Copyrolysis of 1,1-Dimethyl-2-phenyl-1-silacyclobutane and Acrolein

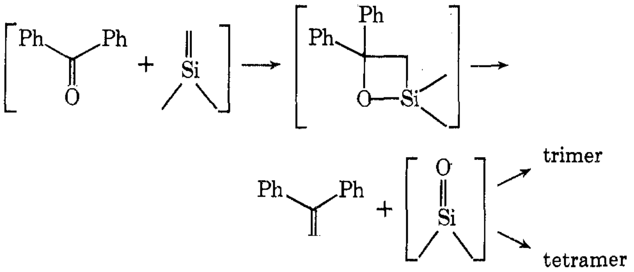
Phillip B. Valkovich and William P. Weber*

Department of Chemistry, University of Southern California, Los Angeles, California 90007

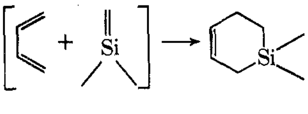
Received July 12, 1974

Copyrolysis at 500° in the gas phase of 1,1-dimethyl-2-phenyl-1-silacyclobutane and acrolein yields hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, 1,2-dihydronaphthalene, naphthalene, and 1,1-dimethyl-1-sila-2-oxa-6-phenyl-3-cyclohexene. 1,2-Dihydronaphthalene was shown to be formed from *trans*-1-phenyl-1,3-butadiene under the reaction conditions. Formation of these products can be accounted for in terms of competing [2 + 2] and [2 + 4] cycloaddition reactions between acrolein and a reactive intermediate [$(CH_3)_2Si{=}HC_6H_5$] possessing a carbon–silicon double bond.

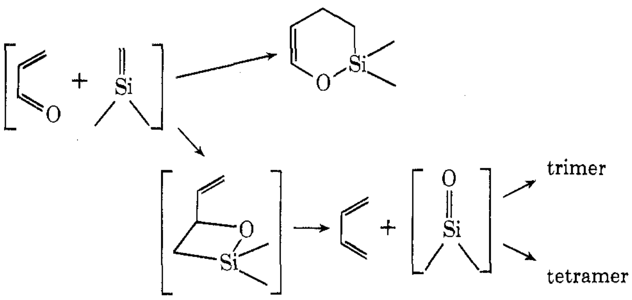
There has been considerable recent interest in the chemical reactions of intermediates possessing a formal carbon–silicon double bond.[1-6] These intermediates may be generated by pyrolysis of silacyclobutanes.[7-10] Photolysis of 1,1-diphenyl-1-silacyclobutane[11] or pentaphenylmethyldisilane[12] also leads to reactive intermediates possessing a formal carbon–silicon double bond. Several pieces of evidence suggest that carbon–silicon double bonded intermediates have significant zwitterionic or ylide character in which the silyl center is positively charged while the carbon is negatively charged. Thus pyrolytic fragmentation of 1,1-dimethyl-1-silacyclobutane (I) in the gas phase yields ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane, the head-to-tail dimer of two silicon–carbon double bonded intermediates.[7-9] This exclusive formation of head-to-tail dimer can be economically rationalized in terms of the polar nature of the intermediates. Copyrolysis of I in the presence of the nonenolizable ketone benzophenone leads to 1,1-diphenylethylene and hexamethylcyclotrisiloxane (trimer) and octamethylcyclotetrasiloxane (tetramer).[2,5] Formation of these products has been explained by the following reaction sequence. A [2 + 2] cycloaddition reaction between the carbon–silicon double bonded intermediate and the ketone yields an unstable silaoxetane which thermally decomposes to yield an olefin and a silanone [$(CH_3)_2Si{=}O$] which undergoes cyclic oligomerization to yield the stable trimer and tetramer observed.[4] Analogous [2 + 2] cycloaddition reactions between carbon–silicon double bonded intermediates and added alkenes to yield new silacyclobutanes[9,13] as well as with imines to yield alkenes and cyclodisilazane[6] have been observed.



On the other hand, copyrolysis of I with dienes such as 1,3-butadiene yields 1,1-dimethyl-1-sila-3-cyclohexene and ethylene. Formation of this product can be explained by a [2 + 4] cycloaddition reaction between a carbon–silicon double bonded intermediate and the diene.[14,15] Similar [2 + 4] cycloaddition reactions have been observed with isoprene and 2,3-dimethyl-1,3-butadiene.



