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SILICON—CARBON MULTIPLE-BONDED (p_π—p_π) INTERMEDIATES

II. CHEMICAL REACTIVITY AND SELECTIVITY OF THERMALLY GENERATED 1,1-DIMETHYL-1-SILAETHENE ($Me_2Si=CH_2$)

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Summary

The order of reactivity and the selectivity of 1,1-dimethyl-1-silaethene ($Me_2Si=CH_2$), generated from 1,1-dimethylsilacyclobutane at 611°, toward a variety of substrates was determined using standard competition experiments. The observed reactivity order was $Ph_2C=O$ > ROH, ArOH ≫ *m*-$ClPhNH_2$ > CH_3CN, which indicates that with these substrates and under the reaction conditions used, $Me_2Si=CH_2$ is behaving like an electrophilic species. Within a given class of substrates, polar effects were found to be generally unimportant, while increased steric effects caused a decrease in rate (up to 50%).

Introduction

In 1967 it was reported [1] that gas phase pyrolysis of 1,1-dimethylsilacyclobutane(I) produced 1,1-dimethyl-1-silaethene ($Me_2Si=CH_2$, II), a very reactive intermediate which, in the absence of suitable substrates, dimerized yielding 1,1,3,3-tetramethyl-1,3-disilacyclobutane. The decomposition of I was inhibited by ethylene [2] and the dimerization of II was completely suppressed by equimolar amounts of water [1] or ammonia [2] (initially yielding trimethylsilanol or trimethylaminosilane). These results indicate that the reaction of II with water or ammonia is much faster than dimerization which in turn appears to be more rapid than, or at least as fast as, the reaction of II with ethylene [2] or propene [3]. In spite of recent activity [4-8] in the area of multiple-bonded (p_π—p_π) silicon intermediates very little information is available concerning the relative reactivity and selectivity of these interesting species in their reactions with organic substrates.

In an attempt to learn more about the chemical nature of the very reactive intermediate, $Me_2Si=CH_2$, we have carried out competition experiments be-

