Synthesis and Reactions of Silacyclopropene or 1-Sila-1,2-Propadiene†

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This brief review deals with the thermal or photochemical synthesis and reactions of silacyclopropene or 1-sila-1,2-propadiene. The novel intramolecular reactions of silacyclopropene or 1-sila-1,2-propadiene are also discussed.

key words: silacyclopropene, 1-sila-1,2-propadiene, intramolecular reaction

INTRODUCTION

The chemical and physical properties of silacyclopropene or 1-sila-1,2-propadiene are attractive subjects from the mechanistic and synthetic viewpoints. Most of silacyclopropene or 1-sila-1,2-propadiene are extremely unstable toward atmospheric oxygen and moisture and they are trapped by acetone or methanol. Silacyclopropenes also react with unsaturated functional groups to give five-membered cyclic organosilicon products. In this review, I will briefly discuss the synthesis and reactions of silacyclopropene or 1-sila-1,2-propadiene including my own studies.

SYNTHESIS OF SILACYCLOPROPENE OR 1-SILA-1,2-PROPADIENE

Seyferth et al. reported the reaction of hexamethylsilirane, which was used as dimethylsilylene source, and bis(trimethylsilyl) acetylene gives 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene, a stable silacyclopropene and tetramethylethylene [1,2].

Subsequent addition of alcohol to the reaction mixture resulted in the formation of the silanol.

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Photochemical synthesis of silacyclopropene or 1-sila-1,2-propadiene was independently reported by Ishikawa [3,4] and Sakurai [5]. Irradiation of (pentamethyldisilanyl)phenylacetylene in the presence of methanol or acetone as trapping agents gives methanol or acetone addition product to silacyclopropene or 1-sila-1,2-propadiene intermediates.

Ishikawa et al. also reported [6] that the photolysis of 1,1-dimesityl-1-trimethylsilylethynyltrimethyldisilane and 1,1-dimesityl-1-phenylethynyldisilane gives stable silacyclopropenes, 1,1-dimesityl-2,3-bis(trimethylsilyl)-1-silacyclopropene and 1,1-dimesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene, respectively, which are not affected by atmospheric oxygen, moisture and alcohols at room temperature.

Shim and Park have recently found that the photolysis of 1-(ortho-substituted-phenyl)-2-pentamethyldisilanylethylene with methanol or acetone affords methanol or acetone addition photoproducts to silacyclopropene or 1-sila-1,2-propadiene intermediate [7-9].
Shim et al. also reported the photolysis of 1-aryl-4-(pentamethylidisilanyl)-1,3-butadiynes which are a very interesting class of organosilicon compounds containing both electron-withdrawing and electron-donating groups in the aryl rings [10-12]. Irradiation of 1-aryl-4-(pentamethylidisilanyl)-1,3-butadiynes in methanol gives the photoaddition products via silacyclopene intermediates.

And, irradiation of 1-aryl-4-(pentamethylidisilanyl)-1,3-butadiynes with acetone yields site specific and regioselective 1:1 adducts via silacyclopene intermediates.

Shim and Park reported the photochemistry of 1,4-bis(pentamethylidisilanyl)-butadiyne [13], 1,4-bis(pentamethylidisilanyl-ethynyl)benzene [14], and 4,4′-bis(pentamethylidisilanyl-ethynyl)biphenyl [15] expecting formation of two successive silacyclopene intermediates.

Irradiation of 1,4-bis(pentamethylidisilanyl)-butadiyne in methanol yields two 1:1 photoaddition products and one 1:2 photoadduct via silacyclopene intermediates [13].

Irradiation of 1,4-bis(pentamethylidisilanyl)lethynyl)benzene in methanol yields two 1:1 photoaddition products via silacyclopene intermediates [14].

Irradiation of 4,4′-bis(pentamethylidisilanyllethynyl)biphenyl in the presence of acetone affords regioselective photoadducts via silacyclopene intermediates [15].

**REACTIONS OF SILACYCLOPROPENE OR 1-SILA-1,2-PROPADIENE**

Ishikawa and co-workers found that the photolysis of 1-(trimethylsilyl-ethynyl)-1,1-diphenyl-2,2,2-trimethylidisilane in the absence of a trapping agent afforded 1,1,2,2-tetraphenyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane via 1-sila-1,2-propadiene intermediate [16].
Seyferth et al. have reported that the silacyclopene 1,1-dimethyl-2,3-bis(trimethylsilyl)disilirene reacts with aldehydes, ketones, styrenes, conjugated terminal acetylenes, benzynes, terminal 1,3-dienes, and a conjugated imine to give five-membered cyclic organosilicon products in which the C=O, C=C, C=N, or C≡N bonds of the organic reactants have inserted into the Si-C bond of the silirene ring [17].

Ishikawa et al. found that the thermolysis of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopene afforded 1-mesityl-3,3-dimethyl-4-phenyl-5-(trimethylsilyl)-1,3-disilacyclo-4-pentene and 1-mesityl-1,3-bis(trimethylsilyl)-1-sila-3-indene [18,19].

Ishikawa et al. have also reported that the nickel- or palladium-catalyzed reaction of silacycloprenes. The reaction of 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopene with a phenylsilylacetylene in the presence of NiCl₂(P埃尔₃)₂ afforded the 1-silacyclopenta-2,4-diene [20]. The reaction of 3-(trimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopene with a catalytic amount of dichlorobis(triethylphosphine)palladium (II) gives 1,4-disilacyclohexa-2,5-diene with high regioselectivity [21].

Although the chemical properties of silacyclopene or 1-sila-1,2-propadiene have been extensively investigated, relatively few examples have been reported on the intramolecular photoreaction of the system.

Shim and Park have recently reported novel photoinduced intramolecular cyclization or cycloaddition reactions of 1-(o-alkoxyphenyl)-2-pentamethyldisilanyl ethyne [22,23,24] and 1-(o-alkoxymethylphenyl)-2-pentamethyldisilanyl ethyne [25].

Park have very recently reported that the photolysis of 1-o-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne [26] and 1-o-acetylamino-2-(pentamethyldisilanyl)ethyne [27] provides novel intramolecular cycloaddition products via silacyclopene or 1-sila-1,2-propadiene, respectively.

REFERENCES


