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Pyrolysis of Methylsilyl Phenyl Ketones. Formation of Silene in the Decomposition of an Intermediate Silaoxetane

Wataru Ando* and Akira Sekiguchi

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

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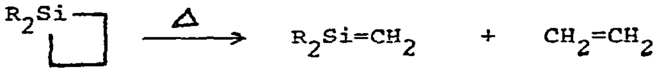
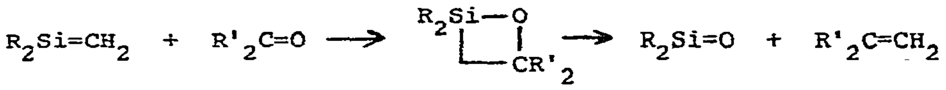
Abstract: Methylsilyl phenyl ketones isomerized thermally to siloxyphenylcarbenes which underwent intramolecular insertion into the C-H bond of a silyl-methyl group to give an unstable silaoxetane intermediate. The thermal decomposition of the silaoxetane proceeded by cleavage of both the silicon-carbon and the silicon-oxygen bonds. The scission of the Si-C bond gave styrene and an Si=O double bonded intermediate which trimerized to a cyclotrisiloxane. On the other hand, the scission of the Si-O bond yielded benzaldehyde and an unstable silene. The intermediacy of the latter was supported by the occurence of a Wittig-type reaction with the starting silyl phenyl ketone or benzophenone.

Intermediates containing a silicon-carbon double bond, silenes, have been postulated frequently to explain some reaction mechanisms[1]. Pyrolyses of silacyclobutanes have been the most convenient method of generation of such short-lived species[2]. Gusel'nikov and Flowers confirmed the existence of such silenes by kinetic studies and chemical trapping experiments in which reactions with water vapor, ammonia, alcohols and a conjugated olefin were used[3]. Barton and Sommer and their coworkers found that copyrolysis of a silacyclobutane with an aldehyde or a ketone yielded a cyclosiloxane and the corresponding new olefin[4]. They suggested silaoxetanes as intermediates in these reactions (eq.1 and 2).



(1)

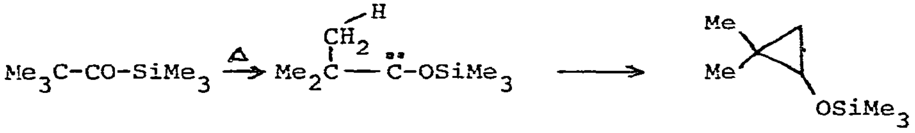


(2)

However, very little is known about the behavior of silaoxetanes. We have begun studies of the preparation of silaoxetanes by intramolecular reactions of siloxycarbenes. Brook had established previously that silyl ketones were photochemically rearranged to siloxycarbenes, which were trapped by a variety of reagents(eq.3)5).

$$R_3SiCOR' \xrightarrow{h\nu} R_3SiO\text{-}\ddot{C}\text{-}R' \xrightarrow{\text{trapping agent}} \text{Product} \qquad (3)$$

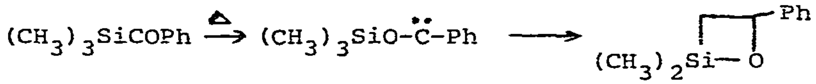
Intramolecular reactions of siloxycarbenes generated photochemically were not observed so far. However, Brook and his coworkers have reported recently that several silyl ketones are rearranged thermally to siloxycarbenes which undergo intramolecular reactions(eq.4 and 5)6)



(4)

$$Me_2CH\text{-}CO\text{-}SiMe_3 \xrightarrow{\Delta} Me_2CH\text{-}\ddot{C}\text{-}OSiMe_3 \longrightarrow Me_2C{=}CHOSiMe_3 \qquad (5)$$

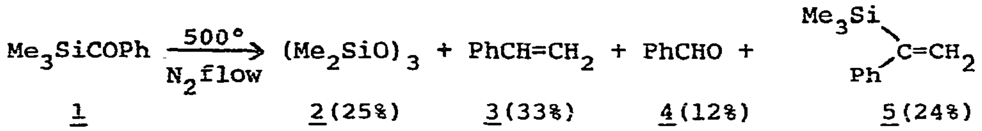
However, these intramolecular reactions of siloxycarbenes are not unusual in that self-insertion into β- or γ-C-H bonds is a well known carbene reaction. A siloxycarbene not having reactive β- or γ-C-H bonds would be expected to produce a silaoxetane by intramolecular insertion into the C-H bond of the silyl-methyl group(eq.6). These considerations led us to study the high temperature pyrolyses of methylsilyl phenyl and methylsilyl naphthyl ketones.