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TABLE 1

COMPETITION REACTIONS BETWEEN PAIRS OF ORGANIC SUBSTRATES FOR $Me_2Si=CH_2$ (II) IN THE GAS PHASE AT 611°

Expt. No.	$(CH_2)_3SiMe_2$ [a] (mmol)	Substrate 1 (mmol)	Substrate 2 (mmol)	Product 1 (% Yield) [b]	Product 2 (% Yield) [b]
1	10.5	$Ph_2C=O$ (10.0)	EtOH (10.1)	$Ph_2C=CH_2$ (44)	$EtOSiMe_3$ (25)
2	9.93	$Ph_2C=O$ (10.3)	Me_3CCH_2OH (10.3)	$Ph_2C=CH_2$ (20) [c]	$Me_3CCH_2OSiMe_3$ (16) [c]
3	10.0	$Ph_2C=O$ (10.6)	PhOH (10.6)	$Ph_2C=CH_2$ (52) [c]	$PhOSiMe_3$ (16) [c]
4	10.0	$Ph_2C=O$ (10.0)	m-ClPhOH (10.0)	$Ph_2C=CH_2$ (49)	$m\text{-}ClPhOSiMe_3$ (17)
5	10.1	$Ph_2C=O$ (10.1)	$m\text{-}ClPhNH_2$ (10.1)	$Ph_2C=CH_2$ (69)	$m\text{-}ClPhNHSiMe_3$ (< 2)
6	10.0	$Ph_2C=O$ (10.0)	CH_3CN (10.0)	$Ph_2C=CH_2$ (74) [c]	Me_3SiCH_2CN (0)
7	2.64	$Ph_2C=O$ (2.26)	$(m\text{-}ClPh)_2C=O$ (2.32)	$Ph_2C=CH_2$ (46)	$(m\text{-}ClPh)_2C=CH_2$ (15)
8	3.60	$Ph_2C=O$ (3.58)	$(p\text{-}MePh)_2C=O$ (3.58)	$Ph_2C=CH_2$ (41)	$(p\text{-}MePh)_2C=CH_2$ (41)
9	2.25	$(p\text{-}MePh)_2C=O$ (1.91)	$(m\text{-}ClPh)_2C=O$ (2.24)	$(p\text{-}MePh)_2C=CH_2$ (32) [d]	$(m\text{-}ClPh)_2C=CH_2$ (30) [d]
10	7.4	$3,5\text{-}Me_2PhOH$ (7.9)	$3,5\text{-}Cl_2PhOH$ (7.9)	$3,5\text{-}Me_2PhOSiMe_3$ (31)	$3,5\text{-}Cl_2PhOSiMe_3$ (33)
11	10.0	$2,6\text{-}Me_2PhOH$ (10.4)	$3,5\text{-}Me_2PhOH$ (10.5)	$2,6\text{-}Me_2PhOSiMe_3$ (25)	$3,5\text{-}Me_2PhOSiMe_3$ (47)
12	10.0	$3,5\text{-}Me_2PhNH_2$ (10.0)	$3,5\text{-}Cl_2PhNH_2$ (10.0)	$3,5\text{-}Me_2PhNHSiMe_3$ (22)	$3,5\text{-}Cl_2PhNHSiMe_3$ (24)
13	10.0	$2,6\text{-}Me_2PhNH_2$ (11.9)	$m\text{-}MePhNH_2$ (11.2)	$2,6\text{-}Me_2PhNHSiMe_3$ (22)	$m\text{-}MePhNHSiMe_3$ (51)
14	10.0	$3,5\text{-}Me_2PhNH_2$ (11.1)	$m\text{-}MePhNH_2$ (11.3)	$3,5\text{-}Me_2PhNHSiMe_3$ (43)	$m\text{-}MePhNHSiMe_3$ (43)

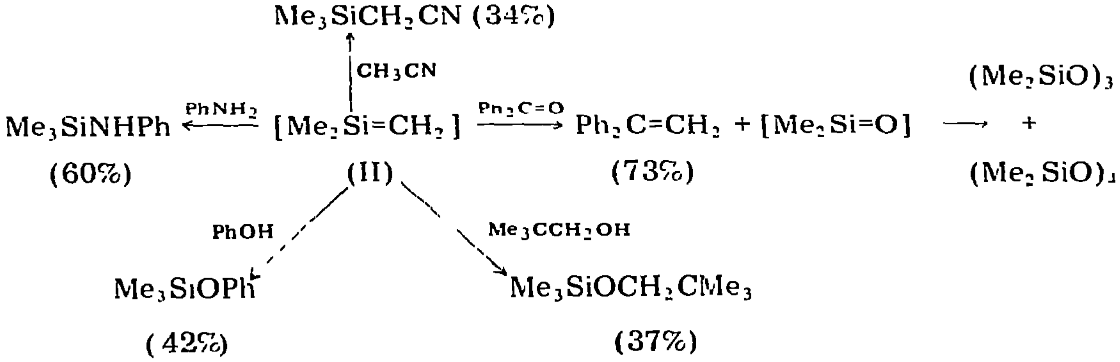
[a] Benzene used as a solvent in all reactions (ca. 3.2 mmol benzene per mmol of 1,1-dimethylsilacyclobutane). [b] Unless otherwise noted yields were determined by analytical GLC using internal standards. [c] Based on material isolated using preparative GLC. [d] Determined by NMR analysis using an internal standard.

tween this intermediate and pairs of appropriately substituted organic substrates. In this manner, the relative reactivity of $Me_2Si{=}CH_2$ toward a variety of substrates was determined from the product distributions.

