

REVIEW

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.

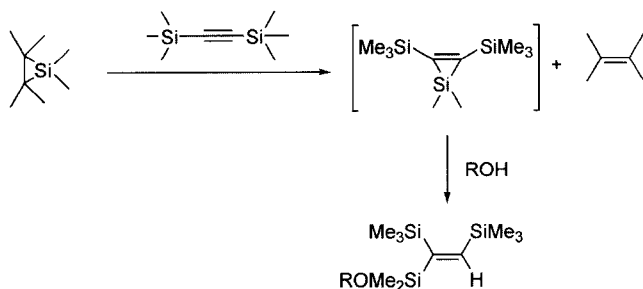
key words: silacyclopropene, 1-sila-1,2-propadiene, intramolecular reaction

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.

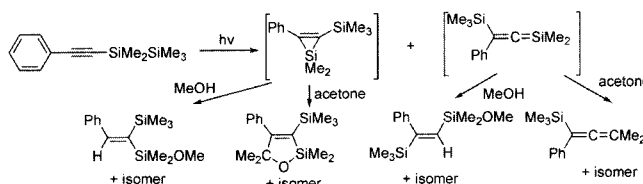
[†] This paper is dedicated to Prof. Sang Chul Shim on the occasion of his 65th birthday.

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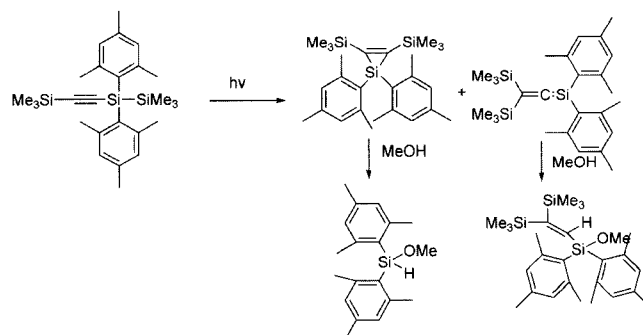
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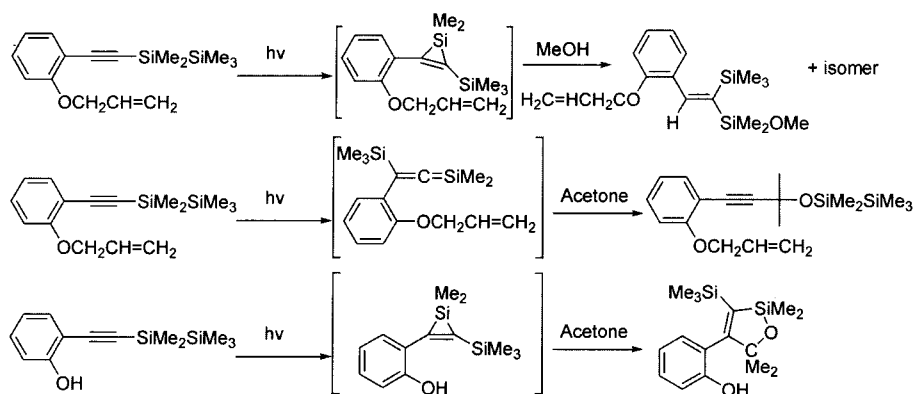
Photochemical synthesis of silacyclopropene or 1-sila-1,2-propadiene was independently reported by Ishikawa [3,4] and Sakurai [5]. Irradiation of (pentamethyldisilanyl)phenylacetylene in the presence of methanol or acetone as trapping agents gives methanol or acetone addition product to silacyclopropene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



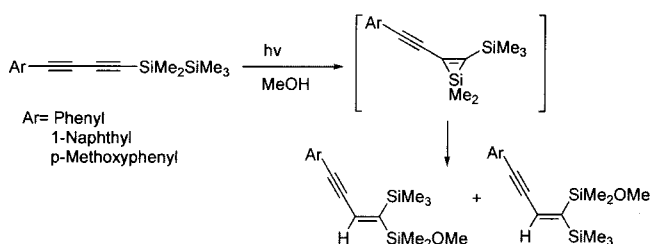
Ishikawa *et al.* also reported [6] that the photolysis of 1,1-dimesityl-1-trimethylsilylethynyltrimethylsilyl silane and 1,1-dimesityl-1-phenylethynyl disilane gives stable silacyclopropenes, 1,1-dimesityl-2,3-bis(trimethylsilyl)-1-silacyclopropene and 1,1-dimesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene,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



