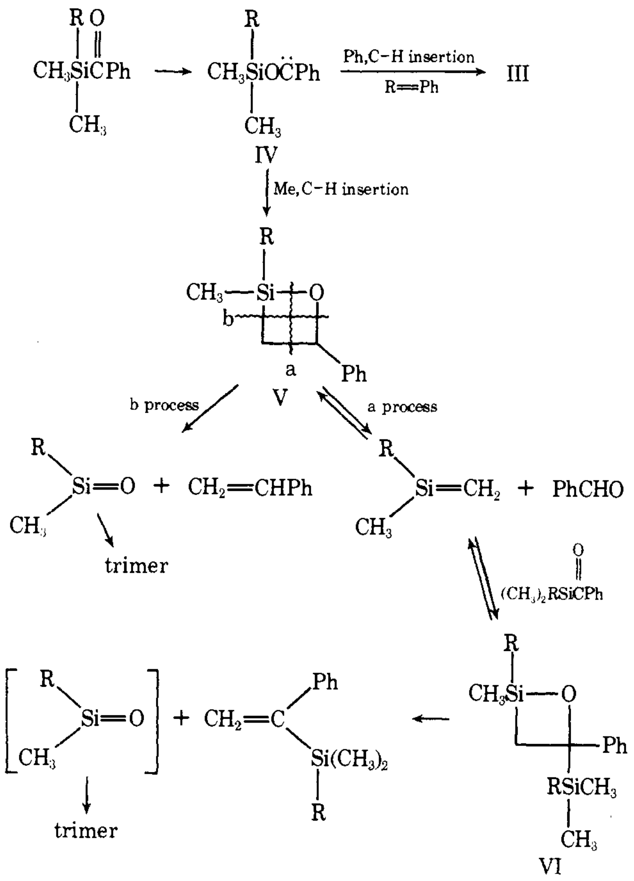
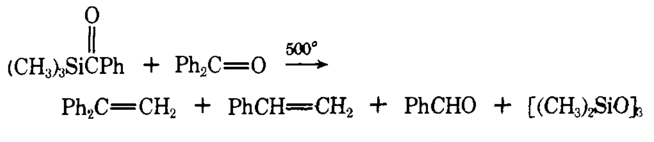
Scheme I



step the expected carbon-carbon rearrangements products were not observed.[13]

The proposed third step in the overall reaction is the cleavage of V to styrene, benzaldehyde, and cyclosiloxane. In this step the lack of stability in the 1,2-silaoxetane (V) causes the silicon-carbon and silicon-oxygen bonds to rupture giving silicon-carbon and silicon-oxygen double bonds. The compounds, α-trimethylsilylstyrene and α-dimethylphenylsilylstyrene are the evident products of cleavage of 1,2-silaoxetane (VI) formed by the reaction of a silicon-carbon double bond and silyl phenyl ketones (I and II). The comparatively low yields of volatile products encountered in the neat pyrolysis of I and II are not suprising, since all of the postulated intermediates should be very prone to polymerization.

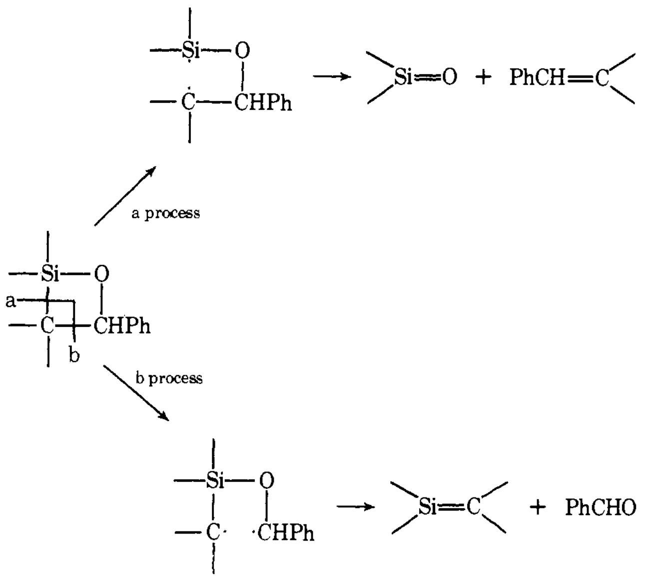
Pyrolysis of I in the presence of benzophenone gave 1,1-diphenylethylene (17%) together with similar yields of $(Me_2SiO)_3$ (24%), styrene (32%), and benzaldehyde (27%).



$$(CH_3)_3Si\overset{\overset{O}{\|}}{C}Ph + Ph_2C{=}O \xrightarrow{500°} Ph_2C{=}CH_2 + PhCH{=}CH_2 + PhCHO + [(CH_3)_2SiO]_3$$

The formation of 1,1-diphenylethylene is due to the cleavage of silaoxetane resulting from the reaction of a silicon-carbon double bond with benzophenone.