Results

In all of the reactions discussed below $Me_2Si{=}CH_2$ was generated in the presence of the appropriate substrates by gas phase pyrolysis (nitrogen flow system, 611°, 760 mm Hg) of mixtures of 1,1-dimethylsilacyclobutane and these reagents. The types of reactions which $Me_2Si{=}CH_2$ undergoes with the individual substrates used in this study, together with isolated yields, are summarized in Scheme 1. The details of the reactions of II with ketones [5, 6] and nitriles [4] have been reported previously and will not be considered further here. Since the reactions of II with anilines and alcohols, while not surprising, have never been reported additional information concerning these reactions is given in the Experimental section.

SCHEME 1



The results of a series of reactions in which pairs of organic substrates were allowed to compete for a limited amount of II are given in Table 1. The high temperatures (611°) required for the generation of II severely limited the choice of organic substrates. For example, compounds containing nitro groups decomposed completely under the reaction conditions used. Except for 3,3'-dichlorobenzophenone which underwent ca. 20% decomposition, all of the substrates and products listed in Table 1 were stable at the reaction conditions ($<$ 5% decomposition). Control experiments demonstrated that the reaction mixtures from the direct competition of pairs of phenols (or anilines) were stable to the reaction conditions. However, phenols could not be competed directly with anilines since complete and rapid silylation of phenol by *N*-trimethylsilylaniline was observed at room temperature. In order to obtain this comparison, each compound was competed individually with benzophenone (Experiments 4 and 5).

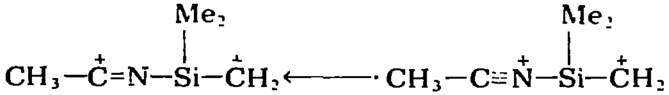
The possibility that prior complexation of I with the substrate might lower the activation barrier for its decomposition was eliminated by the following control experiments. Pyrolysis of a benzene solution containing equimolar quantities of I and benzophenone at a reduced temperature (500°) produced a ca. 5% yield of 1,1-diphenylethylene. Pyrolysis of I alone under identical conditions caused ca. 8% decomposition. These results clearly demonstrate that the presence of benzophenone has no effect on the decomposition of I.

Initial competition reactions between phenol and *meta*-chlorophenol and between *meta*-methylphenol and *meta*-chlorophenol, although not included in Table 1, gave yields within 3% of those obtained for the competition between 3,5-dimethyl- and 3,5-dichlorophenol (Experiment 10, Table 1). GLC analysis showed that in separate reactions 3,3′-dimethyl- and 3,3′-dichloro-benzophenone competed equally well with benzophenone (Experiments 7 and 8, Table 1). A direct competition between 3,3′-dimethyl- and 3,3′-dichloro-benzophenone (Experiment 9, Table 1), analyzed by NMR spectroscopy, because overlapping peaks prevented analysis by GLC, gave a product ratio identical to that obtained from the separate competition reactions of these compounds against benzophenone. Although these experiments provide no new information, they constitute an excellent test of the analytical GLC method used.

Discussion

Results for Experiments 1-6 in Table 1 show that the reactivity order for $Me_2Si{=}CH_2$ (II) with different classes of organic substrates is: $Ph_2C{=}O >$ EtOH, Me_3CCH_2OH, PhOH, *m*-ClPhOH $\gg$ *m*-$ClPhNH_2$ $>$ CH_3CN. Perhaps the most significant competition reaction is Experiment 6, which shows that $Ph_2C{=}O$ is far more reactive towards II than CH_3CN. From this it can be concluded that II is more effective as an electrophile than as a nucleophile. This conclusion involves the reasonable assumption that reaction of CH_3CN with II is initiated via nucleophilic attack of the negatively polarized methylene (see below) in $Me_2Si{=}CH_2$ on an α-hydrogen in CH_3CN, followed by combination of the forming carbanion center with electrophilic positively polarized silicon in II.