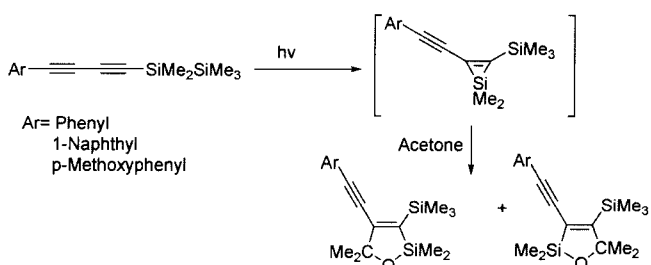
Shim and Park have recently found that the photolysis of 1-(ortho-substituted-phenyl)-2-pentamethyldisilanylethyne with methanol or acetone affords methanol or acetone addition photoproducts to silacyclopropene or 1-sila-1,2-propadiene intermediate [7-9].



Shim *et al.* also reported the photolysis of 1-aryl-4-(pentamethyldisilanyl)-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-(pentamethyldisilanyl)-1,3-butadiynes in methanol gives the photoaddition products via silacyclopropene intermediates.



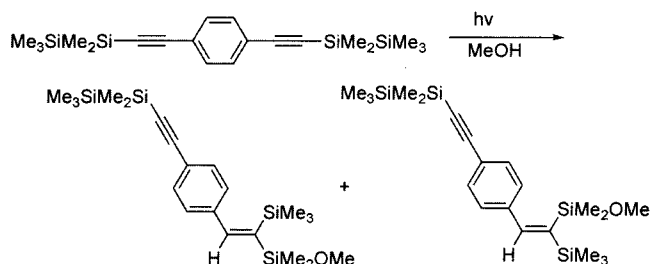
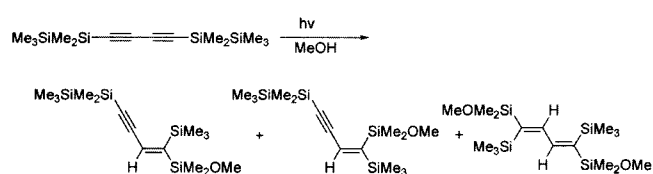
And, irradiation of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes with acetone yields site specific and regioselective 1:1 adducts via silacyclopropene intermediates.



Shim and Park reported the photochemistry of 1,4-bis(pentamethyldisilanyl)-butadiyne [13], 1,4-bis(pentamethyldisilanylethynyl)benzene [14], and 4,4'-bis(pentamethyldisilanylethynyl)biphenyl [15] expecting formation of two successive silacyclopropene intermediates.

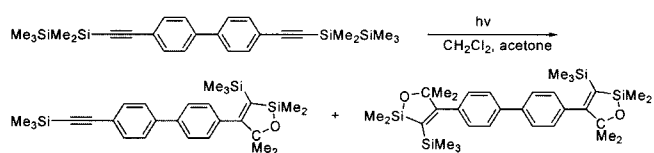
Irradiation of 1,4-bis(pentamethyldisilanyl)-butadiyne in methanol yields two 1:1 photoaddition products and one 1:2 photoadduct via silacyclopropene intermediates [13].

Irradiation of 1,4-bis(pentamethyldisilanylethynyl)benzene in methanol yields two 1:1 photoaddition products via



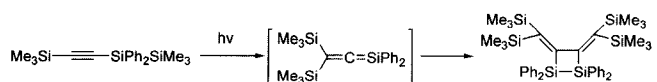
silacyclopropene intermediates [14].

Irradiation of 4,4'-bis(pentamethyldisilanylethynyl)biphenyl in the presence of acetone affords regioselective photoadducts via silacyclopropene intermediates [15].

