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

メタデータ	言語: jpn
	出版者:
	公開日: 2022-10-31
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	キーワード (En):
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URL	https://doi.org/10.24517/00067725

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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
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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.

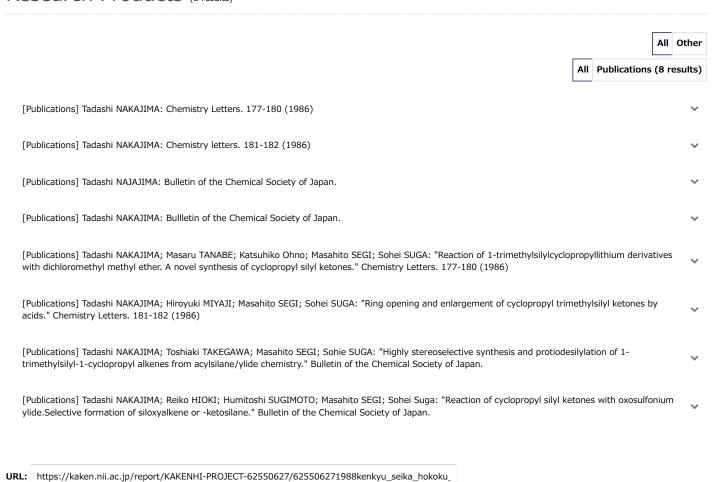
The ketones obtained here react with various halogen acids under milder conditions compared to that of their carbon analogs to give the ring opening products, 3-chloropropyl silyl ketones, or the ring enlargement products, 2-silyl-4,5-dihydrofuran derivatives in some cases. The reaction with sulfuric acid or trifluoromethane sulfonic acid affords only the corresponding 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 comounds 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 protiodesilylation 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)



Published: 1990-03-19