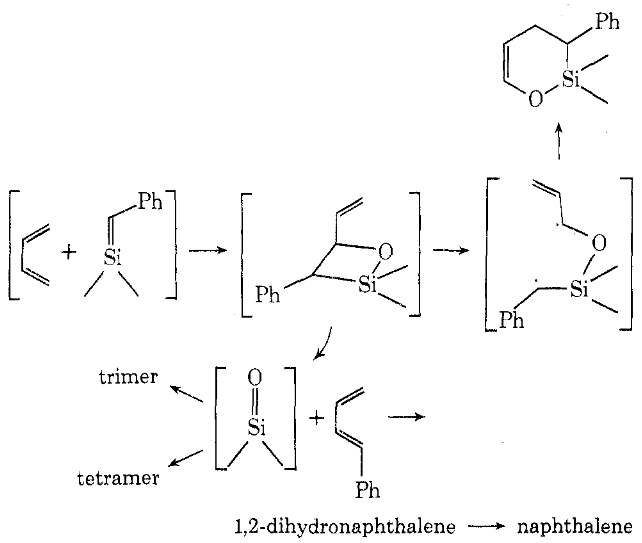
We were interested in the reaction of carbon–silicon double bonded intermediates with nonenolizable α,β-unsaturated aldehydes since both [2 + 2] and [2 + 4] cycloaddition pathways are possible. Only a few cycloaddition reactions are known in which [2 + 2] and [2 + 4] cycloaddition pathways are competitive.[16-20]



The following products were isolated from the copyrolysis of 1,1-dimethyl-2-phenyl-1-silacyclobutane and a tenfold excess of acrolein at 500° and atmospheric pressure in a flow pyrolysis system with purified nitrogen as the carrier gas: 1,2-dihydronaphthalene, naphthalene, trimer, tetramer, and 1,1-dimethyl-1-sila-2-oxa-6-phenyl-3-cyclohexene. Formation of these products may be rationalized in terms of competing [2 + 2] and [2 + 4] cycloaddition reactions between a phenyl-substituted carbon–silicon double bonded intermediate[21] and acrolein. 1,2-Dihydronaphthalene, naphthalene, trimer, and tetramer may be formed *via* an initial [2 + 2] cycloaddition reaction. Thus 1,2-dihydronaphthalene was shown in control experiments to be formed under the reaction conditions from *trans*-1-phenyl-1,3-butadiene, an expected [2 + 2] cycloaddition product. Naphthalene has been shown to be the major pyrolysis product of *trans*-1-phenyl-1,3-butadiene under slightly more stringent conditions (550°),[22] while 1,2-dihydronaphthalene has been converted into naphthalene under more vigorous conditions.[23] On the other hand, formation of 1,1-dimethyl-1-sila-2-oxa-6-phenyl-3-cyclohexene may be economically accounted for by a direct [2 + 4] cycloaddition reaction. However, an alternative possibility exists, namely that the initial silaoxetane adduct formed by [2 + 2] cycloaddition may undergo scission of a carbon–carbon bond to yield an allylic and a benzylic radical pair which recombine to yield 1,1-dimethyl-1-sila-2-oxa-6-phenyl-3-cyclohexene in competition with fragmentation of the siloxetane to yield *trans*-1-phenyl-1,3-butadiene and dimethylsilanone.

The ratio of 1,1-dimethyl-1-sila-2-oxa-6-phenyl-3-cyclohexene to 1,2-dihydronaphthalene and naphthalene is roughly 1:4.

While the system is intriguing, a decision between the two possible mechanisms is not at this time possible.



Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 337 spectrometer and were calibrated against known bands in a polystyrene film. Nmr spectra were recorded on a Varian T-60 spectrometer with methylene chloride (δ 5.28) as internal standard. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer. Conditions used in determination of mass spectra were source temperature 150°; solid inlet 50°; ionizing voltage 70 eV; filament emission 70 μA; target current 50 μA. Vapor phase chromatography was carried out on a Hewlett-Packard F&M 700. Microanalysis was performed by Elek Microanalytical Laboratories. Melting points are uncorrected.