(6)

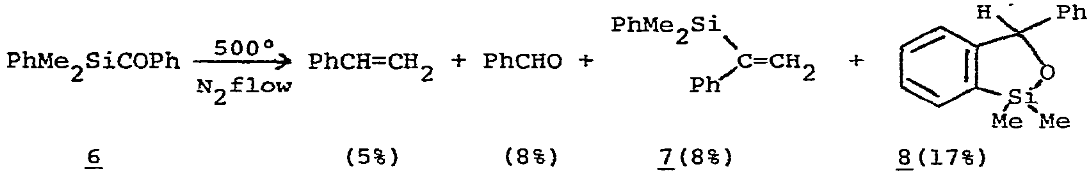
Result and Discussion

The reactions were carried with a stream of nitrogen in a vertical flow system through a 28 cm × 1 cm Pyrex tube packed with Pyrex chips at a nitrogen rate of 30 ml/min. The products were condensed in a trap and analyzed by GLC. Trimethylsilyl phenyl ketone,1, was pyrolyzed at 500°. Separation of the reaction mixture by GLC afforded the products shown in eq.7.



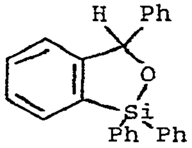
$$\underset{\underline{1}}{Me_3SiCOPh} \xrightarrow[N_2\,flow]{500°} \underset{\underline{2}(25\%)}{(Me_2SiO)_3} + \underset{\underline{3}(33\%)}{PhCH{=}CH_2} + \underset{\underline{4}(12\%)}{PhCHO} + \underset{\underline{5}(24\%)}{(Me_3Si)(Ph)C{=}CH_2} \qquad (7)$$

Pyrolysis of dimethylphenylsilyl phenyl ketone,6, under similar conditions gave analogous products(eq.8).



(8)

1-Sila-2-oxa-cyclopent-4-ene 10 also was obtained in 40% yield in the pyrolysis of triphenylsilyl phenyl ketone,9, at 500°.



