Table I. Infrared Absorptions (cm^{-1}) of $Mo_2(gly)_4Cl_4$. Compound II with H and II with D

$Mo_2(gly)_4Cl_4$	II with H	II with D
3390 (m, br)	3390 (m, br)	3390 (m, br)
3150 (m, vvbr)	3150 (m, vvbr)	3150 (m, vvbr)
	1635 (w, br)	
1600 (m, br)	1600 (m, br)	1600 (m, br)
1545 (m)	1545 (m)	1545 (m)
1460 (s)	1460 (s)	1460 (s)
1420 (s)	1420 (s)	1420 (s)
1345 (s)	1345 (s)	1345 (s)
1310 (m)	1310 (m)	1310 (m)
		1165 (w, br)
1110 (s)	1100 (s)	1100 (s)
1045 (m)	1040 (s)	1040 (s)
	965 (w)	965 (w)
900 (s)	890 (s)	890 (s)
	790 (w, br)	790 (w, br)
700 (m)	690 (m)	690 (m)
	660 (w)	
615 (s)	610 (s)	610 (s)
585 (m)	585 (m)	585 (m)
		472 (w)
425 (m)	435 (s)	435 (s)
340 (w)	345 (m)	345 (m)

addition of concentrated HCl and CsCl as above. The IR spectrum of I obtained in this way still possessed the Mo-D-Mo band[2] at 904 cm^{-1} and not the Mo-H-Mo band at 1245 cm^{-1}.

A crystalline gray-violet precipitate (compound II) separates slowly from an ice-cooled concentrated solution of the violet species in 3 M HCl. Single crystals suitable for x-ray crystallography were not obtained. The IR spectra of II, of deuterated II, and of $Mo_2(gly)_4Cl_4$, measured in Nujol mull and KBr pellets, are presented in Table I. Cotton and Webb[4] proved that the glycine ligands are coordinated to the two molybdenum(II) atoms in $Mo_2(gly)_4^{4+}$ by bridging carboxylates. The striking similarity between the spectrum of $Mo_2(gly)_4Cl_4$ and that of II columns 1 and 2, Table I) indicates that glycine is coordinated in II in the same way. The IR bands of II at 1635 and 660 cm^{-1} probably belong to the Mo-H-Mo vibrations (stretching and bending, respectively). In crystals of II obtained from $Cs_3Mo_2Cl_8D$ these bands are replaced by bands at 1165 and 472 cm^{-1} (Table I, column 3). These shifts are expected for an increase in the reduced mass by a factor of two. Analysis of II (found: Mo, 35.40; C, 9.2; N, 5.2; H, 2.7; Cl, 26.2) conforms to $[Mo_2(gly)_2H]Cl_4 \cdot 3H_2O$ (calcd: Mo, 35.68; C, 8.92; N, 5.20; H, 3.16; Cl, 26.39).

The chemical and spectroscopic evidence presented here indicates that two molybdenum(III) atoms are bridged by two carboxylic ligands, as in $[Mo_2(gly)_4]^{4+}$ [4] and by one hydride ligand as in I[2]. The charge 4+ of the complex ion, rather than 5+, may be due to the existence of an additional OH^- ligand (instead of one H_2O) in a bridging or terminal position. Alternatively, the charge 4+ may be due to the protonation of only one of the two amino groups of the complex ion. Efforts are made to obtain single crystals of II for x-ray analysis.

The difference between the oxidation reactions of the hydride ligand of I and II in aqueous solution may be due to a stronger and shorter metal to metal bond in the latter which enables its conversion to a quadruple bond and the accompanying oxidation of H^- to H^+. A shorter Mo-Mo bond in II is expected on steric grounds; bridging chlorides impede the approach of the Mo atoms to each other,[2] whereas bridging carboxylates fit in, and stabilize very short Mo-Mo bonds, as for example in $Mo_2(OAc)_4$ and $Mo_2(gly)_4(SO_4)_2 \cdot 4H_2O$.