In summary the present work demonstrates that 1,2-silaoxetane resulting from C-H insertion of siloxycarbene undergoes the Si-C and Si-O bond cleavages in almost comparable ratio. Although the strength of the Si-O bond excludes an initial rupture of 1,2-silaoxetane, the product ratio provides evidence for the competitive Si-C and C_2-C_3 bond scission as the initial step of thermal silaoxetane decomposition.[14]



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Wataru Ando*
Department of Chemistry, The University of Tsukuba
Niiharigun, Ibaraki 300-31, Japan

Akira Sekiguchi, Toshihiko Migita
Department of Chemistry, Gunma University
Kiryu, Gunma 376, Japan

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Acidities of Carbon Acids. VII. Conjugation and Strain in Some Cyclopropyl Anions

Sir:

Electron-withdrawing groups (EWG), such as nitro, carbonyl, and sulfonyl, have been shown by equilibrium acidity measurements in dimethyl sulfoxide (DMSO) solution to have acidifying effects of over 30 powers of ten on α-C-H bonds in methane carbon acids, CH_3EWG.[1,2] The present paper extends the study to the SO_2CF_3 group,[3] and to cyclopropane carbon acids, c-PrEWG (Table I).[4]

There is abundant evidence that carbanions α to nitro and carbonyl groups derive much of their stability by rehybridizing from sp^3 to sp^2, thus allowing delocalization of charge to the more electronegative oxygen atoms, but it has

Table I. Equilibrium Acidities of Carbon Acids Measured in Dimethyl Sulfoxide Solution[4]

EWG	p*K* (CH_3EWG)	p*K* (*i*-PrEWG)	p*K* (*c*-PrEWG)	Δp*K*[b]
NO_2	17.20 ± 0.01	16.89 ± 0.02	~27[a]	~9
SO_2CF_3	18.76 ± 0.03	21.80 ± 0.03	26.60 ± 0.03	7.3
COPh	24.70 ± 0.02	26.26 ± 0.02	28.18 ± 0.02[c]	3.0
SO_2Ph	29.04 ± 0.05	>32	>32	>2.5

[a] Rapid decomposition; since equilibrium may not have been reached, this value is probably high by 1 or 2 p*K* units. [b] p*K* (*c*-PrEWG)−p*K* (CH_3EWG) statistically corrected. [c] A referee questioned the validity of this number on the grounds that it is lower than he expected, and is in a range "high for the DMSO system." Actually, the p*K* is almost 7 units below the presently accepted value for the DMSO solvent (35.1).[2] Nevertheless, the value was checked by a different investigator using a freshly purified sample of cyclopropyl phenyl ketone and two different indicators. Against thiaxanthene (p*K* = 28.3) the p*K* observed was 28.22; against diphenylyldiphenylmethane (p*K* = 29.4) it was 28.31 ± 0.01. The value of 28.2 given in the table is probably better than the latter value because it was obtained by several runs with 9-phenylxanthene (p*K* = 27.9) which has a p*K* close to that of cyclopropyl phenyl ketone.

been less clear how important conjugative effects are for the sulfonyl group. It has been known for some time that the sulfonyl group resembles the nitro and carbonyl groups in requiring a σ^- constant to represent its interaction from the para position in anilinium ions, phenols, and thiophenols,[5] and this has been interpreted as evidence for a strong conjugative effect, presumably involving d orbitals on sulfur. On the other hand, theoretical studies suggest little or no need to invoke d-orbital conjugation in most instances,[6] and ab initio calculations on the $CH_2SO_2H^-$ carbanion indicate a pyramidal structure with little or no role assigned to d-orbital conjugation.[7] The present results show that the SO_2CF_3 group has a larger acidifying effect in CH_3EWG acids than does COPh and almost as large an effect as does NO_2, the order being $NO_2 > SO_2CF_3 >$ COPh $> SO_2Ph$. Present evidence indicates that substitution of the SO_2CF_3 group for a hydrogen atom in the methide ion increases its stability by over 60 kcal/mol. It is highly unlikely that a stabilizing effect of this magnitude can be solely a polar effect, and this point of view is supported by evidence pointing to a much smaller acidifying effect by the $N(CH_3)_3^+$ group.[8] We conclude that the SO_2CF_3 group is exerting a large conjugative effect. This conclusion is supported by consideration of its effect on the acidity of a hydrogen atom attached to a cyclopropane ring (Δp*K* in Table I).[9]