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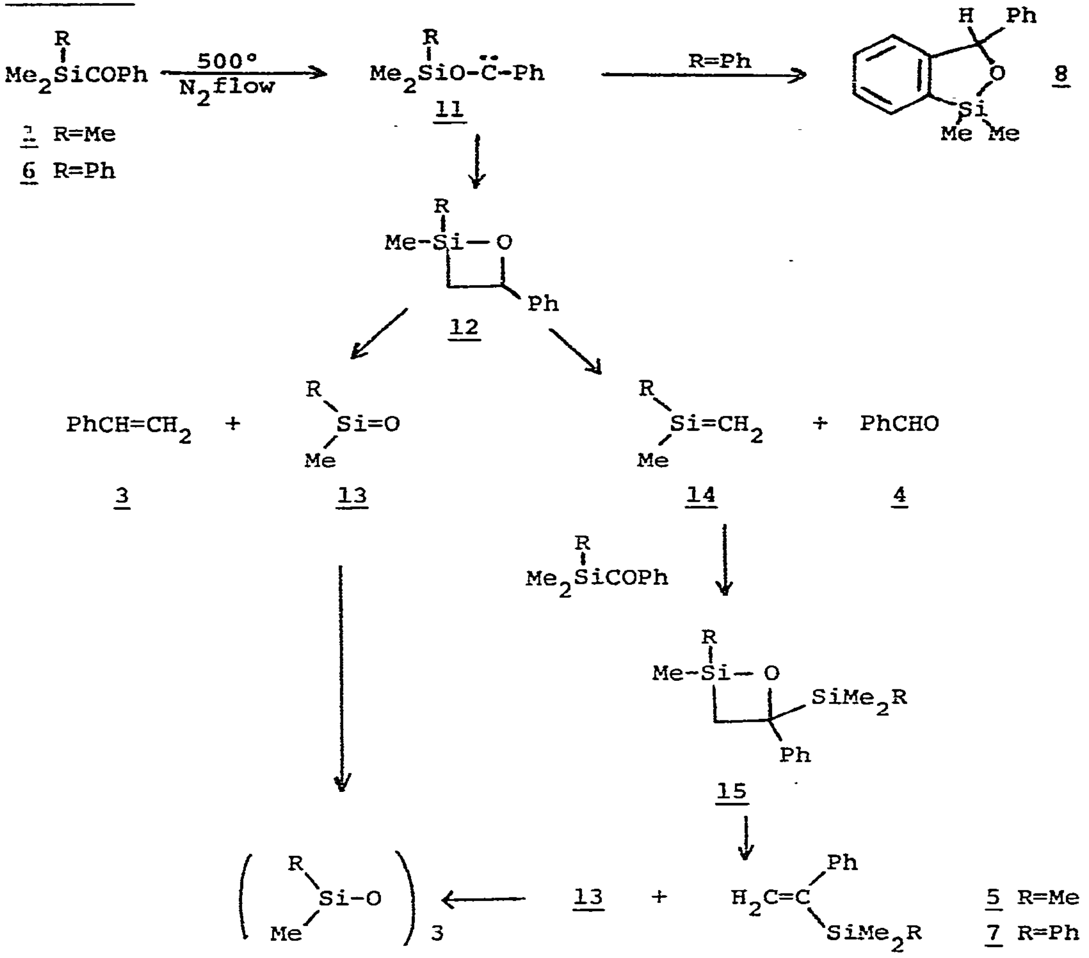
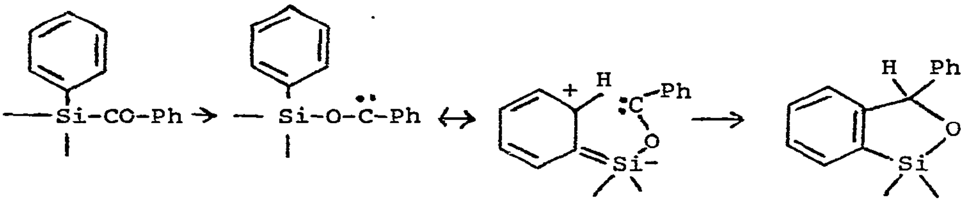
A reasonable pathway for the formation of the products is shown in Scheme 1. The proposed first step is the thermal isomerization of the silyl phenyl ketone to siloxyphenylcarbene 11. Similar thermal rearrangement of a silyl ketone to a siloxycarbene has reported previously by Brook$^{6)}$. Intermediate 12 in the second step is certainly formed by self-insertion of the siloxyphenylcarbene into the proximate C-H bond of the silyl-methyl group. There are not many examples reported of the formation of a four membered ring by intramolecular insertion of a carbene, except for special neighboring group effects, as with α-C-H bonds of an N-alkyl group$^{7)}$.

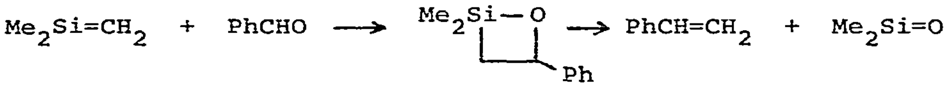
Scheme 1.