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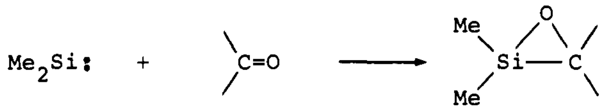
Evidence of the Formation of Oxasilacyclopropane from the Reaction of Silylene with Ketone

Sir:

Strained ring systems containing a silicon atom have long intrigued chemists, owing to their high reactivity resulting from the high strain energy.[1,2] Kumada,[3] Weber,[4] Skell,[5] and Seyferth[6] have provided the data for the evidence of silacyclopropane in the reaction of silylene and carbon-carbon double bond, and, in 1972, Lambert and Seyferth[7] were successful in preparing a stable silacyclopropane. More recently, Gaspar[8] has isolated tetramethyl-1-silacycloprop-2-ene at room temperature, as the addition product of dimethylsilylene to 2-butyne.

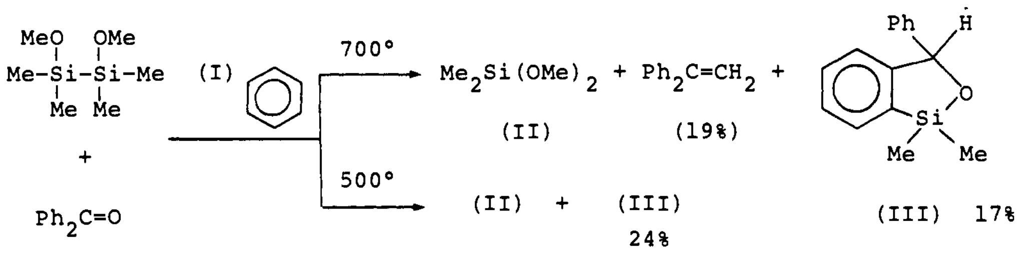
While many routes to silacyclopropanes and silacyclopropenes[9,10] have been investigated, there is no report on the synthesis of small ring compound containing silicon and oxygen. We previously reported evidence for a 1,2-silaoxetane intermediate from the intramolecular C-H insertion of siloxycarbene in the gas phase pyrolysis of silyl phenyl ketone.[11] No successful report of a three-membered-ring compound, with ring silicon and oxygen has appeared. We have strong evidence that it was synthesized as the addition product of dimethylsilylene to ketone.



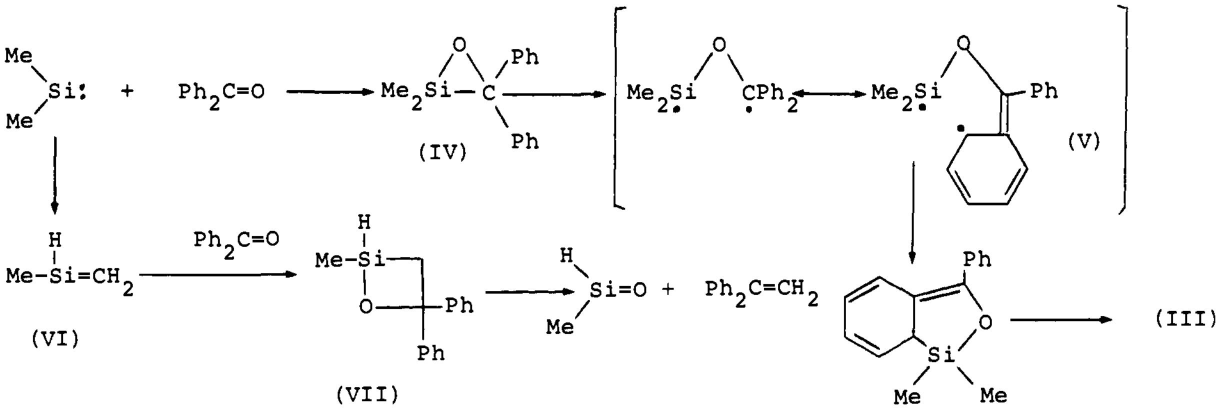
Gas phase flow pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane (I, 3 mmol) in a nitrogen flow system (30 mL/min, at 700 °C) was employed to generate dimethylsilylene in the presence of fivefold excess of benzophenone with 40-fold excess benzene and the pyrolysate collected at −78 °C. Analysis of the pyrolysate by gas chromatography revealed three main components. Separation of these components by preparative gas chromatography afforded dimethyldimethoxysilane (II), 1,1-diphenylethylene (19%), and 1,1-dimethyl-1-sila-2-oxa-3-phenyl-4,5-benzocyclopentene (III, 17%). Pyrolysis of I with benzophenone and benzene at 500 °C gave II and III (24%) as main products (Scheme I). These products were identified by comparison of their GLC retention times and NMR and IR spectra with those of authentic samples.[11] It is possible that the silylene attacks on the π bond of carbonyl to produce the intermediate oxasilacyclopropane (IV) (Scheme II). Such a molecule could thermally cleave the silicon-carbon bond to give 1,5 diradical V followed by recombination to give product III. In this case, direct formation of 1,3 diradical is probably inconsistent with the demonstrated singlet nature of dimethylsilylene.[5,12] It is also known that in gas phase dimethylsilylene partially undergoes 1,2-hydrogen shift to methylsilene (VI).[13] Thus, the formation of 1,1-diphenylethylene may arise from the decomposition of 1,2-silaoxetane (VII) formed from the cycloaddition of the silene and carbonyl of benzophenone.[11,14]