Examination of Table I shows that the cyclopropane carbon acids, *c*-PrEWG, with EWG = NO_2, SO_2CF_3, or COPh, are considerably less acidic than the corresponding CH_3EWG and *i*-PrEWG carbon acids, despite the intrinsically greater acidity of protons attached to a cyclopropane ring.[10] The marked decrease in acidity for *c*-$PrNO_2$ and *c*-PrCOPh, relative to CH_3NO_2 and CH_3COPh, respectively, must be caused primarily by strain in the $C_3H_4{=}NO_2^-$ and $C_3H_4{=}C(Ph)O^-$ anions.[11] The simplest explanation appears to be that removal of the proton on the cyclopropane ring by base is accompanied by rehybridization of the resulting orbital containing the electron pair, its p character being increased so as to permit maximum overlap in the resulting π-bond.[12] Increased p character in this orbital can be achieved, however, only at the cost of decreased p character in the carbon-carbon bonds of the cyclopropane ring, which according to theoretical models, possess a high degree of p character.[13] The result is a sharp increase in ring strain in the anions.[11,12] The SO_2CF_3 group appears to impose the same kind of electronic demand on the cyclopropane ring as does the NO_2 group or the COPh group. The same trend can also be seen with the SO_2Ph group.[14] In other words the SO_2CF_3 and SO_2Ph groups may only exert their maximum effects on sp^2 carbanions. This would imply that retention of asymmetry in α-sulfonyl carbanions is not a result of a high barrier to inversion, but of restricted rotation or asymmetric solvation.[16] The apparent increased conjugative effect of the SO_2CF_3 group, as compared to the SO_2Ph group, is in agreement with predictions of Craig to the effect that increasing the electron-withdrawing power of the group attached to sulfur (replacement of Ph by CF_3 in the present instance) will contract the 3d orbitals of sulfur and make them more available for conjugative overlap.[17] It is also possible to describe the bonding in other ways;[6,7] the one clear point emerging from the experimental results is that conjugation of sulfur in SO_2CF_3 with the carbanion is *strong*.

There have been previous qualitative indications that cyclopropyl anions of the type $C_3H_4EWG^-$ are strained,[11,12] but the present study is the first to provide quantitative data which allow an estimate to be made of the size of the effect. Based on the CH_3EWG model,[9] the strains in the $C_3H_4EWG^-$ anions amount to, ~12, 10.0, 4.1 and >3.4 kcal/mol for the NO_2, SO_2CF_3, COPh, and SO_2Ph groups, respectively.[18] Studies of base-catalyzed exchange rates ("kinetic acidities") for *c*-PrEWG systems have led to the conclusion that some cyclopropyl anions of the type $C_3H_4EWG^-$ are not destabilized by strain.[20] The 10^3-10^4 slower rates observed for all cyclopropene-EWG type compounds did not correlate with the variable cyclopropyl effects on exchange rates and were attributed to antiaromaticity in cyclopropene anions.[20] Since all of our equilibrium measurements show large (10^3-10^{12}) decreases in acidity for *c*-PrEWG compounds due to strain, the lower "kinetic acidities" of cyclopropenyl systems may, after all, also be due to strain, which would not leave much role for antiaromaticity in cyclopropenyl anions of this type.[21]

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F. G. Bordwell,* Noel R. Vanier, Walter S. Matthews[23]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

J. B. Hendrickson,* Paul L. Skipper
Edison Chemical Laboratory, Brandeis University
Waltham, Massachusetts 02154

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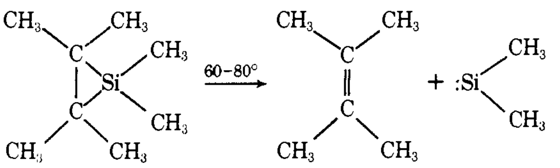
Generation of Dimethylsilylene under Mild Conditions by the Thermolysis of Hexamethylsilirane

Sir:

The generation of divalent silicon species, the silylenes, and their chemical reactivity have received much attention in recent years.[1] Pyrolytic and photolytic processes have served in their production, but these are not wholly satisfactory. The thermolysis reactions require high temperatures, ca. 300°, for substituted 7-silanorbornadienes[2] and ca. 200–250° for polydimethylsilanes with terminal methoxy substituents.[3] The photolysis of $Me(Me_2Si)_nMe$ ($n = 4$–8)[4] and c-$(Me_{12}Si_6)$[5] produces dimethylsilylene at 25–45°, but in such reactions it is possible that the final products obtained will be determined by secondary photoprocesses involving the initial products or by other chemistry involving excited states of the initial products. Clearly, a less strenuous thermal route would be a useful addition to the known procedures of silylene generation.

