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SILICON-BASED NUCLEOPHILE MEDIATED ONE-CARBON RING EXPANSION REACTION OF 1-(TRIMETHYLSILYLMETHYL)CYCLOALKANECARBALDEHYDES

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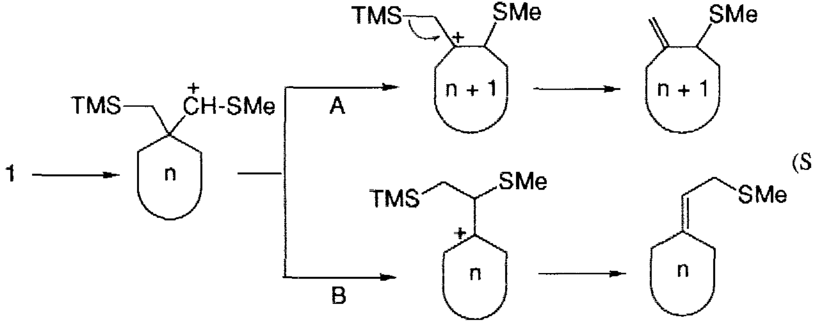
Abstract: Under the influence of an appropriate Lewis acid, TMS sulfide and TMS-OTf induced one carbon ring expansion of 1-(trimethylsilylmethyl)cycloalkanecarbaldehydes to afford the corresponding 2-methylenecycloalkyl sulfides and ethers, or their isomerized ones in good yields.

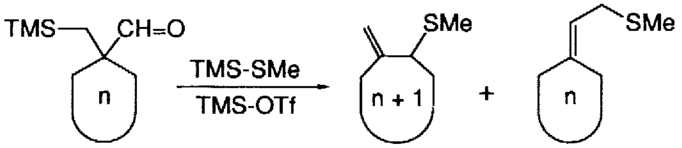
In connection with studies on one-carbon ring expansion reactions of carbocycles,[1,2] we previously reported reaction of 1-(trimethylsilylmethyl)cycloalkanecarbaldehydes **1** with trimethylsilyl ethers in the presence of Lewis acid.[3] Such procedure has made it feasible to generate the corresponding alkoxy-stabilized cationic species in situ which undergoes selective rearrangement of ring carbon to afford 2-methylenecycloalkyl ethers. By using a similar combination of reagents, it seems to be possible to generate various kinds of cationic intermediates, which may react through either path A or path B (Scheme 1) to form the corresponding rearrangement product directly from **1**.



(Scheme 1)

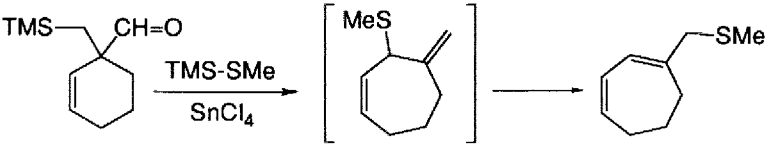
In the present paper, we describe Lewis acid mediated reactions of **1** in the presence of several silicon-based nucleophiles. Thus, on treating with TMS-SMe (2 equiv) and TMS-OTf (1 equiv) , **1a**, **1c**, and **1d** gave the corresponding one-carbon ring enlarged 2-methylenecycloalkyl sulfides **2** in good yields (Eq 1). In contrary, a six-membered substrate **1b** failed to undergo similar rearrangement, but produced **3b** through an exclusive migration of TMS-methyl group (path B).[4] In the presence of $SnCl_4$, however, selective migration of sp^2 carbon could be induced in the reactions of substrates **1e** and **1f** containing vinyl and aromatic group to form seven-membered ring substrates, but they isomerize under these reaction conditions to afford **2e** and **2f** exclusively (Eq 2).

Under the influence of $SnCl_4$ (2 equiv), ketones **4a**, **4c**, and **4d** also gave the corresponding products **5**[5] arising from an initial one-carbon ring expansion followed by isomerization, whereas **4b** gave **6b**[5] as the major product (Eq 3).



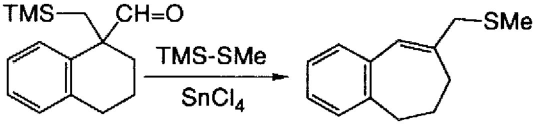
(Eq 1)

1a (n = 5)	**2a** 59%	--
1b (n = 6)	--	**3b** 74%
1c (n = 8)	**2c** 68%	--
1d (n = 12)	**2d** 69%	--



1 e

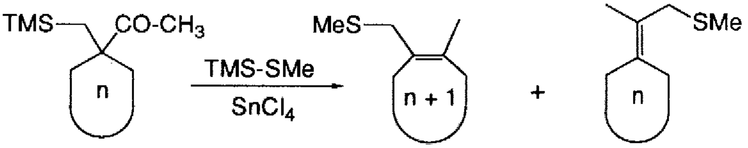
2e 83%



1 f

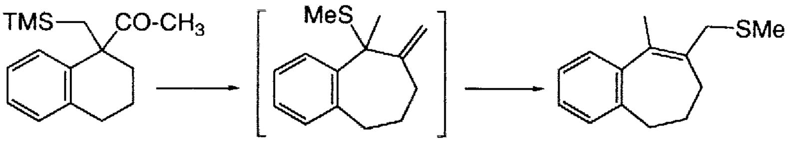
2f 93%

(Eq 2)