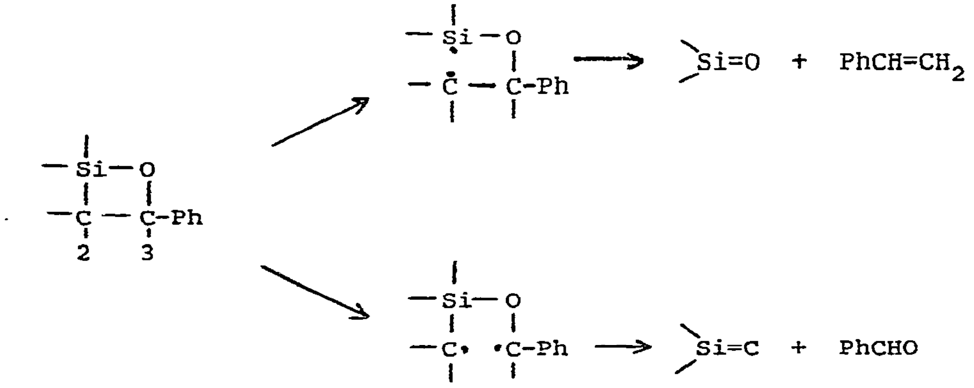
The proposed third step involves cleavage of the Si-C and the Si-O bonds of the silaoxetane. The rupture of the Si-O bond may give benzaldehyde and a silene, 14, which contains a Si=C double bond. The latter may produce α-silyl styrene derivatives 5 and 7 by cleavage of the silaoxetane 15 which is derived from Wittig-type reactions of the silenes with the starting silyl phenyl ketones 1 and 6. The rupture of the Si-C bond in the silaoxetane 12 may give styrene and the Si=O double bond intermediate 13. Intermediates of this type when formed by the decomposition of silaoxetanes, trimerize to produce cyclotrisiloxanes[4]. Final products, 8 and 10, in our reactions apparently are the insertion products of the siloxyphenylcarbene into the C-H bonds of the phenyl groups on silicon (eq.9). Although there are some examples of intramolecular insertions of carbenes into aromatic C-H bond with special conformational requirements8), the insertion into an aromatic C-H bond with probably less steric interaction is quite interesting. It appears that the aromatic ortho hydrogen may be more electrophilic by virtue of the resonance effect of the silicon atom and may be subject to attack by the nucleophilic siloxycarbene, leading to the C-H insertion product.


(9)

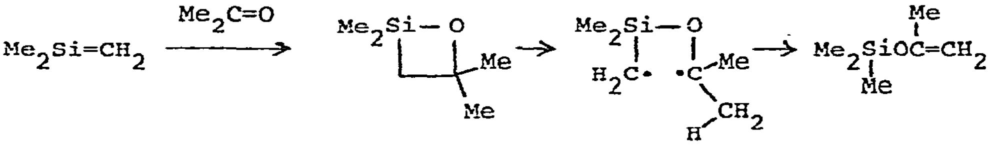
It is reasonable to expect that a siloxycarbene not containing β-or γ-C-H bonds will self-insert into proximate C-H bonds to form a silaoxetane. Barton and Sommer et al. also proposed such silaoxetanes as intermediates in the reactions of silenes with benzaldehyde4) (eq.10).


$$Me_2Si{=}CH_2 + PhCHO \longrightarrow Me_2Si{-}O{-}CH(Ph){-}CH_2 \longrightarrow PhCH{=}CH_2 + Me_2Si{=}O \quad (10)$$

However, they observed only cleavage of Si-C bond in the silaoxetanes as shown. Our results suggest that a silaoxetane derived from intramolecular C-H insertion of a siloxyphenylcarbene undergoes Si-C and Si-O bond cleavage in almost comparable ratio. The product ratio observed provides evidence of competitive Si-C_2 and C_2-C_3 bonds scission as the initial step of the thermal decomposition of the silaoxetane.



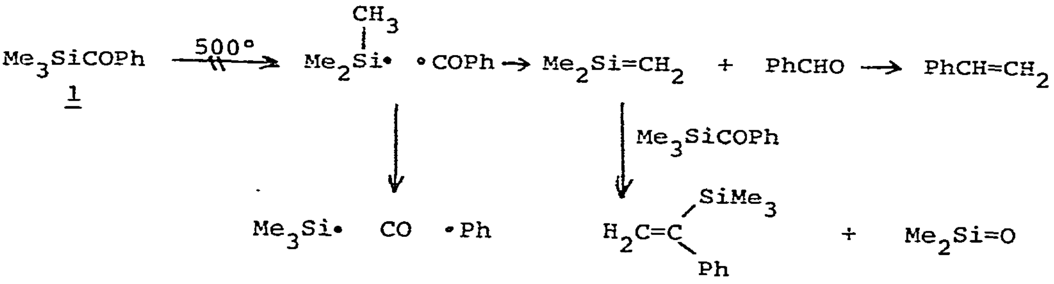
C_2-C_3 Bond scission in a silaoxetane intermediate also was proposed in the copyrolysis of 1,1-dimethyl-1-silacyclobutane with acetone$^{2)}$ (eq.11).