The other alternative, electrophilic attack of II on CH_3CN to give III, seems far less likely, since the geometry of III would make extensive rearrangement a necessary requirement for product formation.



$$CH_3-\overset{+}{C}{=}N-\overset{\overset{\displaystyle Me_2}{|}}{Si}-\overset{-}{C}H_2 \longleftarrow CH_3-C{\equiv}\overset{+}{N}-\overset{\overset{\displaystyle Me_2}{|}}{Si}-\overset{+}{C}H_2$$

(III)

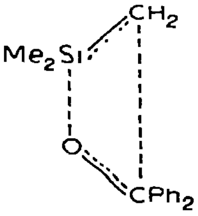
The result of Experiment 6 also indicates, according to this reasoning, that reaction of II with $Ph_2C{=}O$ is initiated via electrophilic attack of positive silicon in $Me_2Si{=}CH_2$ on negative oxygen in $Ph_2C{=}O$, followed by combination of the forming carbonium ion center with nucleophilic negative carbon in II. Similar arguments apply to the reaction of II with phenols or anilines. The dramatic drop in reactivity upon changing the substrate from $Ph_2C{=}O$ to CH_3CN is in good accord with the above mechanistic hypothesis.

The electrophilic nature of II receives further support from the observation that it reacts more rapidly with benzophenone than with ethanol, preferring to attack the greater electron density of the sp^2 hybridized carbonyl oxygen atom.

The observation [5,6] that II behaves analogously to $R_3P{=}CH_2$ in its reactions with a number of aldehydes and ketones is in line with the above assumption that II has considerable dipolar character: $Me_2\overset{\delta+}{Si}{=\!=\!=}\overset{\delta-}{C}H_2$. Results [8] of Hückel treatment of silaethene serve to indicate polarization of the silicon carbon double-bond, $H_2\overset{\delta+}{Si}=\overset{\delta-}{C}H_2$, consistent with formulation of II as a dipolar intermediate. However, it is important to note that the predominantly electrophilic nature of II in the present studies is the opposite to what is observed for its phosphorus analogs, the methylenephosphoranes. Such electrophilic behavior is due, at least in part, to the fact that the silicon center is trisubstituted in contrast to phosphorus, which is tetrasubstituted and more saturated in the dipolar form: $R_3\overset{+}{P}-\overset{-}{C}H_2$. Also, it is important to note the possibility that substrates of different character than those used in the present work, namely, extremely poor nucleophiles, may undergo initial nucleophilic attack by the carbon component of the dipolar silicon—carbon bond.

The greater reactivity of II with phenols relative to anilines despite the much greater basicity of the latter may be partially a reflection of the increased bond energy of a silicon—oxygen bond (ca. 106 kcal) compared to a silicon—nitrogen bond (ca. 76 kcal) and, more importantly, the greater polarity of O—H compared to N—H [9]. A similar reactivity pattern is generally observed in the silylation reactions of alcohols and amines [10].

On the basis of these data we prefer to formulate these reactions as proceeding via a distorted four-centered transition state, IV, as outlined below for the reaction of II with benzophenone. Although the precise degree of concertedness of the reactions leading to IV and also the charge separation present in IV cannot be ascertained from the data currently available, all available information indicates that the initial step of these reactions involves silicon—oxygen bond formation which somewhat exceeds carbon—carbon bond formation. On the basis of data discussed below it would appear that on an absolute basis total bond-formation at the transition state is small.



(IV)

Experiments 9-14 in Table 1, concerning the reactivity of II toward substituted pairs of the same class of organic substrate (phenols, anilines and benzophenones), were designed to determine steric and electronic substituent effects on reactivity.

2,6-Dimethyl substitution in phenols (Experiment 11) and anilines (Experiments 13 and 14) caused a ca. 50% decrease in reactivity towards II compared to the corresponding 3,5-dimethyl derivatives. An attempt to compare the relative reactivities of 4,4'-dimethylbenzophenone and 2,2'-dimethylbenzophenone towards II was unsuccessful because the 2,2'dimethylbenzophenone reacted with II to give substantial yields of non-Wittig-type products [11]. The small rate decreases caused by 2,6-dimethyl substitution in the phenols and anilines are significant since the silylation of 2,6-dimethylphenol by hexamethyldisilazane was reported [12] to be much slower (the data indicated at least a five-fold rate difference) than the silylation of phenol under identical reaction conditions. Although these results would seem to indicate that the steric requirements of II are small, the rate differences may actually be due to a "leveling effect" caused by the high reactivity of II (this is discussed in more detail below).