4a (n = 5)	**5a** 97%	0%
4b (n = 6)	**5b** 20%	**6b** 42%
4c (n = 12)	**5c** 86%	0%

(Eq 3)

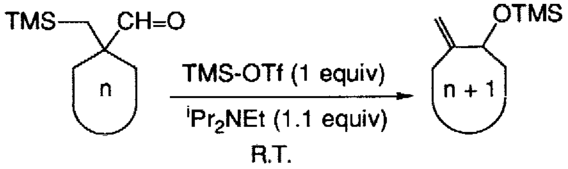


4 d

5d 92%

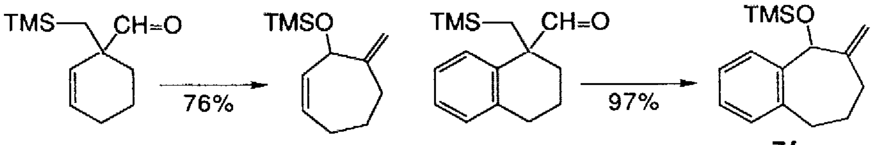
Irrespective of failure with **1b** probably due to an extreme stability of six-membered ring itself,$^{6)}$ the present method seems to be very useful because the allylic sulfides thus obtained are feasible for several synthetic transformation.

Further, a combined use of TMS-OTf (1 equiv) and a slight excess amount of diisopropylethylamine (1.1 equiv) has also effected similar rearrangement reaction to yield the corresponding 2-methylenecycloalkyl trimethylsilyl ethers from **1** (Eq 4 and 5). The reaction usually proceeds at room temperature without any isomerization and the products **7** were obtained in good yields. However, elevated reaction temperature (80 °C) was required to complete the reaction of **1b**. Under such conditions, decomposition of the resulting allylic ether **7b** seems to take place concomitantly to decrease the product yield.



(Eq 4)

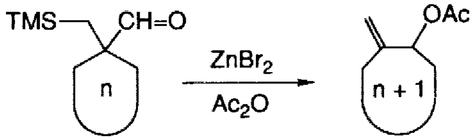
7a (n = 5) 80%
7b (n = 6) 30% (at 80° C)
7c (n = 8) 88%
7d (n = 12) 95%



7e **7f**

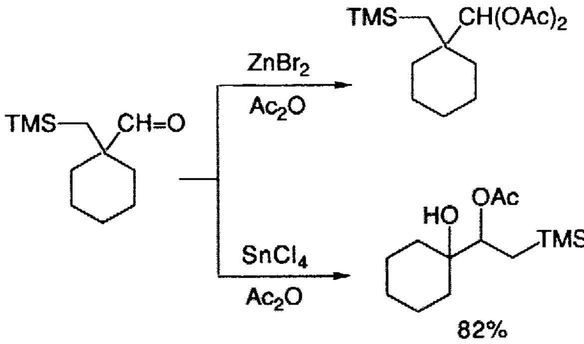
(Eq 5)

Treatment of **1a** or **1d** with acetic anhydride and $ZnBr_2$ similarly afforded the corresponding 2-methylenecycloalkyl acetate **8a** or **8d**, but **1b** failed to undergo ring enlargement (Eq 6). In the presence of $ZnBr_2$, **1b** gave the acylal exclusively, whereas $SnCl_4$ induced a preferential migration of TMS-methyl group (Eq 7).



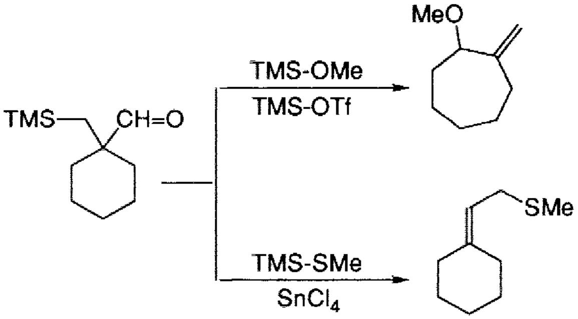
(Eq 6)

8a (n = 5) 67%
8d (n = 12) 63%



(Eq 7)

In conclusion, use of an appropriate combination of silicon-based nucleophilic reagents (TMS-X) and a Lewis acid has usually facilitated one carbon ring enlargement reaction of **1** through in situ generation of hetero atom substituted carbocationic species to afford 2-substituted methylenecycloalkanes. However, in the reaction of six-membered substrate **1b**, the mode of rearrangement course of the cationic intermediates has been greatly influenced by a substituent X (Scheme 1).



The more-stabilized species (X = OMe) undergoes selective migration of the ring carbon (path A),$^{3)}$ whereas the path B is followed by less-stabilized intermediate (X = SMe).

We are currently studying on synthetic application of these ring enlargement reactions.

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3) Katoh, T.; Tanino, K.; Kuwajima, I. *Tetrahedron Lett.*, **1988**, *29*, 1819.

4) On a greater migratory aptitude of TMS-methyl group, see Tanino, K.; Hatanaka, Y.; Kuwajima, I. *Chem. Lett.*, **1987**, 385.

5) The products **5b** and **6b** were determined by comparison with the authentic samples prepared by treatment of the corresponding silyl ethers with TMS-SMe in the presence of $SnCl_4$.

6) In several ring expansion reactions, 6-membered ring substrates exhibit different behaviors from other ring-sized compounds. See, for example: Trost, B. M.; Mikhail, G. K. *J. Am. Chem. Soc.*, **1987**, *109*, 4124.

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