(11)

The silyl vinyl ether might be formed by isomerization of the silaoxetane resulting from 1,5 hydrogen migration in the biradical formed by cleavage of the C-C bond.

Brook and his coworkers suggested that photolyses of silyl ketones in non-polar solvents involved Norrish-type 1 cleavage of the Si-C bond and formation of silyl and acyl radicals$^{9)}$. The possible involvement of silyl and benzoyl radicals also must be considered in our reactions. A reasonable route can be written by assuming homolytic rupture of the Si-C bond followed by hydrogen abstraction from the silyl radical to give benzaldehyde and a silene shown in Scheme 2. Styrene and α-silylstyrene could be formed by a Wittig—type reaction with benzaldehyde and trimethylsilyl phenyl ketone, respectively.

Scheme 2.



We intended to pyrolyze a carbon tetrachloride solution of 1 to trap the silyl and benzoyl radicals. However, the total decomposition of carbon tetrachloride at 500° made this approach unfeasible. A mechanism involving radicals is unlikely since the benzoyl radical would easily decarbonylate before hydrogen abstraction under these conditions. In addition, the formation of 1-sila-2-oxa-cyclopent-4-enes 8 and 10 provides support that the reaction proceeds through a siloxycarbene.

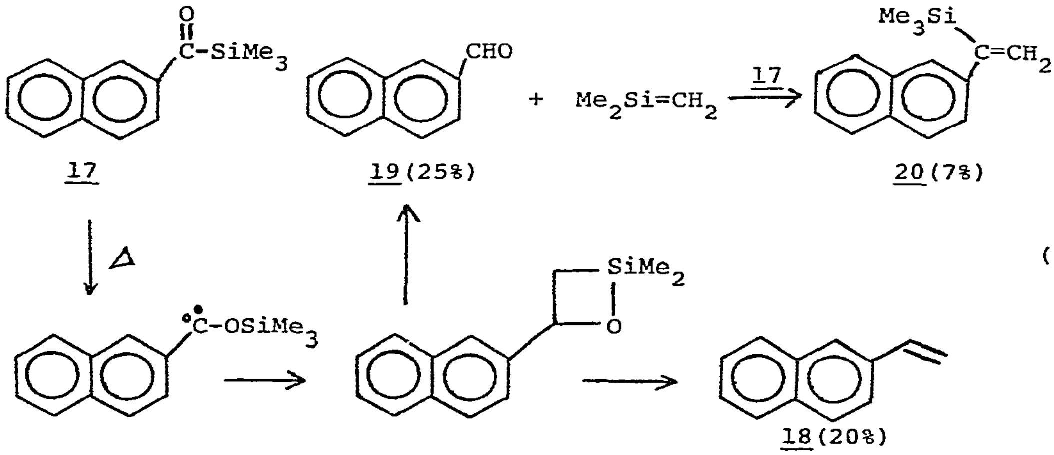
A photochemical reaction of a silyl ketone also was examined. When a benzene solution of 1 was irradiated with a 400W high pressure mercury lamp for 24 hr, almost all of the starting material was recovered. This indicates that the siloxycarbene generated photochemically may revert to 1 5),9) since it has activation energies not enough to insert into the C-H bond leading to the silaoxetane.