All of the data from the competitions between pairs of substituted phenols, anilines, and benzophenones, for II indicate that these reactions are insensitive to polar effects.

At present, insensitivity of these reactions to polar effects may be explained by the high reactivity of $Me_2Si=CH_2$ (II) which gives rise to activation barriers for all of the reactions studied which are less than ca. 9 kcal/mole (the assumptions used to calculate this value are discussed below). Consideration of these low activation barriers together with the realization that the reactions of II with any of the substrates used in this study must be highly exothermic leads to formulation of an activated complex which resembles the reactants more than the products, and, therefore, one in which the effects of polar substituents on the reactivity should be minimal. The severe (611°) reaction conditions used are an additional factor which may also contribute to this leveling effect.

The possibility that II is reacting as a diradical which might be expected to be insensitive to electronic effects is eliminated since II does not react with toluene and also because the observed *A* factor ($\log A = 15.8\ \text{sec}^{-1}$) for the formation of II from 1,1-dimethylsilacyclobutane is not in accord with a reaction involving spin inversion [2].

The value of ca. 9 kcal/mole as an upper limit to the activation energy for the reaction between II and the substrates used in this study is based on a calculated value of ca. 11 kcal/mole for the activation energy for the dimerization of II and the experimental observation that the reaction of II with the substrates used is at least one hundred times faster than its dimerization (i.e., less than 0.5% dimer present in the pyrolysates).

The calculated value of ca. 11 kcal/mole for the activation energy for the dimerization of II was reported by Flowers and Gusel'nikov on the basis of their gas phase kinetic data and an assumed value of 20 kcal/mole for the activation energy for the reaction between II and ethylene [2]. A similar value of ca. 9 kcal/mole for the activation energy for the disappearance of II can be calculated using the data reported in a separate study in which II, trapped at −196°, reacted upon warming to ca. −120° [13].

Additional support for the low activation energies for the reactions of II is provided by the fact that gas phase reactions between Lewis acids and bases such as BF_3 and CH_3NH_2 occur with activation energies close to zero [14] (we reiterate that extended Hückel calculations [8] indicate that $Me_2\overset{+}{Si}—\overset{-}{C}H_2$ is a major contributing resonance structure for 1,1-dimethyl-1-silaethene).

It should be emphasized that although the activation energies discussed above are approximate, an increase in these estimated values by as much as 5 kcal/mole does not alter our basic argument.

In conclusion, it is our opinion that II is best described as a highly reactive dipolar intermediate, $Me_2\overset{\delta+}{Si}=\overset{\delta-}{C}H_2$, which behaves as an electrophile toward such substrates as ketones, alcohols, phenols, and amines. In the case of acetonitrile the less potent nucleophilic character of II is involved.

We are continuing our investigations into the reactivity and selectivity of multiply bonded silicon—carbon intermediates using different substituents on silicon and lower substrate concentrations in an effort to moderate these reactions so that the polar effects of organic substrates can be observed.

Experimental

NMR spectra were recorded on a Varian A60-A spectrometer. Infrared spectra were obtained using a Beckman IR-8 spectrometer. Reaction mixtures were analyzed by GLC on a HP 7620A (FID) using a 6 ft. × 1/8 in. 10% UC-W98 column. Preparative GLC separations were made on a Varian 920 (TCD) using a 10 ft. × 3/8 in. 20% SE 30 on Chromosorb W column. Melting points were taken in capillary tubes, and are uncorrected.

