Ruthenium-(C=NMe$_2$) bond lengths are symmetrical, with Ru(11)-C(1) = 2.039 (4) Å, Ru(12)-C(1) = 2.018 (4) Å, Ru(21)-C(2) = 2.034 (5) Å, and Ru(22)-C(2) = 2.037 (5) Å. Distances within the Me$_2$NC ligand (C(1)-N(1) = 1.279 (5) Å, C(2)-N(2) = 1.280 (6) Å and N-Me = 1.455 (7)-1.481 (7) Å) are consistent with there being a C=N linkage. Since the ligand acts as a three-electron donor, it should presumably be written as $Me_2N^+ \rightleftarrows {}^-C\!:$.

Finally, we note that a species initially formulated as $HFe_3(CO)_{11}(NMe_2)$[16] has more recently been characterized as $HFe_3(CO)_{10}(CNMe_2)$[17] by spectroscopic methods, although details of the metal-(CNMe$_2$) bonding were not considered. This complex appears to be the iron analogue of our present ruthenium complex.

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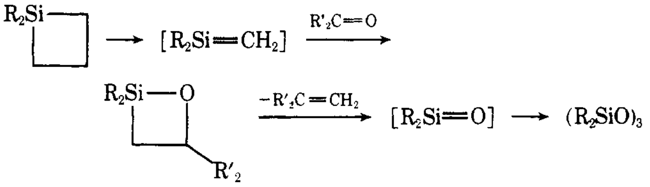
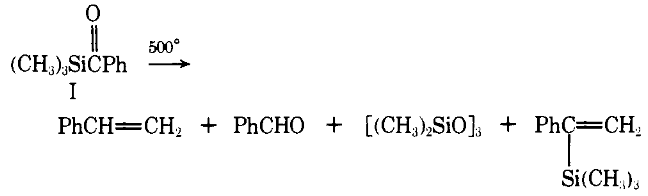
The Chemistry of Silylcarbene. V. 1,2-Silaoxetane Intermediate in the Gas Phase Decomposition of Silyl Phenyl Ketones. New Route for the Formation of a Silicon-Carbon Double Bond[1]

Sir:

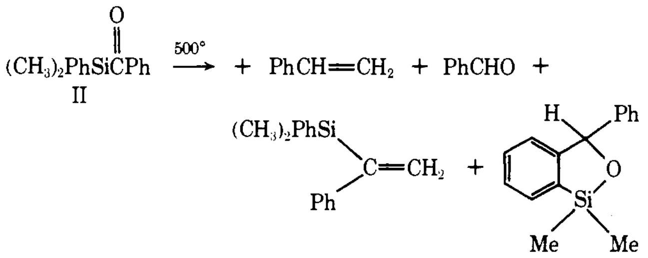
A number of reactions suggest the formation of short-lived silicon olefin analogues during the pyrolysis and the photolysis of silacyclobutane,[2,3] disilane,[4,5] silabicyclooctadiene,[6,7] and silyldiazomethane.[1,8-10] Some chemical evidence for the existence of silicon analogues of olefins is the reaction of monosilacyclobutane with water vapor, ammonia, alcohols, imines, nitriles, and dienes.[2] Barton and Kline[11] found that the copyrolysis of 1,1-dimethyl-1-silacyclobutane with isobutyl methyl ketone resulted in the formation of cyclosiloxane (mainly, trimer), ethylene, and a corresponding new olefin, and suggested a possible 1,2-silaoxetane intermediate as an adduct of Me$_2$Si=CH$_2$ and the carbonyl compound. We wish to report here the reversible formation of a silicon-carbon double bond from a 1,2-silaoxetane intermediate generated in the decomposition of silyl phenyl ketones.



Complete pyrolysis of trimethylsilyl phenyl ketone (I) was conducted in a nitrogen flow system (30 cm^3/min, 500°) and the pyrolysate collected at −196°. Analysis of the pyrolysate by gas chromatography revealed four main components and a total absence of silyl phenyl ketone. Separation of the four components by preparative gas chromatography afforded pure samples of cyclosiloxane (25%), styrene (33%), benzaldehyde (12%), and α-trimethylsilylstyrene (24%). These products were identified by comparison of their GLPC retention times and NMR and ir spectra with those of authentic compounds. Pyrolysis of II at 500° led to α-dimethylphenylsilylstyrene (8%), together with the styrene (5%), benzaldehyde (8%), and the siloxy derivative III (17%).