Further support for the formation of the silene, 14, comes from the copyrolysis of 1 with an excess of benzophenone(eq.12).

$$\underset{\underline{1}}{Me_3SiCOPh} + Ph_2CO \xrightarrow[N_2\,flow]{500^\circ} \underset{\underline{16}(17\%)}{Ph_2C{=}CH_2} + \underset{(24\%)}{(Me_2SiO)_3} + \underset{(32\%)}{PhCH{=}CH_2} + \underset{(27\%)}{PhCHO} \qquad (12)$$

1,1-Diphenylethylene is formed by cleavage of the silaoxetane derived from the silene and benzophenone. However, an attempt to trap the silene with a conjugated olefin failed. Products formed in the copyrolysis of 1 with 2,3-dimethyl-1,3-butadiene at 500° were identical with those of the pyrolysis of 1. The silene was trapped by 1, not the diene as a result of the higher reactivity of a silene toward a carbonyl compound than toward a diene.

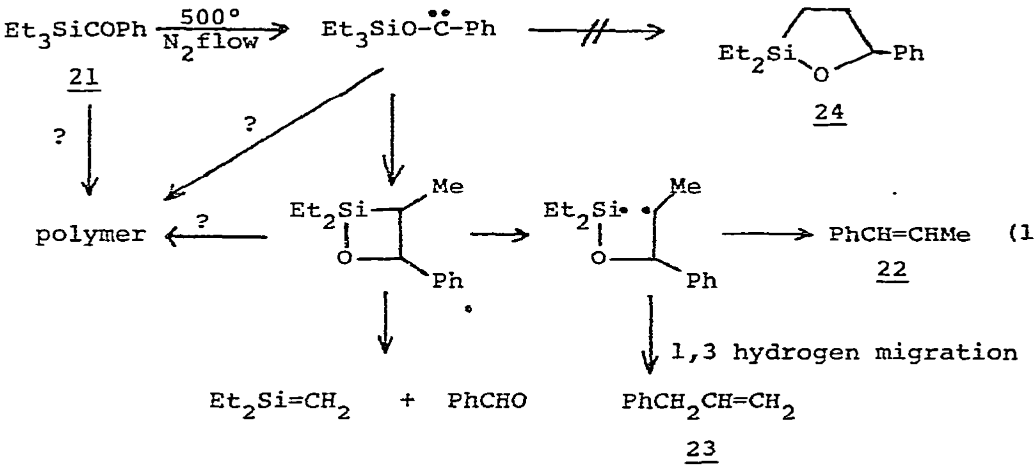
Our studies were extended to similar pyrolyses of trimethylsilyl 2-naphthyl ketone and triethylsilyl phenyl ketone. Gas phase pyrolysis of trimethylsilyl 2-naphthyl ketone, 17, at 500° gave similar products(eq.13).



(13)

Their formations can be rationalized as shown in terms of isomerization of the siloxycarbene to a silaoxetane which then decomposes to give products, 18, 19 and the silene, which again reacts with ketone 17 to produce 20.

Pyrolysis of triethylsilyl phenyl ketone, 21, afforded mainly unidentified polymeric products, which had no carbonyl absorption, but very strong Si-O-C absorption at 1000-1100 cm^{-1}. Some β-methylstyrene (cis,3%, and trans,4%), allylbenzene(4%) and benzaldehyde(4%) also were obtained as minor products. Since β-methylstyrene did not isomerize to allylbenzene under the reaction conditions, the latter may have been formed via cleavage of the Si-C bond of the silaoxetane followed by 1,3 hydrogen migration and C-O cleavage. A long-range insertion product such as 24, which might have been expected from the siloxycarbene, was not obtained(eq.14).



(14)

Experimental

General:

Nmr data were obtained on a Varian A-60D spectrometer. Infrared spectra were obtained using a Hitachi EP-1-G3 spectrometer. Mass spectra were obtained either JEOL JNF-07 or Hitachi RMU-7M spectromete at 70eV. Preparative GLC was accomplished using a Ohkura gas chromatography. Separation was done by 2 m × 5 mm or 30 cm × 5 mm stainless columns with 15% SF-96 and 1.5 m × 5 mm stainless column with 10% Apiezon Grease on Celite 545. Yields were done by GLC.

A known amount of standard sample was added to the reaction mixture and used to calculate yield.

Reagents:

Silyl ketones were prepared by hydrolysis of the corresponding dibromide with silver acetate in water-acetone-ethanol system using the Brook method[10],[11].