Chemicals

Reagent grade neopentyl alcohol, phenol, *m*-chlorophenol, *m*-chloroaniline, acetonitrile, 3,5-dimethylphenol, 3,5-dichlorophenol, 3,5-dimethylaniline, 3,5-dichloroaniline, 2,6-dimethylaniline, *m*-methylaniline, and aniline were obtained from either the Aldrich, Eastman, or Baker chemical companies. Except for the liquid amines which were distilled before use, all of the above reagents were of sufficient purity to be used as obtained.

Hexamethyldisilazane was generously donated by the Dow Corning Corporation. 1,1-Dimethylsilacyclobutane was prepared by the method of Damrauer [15]. 4,4′-Dimethylbenzophenone m.p. 91.5-93° (lit. 95°) [16] and 3,3′-dichlorobenzophenone m.p. 122-124° (lit. 123-124°) [17] were prepared from the corresponding acid chlorides and the substituted bromobenzenes via the organocadmium reagent [18].

All of the products of the competition experiments such as phenoxytrimethylsilane were made independently by reaction of substrate with hexamethyldisilazane followed by isolation by preparative GLC. These products were then used as references for GLC retention times and also to determine yields by quantitative GLC (see below).

The Wittig products of the competition experiments were made by independent pyrolysis of the starting ketone and 1,1-dimethylsilacyclobutane at 611°, then isolated by preparative GLC.

General pyrolysis procedure

The apparatus and procedure used for all of the pyrolyses described above have been described in detail in a previous publication [6].

Competition reactions

The following is a specific example of a competition reaction but in general all of the competition reactions in this paper were carried out in this manner.

1,1-Dimethylsilacyclobutane (10.0 mmol), *m*-chlorophenol (10.0 mmol) and benzophenone (10.0 mmol) were pyrolyzed in 2.05 g of benzene at 611° yielding 5.42 g of pyrolysate (96.5% mass recovery corrected for ethene loss). Quantitative GLC analysis of the pyrolysate was carried out by first measuring the areas of the product peaks. Then a known weight of one of the products was added and the peak areas were again measured. This information coupled with the flame factors of the two products, determined from standard solutions of the products, was used to calculate the absolute product yields. These analyses, done two or three times for each competition reaction, were consistent to ca. ± 3%. The yields of 3-chlorophenoxytrimethylsilane and 1,1-diphenylethene were 17.3 and 49.0%, respectively.

Pyrolysis of neopentyl alcohol with 1,1-dimethylsilacyclobutane

Pyrolysis of neopentyl alcohol (14.9 mmol) with 1,1-dimethylsilacyclobutane (7.34 mmol) in 3.69 g of benzene at 611° afforded 5.26 g of pyrolysate (98% mass recovery corrected for ethene loss). Preparative GLC gave 0.435 g of trimethylneopentoxysilane (37%) and 0.605 g of neopentyl alcohol (46.2%), identified by their IR and NMR spectra which were identical to those of the authentic compounds.

Pyrolysis of phenol with 1,1-dimethylsilacyclobutane

Pyrolysis of phenol (25.7 mmol) with 1,1-dimethylsilacyclobutane (12.8 mmol) in 2.13 g of benzene at 611° afforded 5.32 g of pyrolysate (99% mass recovery corrected for ethene loss). Preparative GLC gave 0.888 g trimethylphenoxysilane (41.8%) and 0.598 g of phenol (24.8%), identified by their IR and NMR spectra which were identical to those of the authentic compounds.

Pyrolysis of aniline with 1,1-dimethylsilacyclobutane

Pyrolysis of freshly distilled aniline (31.0 mmol) with 1,1-dimethylsilacyclobutane (9.16 mmol) in 2.30 g of benzene at 611° afforded 5.36 g of pyrolysate (92% mass recovery corrected for ethene loss). Preparative GLC gave 0.901 g *N*-trimethylsilylaniline (60%) and 2.06 g of aniline, identified by their IR and NMR spectra which were identical to those of the authentic compounds.

Acknowledgment

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