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

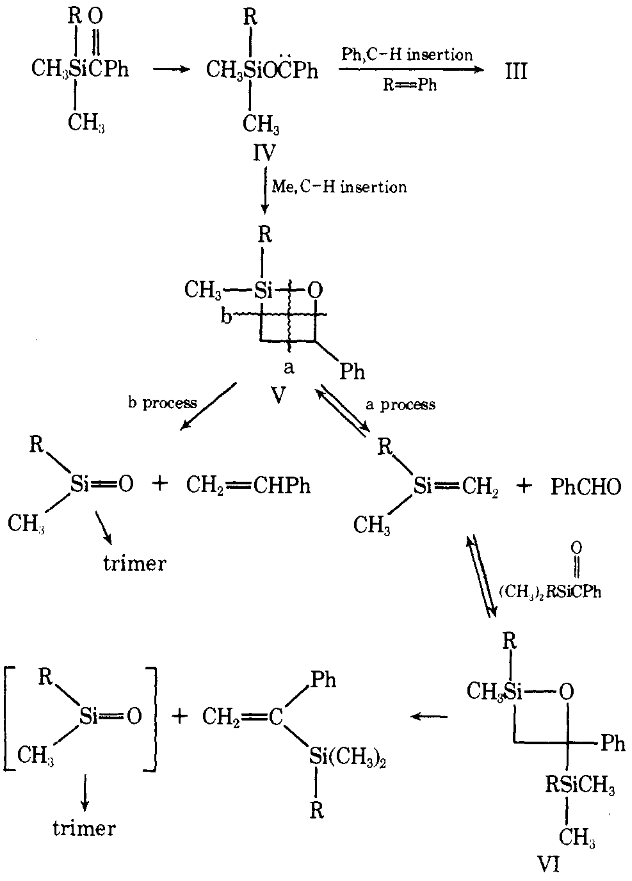


III

The structure of III follows from the ^{1}H NMR spectrum (CCl$_4$, τ 9.58, s, 3 H; 9.52, s, 3 H; 3.92, s, 1 H; 3.20-2.27, m, 9 H) and the presence of infrared bands at 1020 and 1045 cm^{-1}. A reasonable pathway for the formation of these products is shown in Scheme I. The proposed first step, the rearrangement of silyl phenyl ketone to form siloxyphenylcarbene, is very similar to the photoisomerization of silylketone in a polar solvent previously reported by Brook.[12]

The intermediate (V) in the second step is almost certainly formed by an insertion of carbene (IV) into the proximate carbon-hydrogen bond of the silyl methyl group. The source of III is apparently the insertion of siloxycarbene into the C-H bond of the phenyl group on silicon. In this

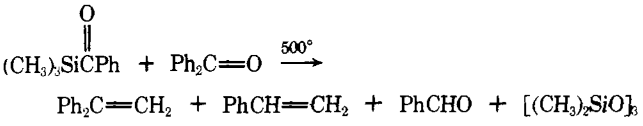
Scheme I



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.

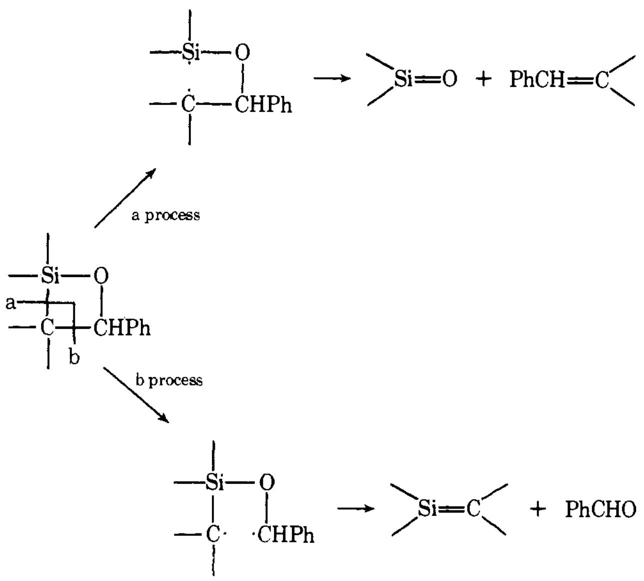
Pyrolysis of I in the presence of benzophenone gave 1,1-diphenylethylene (17%) together with similar yields of $(Me_2SiO)_3$ (24%), styrene (32%), and benzaldehyde (27%).



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

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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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