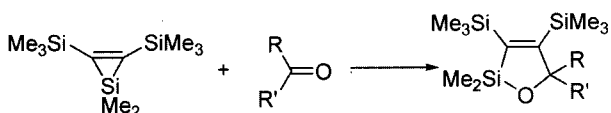


REACTIONS OF SILACYCLOPROPENE OR 1-SILA-1,2-PROPADIENE

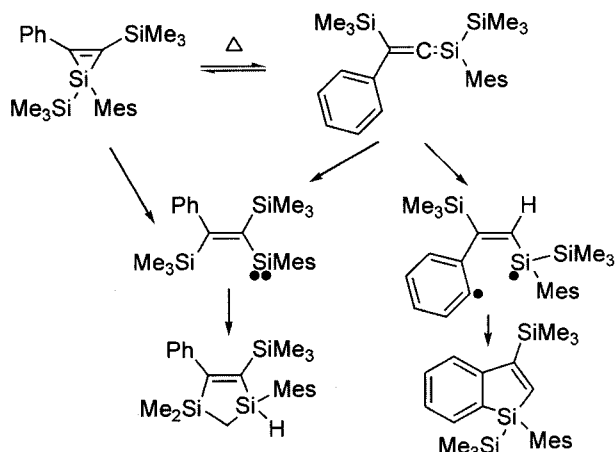
Ishikawa and co-workers found that the photolysis of 1-(trimethylsilylethynyl)-1,1-diphenyl-2,2,2-trimethyldisilane in the absence of a trapping agent afforded 1,1,2,2-tetraphenyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane via 1-sila-1,2-propadiene intermediate [16].



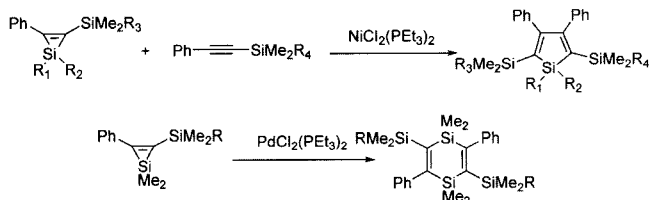
Seyferth *et al.* have reported that the silacyclopropene 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene reacts with aldehydes, ketones, styrenes, conjugated terminal acetylenes, benzyne, terminal 1,3-dienes, and a conjugated imine to give five-membered cyclic organosilicon products in which the C=O, C=C, C≡C, 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-silacyclopropene afforded 1-mesityl-3,3-dimethyl-4-phenyl-5-(trimethylsilyl)-1,3-disilacyclo-4-pentene and 1-mesityl-1,3-bis(trimethylsilyl)-1-silaindene [18,19].



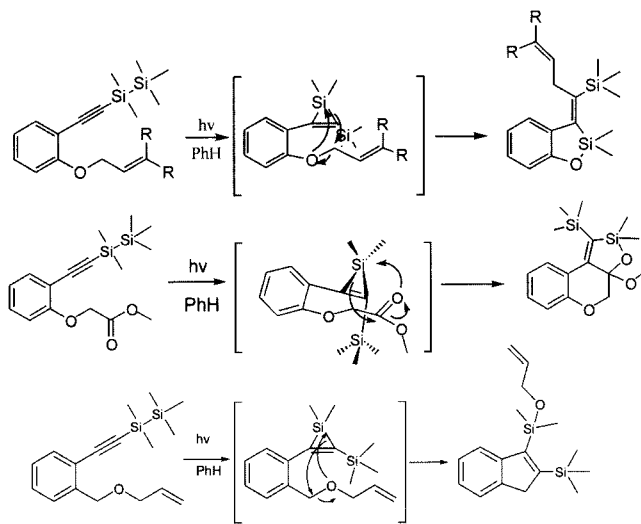
Ishikawa *et al.* have also reported that the nickel-, or palladium-catalyzed reaction of silacyclopropenes. The reaction of 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene with a phenylsilylacetylene in the presence of $\text{NiCl}_2(\text{PEt}_3)_2$ afforded the 1-silacyclopenta-2,4-diene [20]. The reaction of 3-(trimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopropene with a catalytic amount of dichlorobis(triethylphosphine)palladium (II) gives 1,4-disilacyclohexa-2,5-diene with high regioselectivity [21].



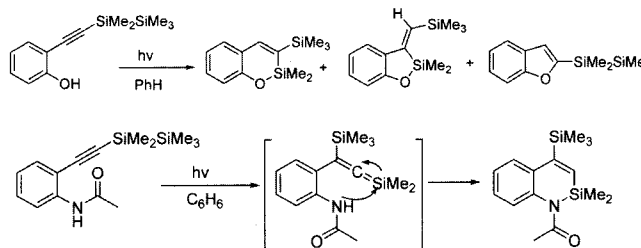
Although the chemical properties of silacyclopropene or 1-sila-1,2-propadiene have been extensively investigated, relatively few examples have been reported on the intramolecular photo-

reaction 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 silacyclopropene or 1-sila-1,2-propadiene, respectively.



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