1,1-Dimethyl-2-phenyl-1-silacyclobutane was prepared from allylbenzene and dimethylchlorosilane in 50% yield by the method of Valkovich, *et al.*[21]

Copyrolysis of 1,1-Dimethyl-2-phenyl-1-silacyclobutane (II) and Acrolein. The pyrolysis was performed using a vertical tube oven. The pyrolysis tube consisted of a 30-cm long Pyrex glass tube (12.5 mm o.d., 9 mm i.d.) packed with 1-cm long pieces of 3-mm Pyrex tubing. Due to a premature reaction upon standing at room temperature of acrolein and II leading to polymeric material, it was necessary to mix the two together immediately prior to pyrolysis. This was accomplished by use of the following apparatus. A 25-ml, three-neck, pear-shaped flask was adapted by placing a stopcock at the bottom, the exit of which was connected to the top of the pyrolysis tube. In two of the three necks of the flask were placed pressure equalizing addition funnels. A nitrogen inlet was placed in the third neck. Nitrogen also entered the pyrolysis tube just before the oven, so that there was a continuous flow of nitrogen in the pyrolysis tube even when the stopcock of the mixing flask was closed. The exit of the pyrolysis tube was connected to a 50-ml two-neck flask which was immersed in a Dry Ice–acetone bath. The second neck of the flask was connected to another Dry Ice–acetone trap. The nitrogen flow rate was adjusted to 0.5 ml/sec. The column was allowed to reach a temperature of 500°. The entire apparatus was flame dried. At this point 6.38 g of freshly distilled acrolein was placed in one addition funnel, while 2.0 g of II was placed in the other. The pyrolysis was carried out as follows. One drop of II was added to 3–4 drops of acrolein in the mixing flask. This mixture was added all at once to the pyrolysis tube. This procedure was repeated. The addition was complete within 0.5 hr. The apparatus was allowed to cool, and the pyrolysis tube was rinsed with 1 ml of benzene. The material collected in the two traps was purified as follows. Benzene and excess acrolein were removed by distillation at atmospheric pressure. The residue, 2.63 g was purified by bulb-to-bulb distillation at 0.1 mm. This material (2.43 g) was separated by preparative glpc on a ¼ in. × 4 ft 20% SE-30 on Chromosorb P column at 120°. The following compounds were isolated and identified. A number of additional components were present in very small amounts. All yields are based on recovered starting material generally about 40%.

Hexamethylcyclotrisiloxane: 49.9% yield; properties (mp 64°; ir, and glpc retention time) identical with those of an authentic sample.[24]

Octamethylcyclotetrasiloxane: 7.7% yield; properties (ir and glpc retention time) identical with those of an authentic sample.[24]

A mixture of 1,2-dihydronaphthalene and naphthalene was next collected. This mixture was separated on a ¼ in. × 10 ft 20% DC-QF-1 on Chromosorb W column at 110°. The ratio of 1,2-dihydronaphthalene to naphthalene was 14:1.

Naphthalene: 4% yield, mp 80–81° (lit. mp 80.5°);[25] its nmr was identical with that of an authentic sample.

1,2-Dihydronaphthalene: 58% yield; its ir was identical with that of authentic 1,2-dihydronaphthalene;[26] nmr δ 2.66 (m, 4 H), 6.03 (m, 1 H), 6.51 (m, 1 H), 7.12 (m, 4 H).

1,1-Dimethyl-1-sila-2-oxa-6-phenyl-3-cyclohexene. Final purification was accomplished by preparative glpc on a ¼ in. × 10 ft Silar 5 CP on Gas-Chrom Q column at 110°: 16.6% yield; mp 40–41°; nmr (CCl_4) δ 0.16 (s, 3 H), 0.32 (s, 3 H), 2.60 (m, 3 H), 4.82 (m, 1 H), 6.42 (d, 1 H, J = 6.2 Hz), 7.27 (m, 5 H). The following decoupling experiments were performed. Irradiation at δ 2.6 caused the multiplet at δ 4.82 to collapse to a doublet, J = 6 Hz, while irradiation at δ 4.82 caused the doublet at 6.42 to collapse to a singlet: ir (film) 1254 ($Si{-}CH_3$), 1071, 1081, and 1125 (Si–O and C–O, and 1635 cm^{-1} (C = C); mass spectrum parent at m/e 204 (44.6%).

Anal. Calcd for $C_{12}H_{16}SiO$: C, 70.53; H, 7.83. Found C, 70.45; H, 7.89.

***trans*-1-Phenyl-1,3-butadiene** was prepared by the method of Grummitt and Becker.[27] It was pyrolyzed at 500° using the apparatus previously described. 1,2-Dihydronaphthalene and naphthalene were obtained in 81% yield in a ratio of 8:1.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research Grant No. 73-2424.

Registry No.—II, 52500-06-8; acrolein, 107-02-8; hexamethylcyclotrisiloxane, 541-05-9; octamethylcyclotetrasiloxane, 556-67-2; naphthalene, 91-20-3; 1,2-dihydronaphthalene, 447-53-0; 1,1-dimethyl-1-sila-2-oxa-6-phenyl-3-cyclohexene, 53210-17-6; *trans*-1-phenyl-1,3-butadiene, 16939-57-4.

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