Alkyl ketones (VIII) such as diethyl ketone, cyclohexanone, and acetophenone were found to react with dimethylsilylene generated from the gas phase flow pyrolysis of I with benzene

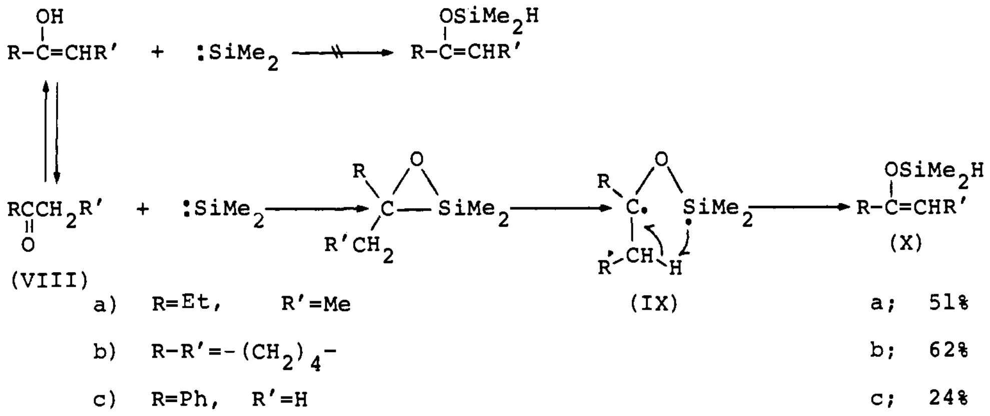
Scheme I



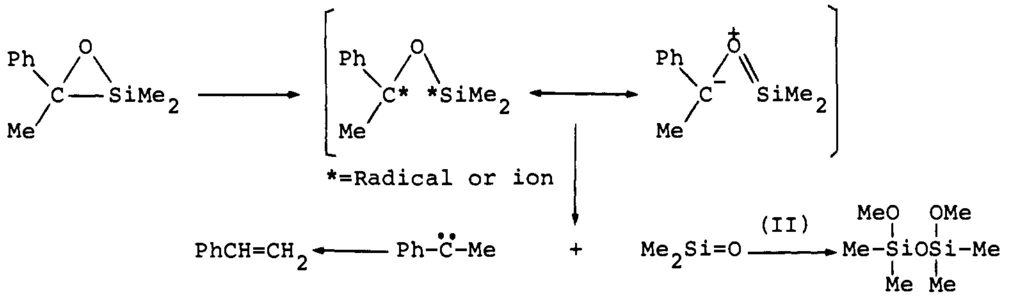
Scheme II

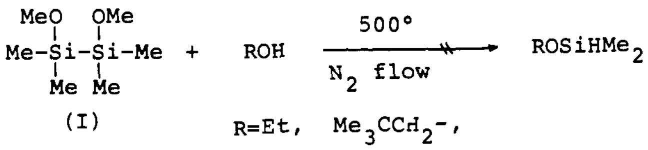


Scheme III

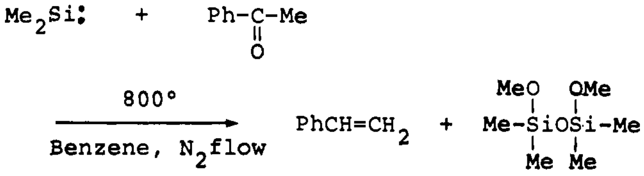


Scheme IV





under a nitrogen flow system (30 mL/min, at 500 °C). The silyl enol ether X, along with some decomposition, was obtained in moderate yield. While the silyl enol ether is formally the insertion product of silylene into enol O-H bond, presently we favor the reaction path involving prior formation of oxasilacyclopropane followed by γ-hydrogen abstraction of silyl radical IX through the homolytic cleavage of silicon-carbon ring bond (Scheme III). Examination of the reactivity of dimethylsilylene has shown that alcohols, such as ethyl or neopentyl alcohol, did not intercept this species under the gas phase conditions, in contrast to silylene reaction under the liquid phase.[15,16,17] When I was pyrolyzed with fivefold excess of acetophenone and 40-fold excess of benzene in a nitrogen flow system at 800 °C, the products included tetramethyldimethoxysiloxane (10%), styrene (31%), some polysilanes, and unreacted acetophenone. The possibility that styrene arises from the 1,2-hydrogen shift of phenylmethylcarbene must be considered. A reasonable route can be written in Scheme IV