We have found that hexamethylsilirane, **1**, whose preparation we reported recently,[6] decomposes at around 60–80° to generate dimethylsilylene, eq 1. The initial indication of such a mode of decomposition was provided by the mass spectrum of hexamethylsilirane which showed no molecular ion. The largest fragment, *m/e* 84, was attributable to $[Me_2C{=}CMe_2]^+$. An experiment in which the decomposition of hexamethylsilirane in benzene-d_6 under argon at 60° was monitored by proton NMR spectroscopy showed that two products were formed when hexamethylsilirane decomposed: tetramethylethylene (δ 1.78 ppm) and a methylsilicon compound (δ 0.28 ppm). The half-life of the silirane under these conditions was 11 hr. In a larger scale experiment carried out in benzene (15 hr at 73°), the tetramethylethylene yield was determined by gas chromatography (GLC) to be 77%, and this product was isolated and identified by comparison of its GLC retention time, NMR spectrum, and refractive index with those of an authentic sample. Invariably lower yields of tetramethylethylene (46% in one such experiment) were obtained when the thermolysis of hexamethylsilirane was carried out in THF. The organosilicon product of the decomposition was isolated as a nonvolatile oil, probably polymeric polydimethylsilylene.



1

(1)

Dimethylsilylene produced in the thermolysis of hexamethylsilirane may be trapped by various substrates when the decomposition is carried out in their presence. The hexamethylsilirane may be used in the form of the THF solution in which it is formed,[6] as the neat reagent, or in benzene solution. Orientational experiments are required to determine which of these possibilities gives the best results for a given type of substrate. Also, the optimum substrate/hexamethylsilirane ratio must be determined in such experiments for the different types of substrate used.

Our initial trapping experiments have been carried out with classes of substrates which had been shown by previous workers to react with dimethylsilylene. The reaction of dimethylsilylene with dimethyldimethoxysilane is described in detail to illustrate the procedure used. (It must be emphasized that all operations must be carried out under an atmosphere of dry argon or nitrogen since hexamethylsilirane is highly reactive toward atmospheric oxygen and moisture.[6] All substrates and solvents used must be degassed prior to their mixing with the silirane.)

Seven milliliters of a solution of hexamethylsilirane in THF[6] was concentrated at room temperature and 65–70 mmHg during a 3-hr period to remove THF and argon was admitted into the flask containing the silirane which remained. An aliquot of the silirane was added to benzene-d_6 containing toluene as internal standard and the amount of silirane present was determined by NMR. An added check was provided by methanolysis of the silirane[6] in the NMR sample and determination of the yield of the methanolysis product, $MeOSiMe_2CMe_2CHMe_2$, by GLC. In this way it was established that 1.18 mmol of hexamethylsilirane was available for reaction. To this was added 75 mmol of degassed dimethyldimethoxysilane[7] and the resulting solution was heated at 73° for 15 hr, with stirring under argon. Subsequent GLC analysis showed that tetramethylethylene was present in 95% yield and that the Si–OMe insertion product, $MeOSiMe_2SiMe_2OMe$,[8,9] had been formed in 71% yield.

Organosilicon hydrides also react readily with silylenes,[1] and we have intercepted the dimethylsilylene released in hexamethylsilirane thermolysis with several substrates containing Si–H bonds. In all cases no inert diluent was present and the silicon hydride, present in large excess, served as reaction medium. The results are shown in Scheme I. Finally, we have examined reactions of hexamethylsilirane with 1,3-dienes which have been shown to react with silylenes,[1] via 1,2-addition followed by subsequent rearrangement of the initially formed vinylsilacyclopropanes, usually to 1-silacyclopent-3-enes.[12] Here the results were not straightforward. The best product yield with 2,3-dimethyl-1,3-butadiene was obtained when a THF solution containing the silirane and 5.3 molar equivalents of the diene was heated at 66° for 17 hr. Tetramethylethylene was obtained in 37% yield and 1,1,3,4-tetramethyl-1-silacyclopent-3-ene[8,13] in

Scheme I