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A HIGHLY SELECTIVE ONE-CARBON RING ENLARGEMENT REACTION DIRECTED BY SILICON

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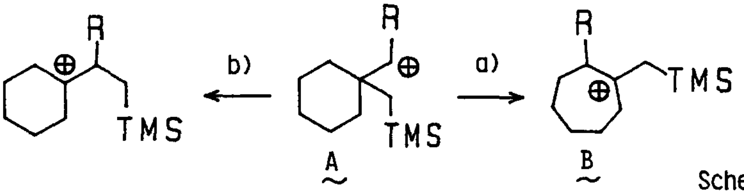
Summary: On treatment with dichloroaluminum phenoxide, 1-(trimethylsilyl)-methylcycloalkanecarbaldehydes undergo selective rearrangement of ring carbons to give the corresponding one-carbon ring enlarged 2-(trimethylsilyl)methyl-cycloalkanones in excellent yields.

A variety of synthetic organic reactions have been developed on the basis of the cation-stabilizing effects of a silyl group.[1] Such effects are also expected to play important roles both for acceleration and control of several cationic carbon skeleton rearrangement reactions.[2,3]

According to our previous findings,[3] a silyl group exhibits two different roles to determine the rearrangement courses: (i) a greater migration tendency of TMS-methyl group, and (ii) a well-documented β-cation stabilizing effect. Thus, on generation of a cationic species **A**, two different reaction courses may be conceivable (Scheme 1). By utilizing the second effect, we attempted to develop a useful one-carbon ring enlargement process.



Scheme 1

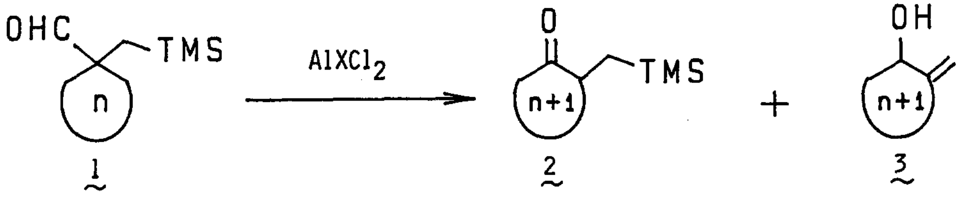
Examinations on various cationic species led us to a finding that the reaction of 1-(TMS-methyl)cycloalkanecarbaldehyde **1**[4] proceeds selectively through path a) to afford the corresponding one-carbon ring enlargement product **2**. Thus, on treating with $MeAlCl_2$ in hexane at room temperature, the cyclohexanecarbaldehyde **1a** can be converted to 2-(TMS-methyl)cycloheptanone **2a** in 77% yield.

In this reaction, a silyl group clearly exerts a strong directing influence[5] on an initial rearrangement step so as to form the β-silicon stabilized cationic species **B**. The resulting intermediate **B** exhibits an unprecedented behavior such as a preferential 1,2-hydride shift without removal of TMS group, which makes a remarkable contrast with a well established behavior of β-silicon substituted cationic species, and may broaden the synthetic utility.[6]

Aldehydes bearing other ring-sized carbon skeletons **1b** and **1c** also gave **2b** and **2c**, but the yield were decreased accompanied with formation of the corresponding 2-methylenecycloalkanols **3b** and **3c**, respectively.

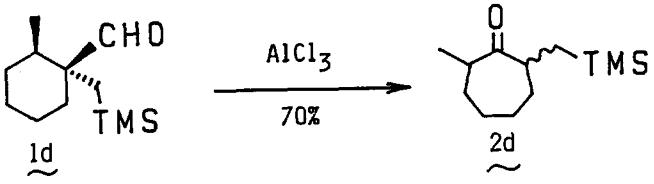
Various aluminum-based Lewis acids were examined to exclude the formation of 3, and $Al(OPh)Cl_2$[7] is found to be the most preferable for conversion of 1 to 2 as shown in Table 1.