$$\mathrm{Me_2Si{:}} + \mathrm{Ph{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Me} \xrightarrow[\text{Benzene, } N_2\text{flow}]{800^\circ} \mathrm{PhCH{=}CH_2} + \mathrm{Me{-}\overset{\overset{\displaystyle MeO}{|}}{\underset{\underset{\displaystyle Me}{|}}{Si}}O\overset{\overset{\displaystyle OMe}{|}}{\underset{\underset{\displaystyle Me}{|}}{Si}}{-}Me}$$

either by the cleavage of silicon-carbon ring bond of intermediate oxasilacyclopropane followed by the rupture of carbon-oxygen bond, or by [3 → 2 + 1] cycloelimination to give a primarily phenylmethylcarbene, which rearranges to styrene.[18] The resulting dimethylsilanone could react with dimethyldimethoxysilane to give tetramethyldimethoxysiloxane.[19,20]

In summary the present work demonstrates that silylene could attack on carbonyl to produce oxasilacyclopropane. Thermal cleavage of the silicon-carbon ring bond of oxasilacyclopropane gives a 1,3 diradical or zwitterion which may undergo either intramolecular hydrogen abstraction or addition to the π bond of aromatic ring. The deoxygenation of carbonyl compounds also occurs to give the carbenes.

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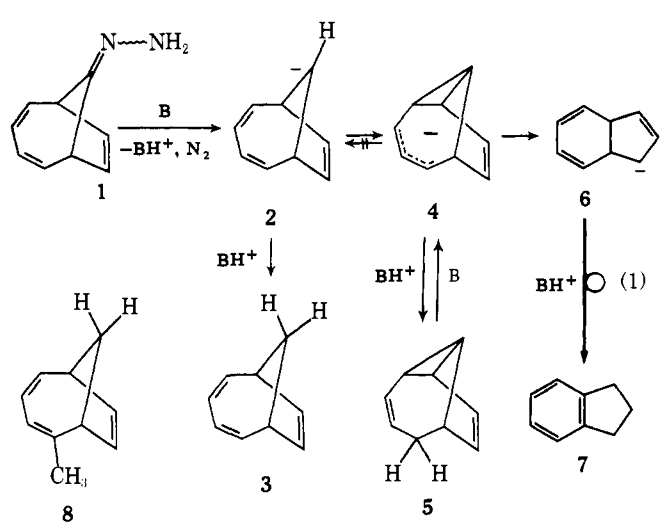
Surprises in Base-Catalyzed Decompositions of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Hydrazone