$Me_3SiCOPh$: b.p. 61-65°/1mmHg in 97% yield (lit. b.p. 61°/1mmHg[10]);
$PhMe_2SiCOPh$: m.p. 51-53° in 67% yield (lit. m.p. 54-55°[10]);
$Ph_3SiCOPh$: m.p. 97-99° in 88% yield (lit. m.p. 103°[11]);
$2\text{-}C_{10}H_7COSiMe_3$: b.p. 140°/2mmHg in 57% yield (lit. 113°/0.1mmHg[12]);
$Et_3SiCOPh$: b.p. 106-109°/4mmHg in 61% yield. Nmr(CCl_4): δ 0.7-1.2 (15H,m,$SiCH_2CH_3$), 7.2-7.9(5H,m,ArH). Ir(neat): 2950, 2875, 1612(C=O), 1590, 1578 and 1210 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_1Si_1$: C,70.85; H,9.15: Found: C,70.79; H,9.16.

General Pyrolysis Procedure:

The pyrolyses were performed using a vertical tube oven (inside diameter,3 cm; length,33 cm). The pyrolysis apparatus consisted of a 28 cm × 1 cm Pyrex tube packed with Pyrex chips. The upper end of the appratus was equipped with a rubber cap for sample introduction by syringe, and a nitrogen inlet. The sample was dripped in using a one ml syringe with a stream of nitrogen passing through the Pyrex tube at a rate of 30 ml/min. The temperature of the oven was measured by a thermocouple. The residence time of the sample was 1.4 sec. The pyrolysate was trapped in a dry ice-acetone or a liquid nitrogen trap, concentrated, and then separated by preparative GLC.

Pyrolysis of Trimethylsilyl phenyl ketone:

Trimethylsilyl phenyl ketone(0.486g) was pyrolyzed in the gas phase at 500°. One ml of benzene was passed through the reaction tube as a wash after cooling. Separation of the product mixture by GLC gave four products, hexamethylcyclotrisiloxane(25%), styrene(33%), benzaldehyde(12%) and α-trimethylsilylstyrene(24%). Hexamethylcyclotrisiloxane[13], styrene and benzaldehyde were identified by comparison of their nmr, ir spectra and retention times with those of authentic samples. α-Trimethylsilylstyrene[14] was identified by its nmr, ir and mass spectra. Nmr(CCl_4): δ 0.15(9H,s, SiMe), 5.57 and 5.78(2H,d,J=3Hz,$C=CH_2$) and 6.9-7.4(5H,m,ArH). Ir(neat): 3050, 2950, 1490, 1410, 1249 and 932 cm^{-1}. Mass: m/e, M^+ 176(rel. int. 80), 162(15), 161(100), 135(30) and 73(63); high resolution mass: m/e Calcd for $C_{11}H_{16}Si_1$: 176.1021; Found: 176.1009.

Pyrolysis of Dimethylphenylsilyl phenyl ketone:

Dimethylphenylsilyl phenyl ketone(0.956g) was pyrolyzed at 500°. The products were analyzed by GLC, which showed the formation of styrene(5%), benzaldehyde(8%), α-dimethylphenylsilylstyrene(8%) and 1-sila-2-oxa-cyclopent-4-ene 8(17%). α-Dimethylphenylsilylstyrene was identified by its nmr, ir, mass and elemental analyses. Nmr(CCl_4): δ 0.38(6H,s,SiMe), 5.62 and 5.92(2H,d,J=3Hz,$C=CH_2$) and 6.8-7.6(10H, m,ArH). Ir(neat): 3055, 2945, 1427, 1249, 1110 and 934 cm^{-1}. Anal. Calcd for $C_{16}H_{18}Si_1$: C,80.29; H,7.19: Found: C,80.02; H,6.99. 1-Sila-2-oxa-cyclopent-4-ene 8 was identified by its nmr, ir, mass ans elemental analyses. Nmr(CCl_4): δ 0.42(3H,s,SiMe), 0.48(3H,s,SiMe), 6.08(1H,s,Ar-CH-O) and 6.8-7.7(9H,m,ArH). Ir(neat): 3045, 1590, 1490, 1250, 1135, 1040(Si-O-C) and 1015 cm^{-1}(Si-O-C). Mass: m/e, M^+ 240(100), 239(88), 225(43), 165(30) and 105(18); high resolution mass: m/e Calcd for $C_{15}H_{16}O_1Si_1$: 240.0970; Found: 240.0945. Anal. Calcd.: C,74.95; H,6.71: Found: C,74.72; H,6.85.

