series of aryldimethylsilanes has been oxidized by ozone to yield the aryl-dimethylsilanols. The reaction occurs rapidly at -78° in methylene dichloride. Competitive studies of pairs of aryldimethylsilanes for a deficient quantity of ozone has been carried out. The rate of reaction is first order in the silane. However, the order with respect to ozone is unknown. A correlation of relative rates with σ of the aryl-ring substituent has been established with $\rho = -1.43$. The reaction is postulated to involve electrophilic attack of ozone on the silane.

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