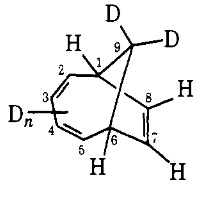
Sir:

Bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone (**1**) is converted by aqueous sodium hydroxide/diethylene glycol at reflux and then at 210 °C to tricyclo[6.1.0.0^{4,9}]nona-2,6-diene (**5**, homosemibullvalene; 95%).[1] This excellent synthesis of **5** is presumed[1] to involve Wolff-Kishner conversion[2] of **1** to the bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (**2**), a supposed bicycloaromatic carbanion,[3] and then the tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-yl anion (**4**, homosemibullvalenyl anion) which protonates to **5** (eq 1). We now communicate further study of decomposition of **1** in the presence of bases because the system is replete with significant surprises.



In the present investigations in which repetition of the prior work[1] was attempted, reaction of **1** with aqueous potassium hydroxide/diethylene glycol at reflux to 210 °C is observed to give bicyclo[4.2.1]nona-2,4,7-triene (**3**, 7%) along with **5** (93%).[4a] In subsequent experiments in which enhanced partitioning of **2** to **3** during decomposition of **1** at lower temperatures was the presumed mechanistic objective, potassium *tert*-butoxide/*tert*-butylalcohol (2 equiv)/dimethyl sulfoxide at 74 °C is found to convert **1** to **3** (>69%)[5] and **5** is not obtained.[4a] When added *tert*-butyl alcohol is absent, however, conversion of **1** to **3** is lowered and 2-methylbicyclo[4.2.1]nona-2,4,7-triene (**8**, 10%) is formed.[4a,6a] During the above reactions of **1**, **5** is not isomerized to **3**;[4b] potassium *tert*-butoxide/*tert*-butyl alcohol/dimethyl sulfoxide however does rearrange **5** slowly to indan (**7**) at 74 °C, presumably via **4**[7] and then the dihydroindenyl anion (**6**). Potassium *tert*-butoxide/*tert*-butyl alcohol/dimethyl sulfoxide does not convert **3** nor **5** to **8** nor effect methylation of **1** prior to development of the reduction processes.

Base-catalyzed decompositions of **1** were then investigated to explain the product differences when the reactions are effected with different bases in dimethyl sulfoxide and in diethylene glycol. Upon determining that potassium *tert*-butoxide (1 equiv)/*tert*-butyl alcohol-*O*-*d* does not exchange deuterium into triene **3** at 74 °C,[8] it was of interest to demonstrate the intermediacy of anion **2** in the reduction systems of **1** by deuterium capture at C_9. Bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone-*N*-d_2[9] containing 20% **1** does react with potassium *tert*-butoxide/*tert*-butyl alcohol-*O*-*d*/dimethyl sulfoxide-d_6 at 74 °C to give bicyclo[4.2.1]nona-2,4,7-triene (**9**) with ~100% deuterium incorporation at c_9 and no deuterium at the bridgehead positions (C_1 and C_6).[6b] It was of great surprise, however, that **9** forms with ~80% exchange (3.20 D) on its C_2–C_5 diene bridge and with none on C_7–C_8.[6b] Similar results are obtained for methyltriene **10** with the minor difference that exchange of its diene hydrogens is ~83% (2.50 D).[4b] Deuterium exchange into the diene bridge of **1** by potassium *tert*-butoxide/*tert*-butyl alcohol-*O*-*d*/dimethyl sulfoxide-d_6 at 74 °C *prior* to the supposed Wolff-Kishner reactions could not be determined because of the rapid disappearance of the hydrazone under the conditions. Bicyclo-



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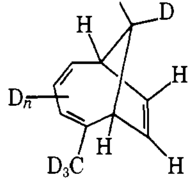

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