Pyrolysis of Triphenylsilyl phenyl ketone:

A benzene solution of triphenylsilyl phenyl ketone(0.550g) was pyrolyzed at 500°. 1-Sila-2-oxa-cyclopent-4-ene 10 was obtained by GLC as resinous liquid in 40% yield. Nmr(CCl_4): δ 6.27(1H,s,Ar-CH-O) and 6.9-7.9(19H,m,ArH). Ir(CCl_4): 3060, 1590, 1430, 1267, 1185, 1122 and 1010 cm^{-1}(Si-O-C); high resolution mass: m/e Calcd for $C_{25}H_{20}O_1Si_1$: 364.1283; Found: 364.1296. Anal. Calcd.: C,82.38; H,5.53: Found: C,82.12; H,5.37.

Copyrolyses of Trimethylsilyl phenyl ketone with Benzophenone and 2,3-Dimethyl-1,3-butadiene:

A mixture of 0.435g(2.44m mol) of trimethylsilyl phenyl ketone and 2.54g(14m mol) of benzophenone was pyrolyzed at 500°. 1,1-Diphenylethylene was obtained in 17% yield together with hexamethylcyclotrisiloxane(14%), styrene(32%) and benzaldehyde(27%). 1,1-Diphenylethylene was identified by comparison of its nmr, ir spectr and retention time with those of an authentic sample.

Copyrolysis of trimethylsily phenyl ketone with an excess of 2,3-dimethyl-1,3-butadiene also was done at 500°. Products and yields were identical with those of the pyrolysis of trimethylsilyl phenyl ketone.

Pyrolysis of Trimethylsilyl 2-naphthyl ketone:

Trimethylsilyl 2-naphthyl ketone(0.22g) was pyrolyzed at 500°. 2-Vinylnaphthalene(20%), 2-naphthaldehyde(25%) and 1-trimethylsilyl-1-(2-naphthyl)ethylene(7%) were obtained by GLC. 2-Vinylnaphthalene (m.p. 61-62°, lit.[15] 60-62°) and 2-naphthaldehyde (m.p. 58-60°, lit.[16] 59-62°) were identified by comparison of their nmr and ir spectra with those of authentic samples. 1-Trimethylsilyl-1-(2-naphthyl)-ethylene was identified by its nmr, ir and mass spectra. Nmr(CCl_4): τ 0.25(9H,s,SiMe), 5.63 and 5.87(2H,d,J=3Hz,$C=CH_2$) and 7.1-8.1(7H, m,Np-H). Ir(CCl_4): 3050, 2950, 1250, 930 and 890 cm^{-1}. Mass: m/e, M^+ 226(61), 211(27), 153(23), 152(52) and 73(100); high resolution mass: m/e Calcd for $C_{15}H_{18}Si_1$: 226.1178; Found: 226.1181. The product has only been identified by the above spectroscopic means because of the small yield.

Pyrolysis of Triethylsilyl phenyl ketone:

Triethylsilyl phenyl ketone(0.569g) was pyrolyzed at 500°. Four products were found by GLC; β-methylstyrene(cis,3%, and trans,4%), allylbenzene(4%) and benzaldehyde(4%). The major product was an unidentified polymeric material which had strong Si-O-C absorption at 1000-1100 cm^{-1}. β-Methylstyrene did not isomerize to allylbenzene under the reaction conditions.

Photolysis of Trimethylsilyl phenyl ketone in Benzene:

Trimethylsilyl phenyl ketone(0.199g) and 3 ml of benzene was placed in 8 mm × 30 cm Pyrex tube, and then the mixture was irradiated with a 400W high pressure mercury lamp for 24 hr. GLC showed the presence of trimethylsilyl phenyl ketone(86%) and benzaldehyde(9%).

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