

# Novel preparation method and synthetic applications of cyclopropyl trimethylsilyl ketones

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# 1988 Fiscal Year Final Research Report Summary

## Novel preparation method and synthetic applications of cyclopropyl trimethylsilyl ketones

Research Project

### Project/Area Number

62550627

### Research Category

Grant-in-Aid for General Scientific Research (C)

### Allocation Type

Single-year Grants

### Research Field

Synthetic chemistry

### Research Institution

Kanazawa University

### Principal Investigator

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### Project Period (FY)

1987 – 1988

### Keywords

Cyclopropyl silyl ketones / 1-Silyl-1-cyclopropylalkenes / Siloxyalkenes / -Ketosilanes / Alkylidenephosphoranes / オキソスルホニウムメチリド

### Research Abstract

A series of new cyclopropyl trimethylsilyl ketones has been prepared in moderate yield from the novel reaction of 1-trimethylsilylcyclopropyllithium derivartives with dichloromethyl methyl ether. This reaction involves the intramolecular 1,2-silicon shift from carbon to carbon. The spectroscopic properties of these silyl ketones have been measured.

The ketones obtained here react with various halogen acids under milder conditions compared to that of their carbon analogs to give the ring opening products, 3-chloropropyl silyl ketones, or the ring enlargement products, 2-silyl-4,5-dihydrofuran derivatives in some cases. The reaction with sulfuric acid or trifluoromethane sulfonic acid affords only the corrensponding silyldihydrofurans in good yield. Especially, it is noteworty that the reaction of 2-

phenylcyclopropyl silyl ketone with sulfuric acid yields 2-phenylcyclobutanone. The formation of these compounds is interpreted on the basis of the effect that silicon stabilizes a cation to it .

Wittig reactions of cyclopropyl silyl ketones with alkylidene-triphenylphosphoranes proceed stereoselectively to give the corresponding Z-1-silyl-1-cyclopropyl alkenes. The protodesilylation of silyl cyclopropyl alkenes with tetrabutylammonium fluoride proceeds with retention of configuration to give E-cyclopropyl alkenes, although the reaction with hydrogen halides was unsuccessful due to the cleavage of the three membered ring.

The reaction of sulfur ylides in THF with cyclopropyl silyl ketones resulted in the formation of the corresponding siloxyalkenes or -ketosilanes. The relative ratio of these compounds varies with the reaction temperature, the porality of solvents used, and the preparation method of ylide. It is noteworthy that the reaction with salt free ylide affords siloxyalkenes and that of the ylide containing inorganic salt -ketosilanes, selectively. These two type of products would be formed by the anionotropic and cationotropic rearrangement of silyl group in the betaine intermediate.▲ Less

## Research Products (8 results)

		All	Other
		All	Publications (8 results)
[Publications]	Tadashi NAKAJIMA: Chemistry Letters. 177-180 (1986)		▼
[Publications]	Tadashi NAKAJIMA: Chemistry letters. 181-182 (1986)		▼
[Publications]	Tadashi NAJAJIMA: Bulletin of the Chemical Society of Japan.		▼
[Publications]	Tadashi NAKAJIMA: Bulletin of the Chemical Society of Japan.		▼
[Publications]	Tadashi NAKAJIMA; Masaru TANABE; Katsuhiko Ohno; Masahito SEGI; Sohei SUGA: "Reaction of 1-trimethylsilylcyclopropyllithium derivatives with dichloromethyl methyl ether. A novel synthesis of cyclopropyl silyl ketones." Chemistry Letters. 177-180 (1986)		▼
[Publications]	Tadashi NAKAJIMA; Hiroyuki MIYAJI; Masahito SEGI; Sohei SUGA: "Ring opening and enlargement of cyclopropyl trimethylsilyl ketones by acids." Chemistry Letters. 181-182 (1986)		▼
[Publications]	Tadashi NAKAJIMA; Toshiaki TAKEGAWA; Masahito SEGI; Sohei SUGA: "Highly stereoselective synthesis and protodesilylation of 1-trimethylsilyl-1-cyclopropyl alkenes from acylsilane/ylide chemistry." Bulletin of the Chemical Society of Japan.		▼
[Publications]	Tadashi NAKAJIMA; Reiko HIOKI; Humitoshi SUGIMOTO; Masahito SEGI; Sohei Suga: "Reaction of cyclopropyl silyl ketones with oxosulfonium ylide.Selective formation of siloxyalkene or -ketosilane." Bulletin of the Chemical Society of Japan.		▼

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