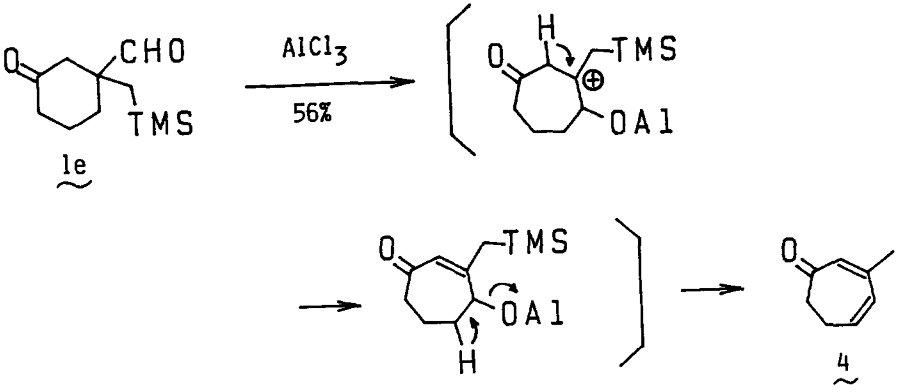
Table 1



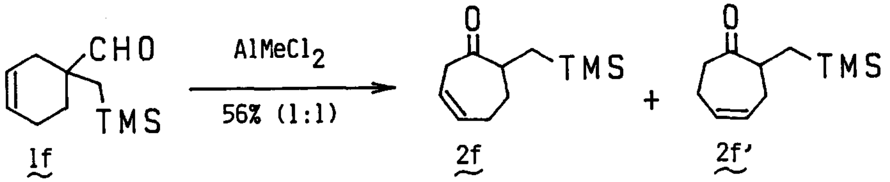
a: n = 6	$AlMeCl_2$	77%	trace
	$Al(OPh)Cl_2$	100%	-
b: n = 8	$AlMeCl_2$	67%	8%
	$Al(OPh)Cl_2$	97%	-
c: n = 12	$AlMeCl_2$	57%	15%
	$Al(OPh)Cl_2$	85%	-

Regiochemical outcome of this rearrangement has been briefly examined. A migration aptitude of primary vs. secondary or possibly tertiary alkyl groups seems to be different enough to induce a selective rearrangement of a more substituted group. For example, the reaction of an aldehyde **1d**[8] bearing 2-methyl group gave 2-methyl-7-(TMS-methyl)cycloheptanone **2d** in 70% yield as a mixture of cis- and trans-isomers. Further, a migration of an alkyl group takes place preferentially over that of 2-oxoalkyl group in the reaction of the 3-oxocyclohexanecarbaldehyde **1e**, which afforded 3-methylcycloheptadienone **4**. The formation of **4** may be explained by assuming a subsequent removal of an acidic proton from the resulting rearrangement intermediate followed by dehydration and desilylation.

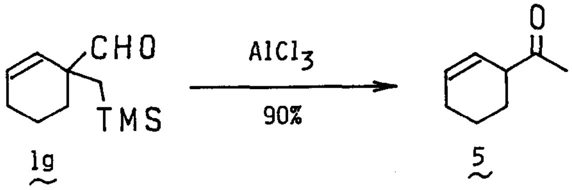




Difference of migration aptitude between an alkyl and an allyl group may be expected, but the 3-cyclohexenecarbaldehyde 1f gave a mixture of **2f** and **2f'** in almost 1:1 ratio.



In contrast, the 2-cyclohexenecarbaldehyde **1g** failed to undergo such ring expansion, but yielded cyclohexenyl methyl ketone **5** selectively. Different behavior of **1g** may attract much attention from mechanistic point of view. A larger migration aptitude of the TMS-methyl group as well as a resulting formation of a relatively stable allyl cationic intermediate may account for the unusual mode of rearrangement observed with **1g**.



In conclusion, an appropriate choice of substrates has allowed to induce selective carbon skeleton rearrangement by the cation-stabilizing effect of silicon, and may further lead to the development of a facile construction of carbocycle frameworks.

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2) I. Fleming and I. P. Michael, J. Chem. Soc., Chem. Commun., **1978**, 245. I. Fleming and S. K. Patel, Tetrahedron Lett., **22**, 2321 (1981).
3) K. Tanino, Y. Hatanaka, and I. Kuwajima, Chem. Lett., **1987**, 385.
4) These aldehydes were easily prepared by treating the corresponding lithiated carbonitriles with iodomethyltrimethylsilane followed by DIBAL reduction. The overall yields from the carbonitriles were about 80%.
5) In addition to a direction control, the silyl group has an accelerating effect. In the reaction of 1-methylcyclohexanecarbaldehyde, $AlCl_3$ induced a selective migration of methyl group extremely slowly.
6) For conversion of these ketones to α-methylene ketones: I. Fleming and J. Goldhill, J. Chem. Soc., Chem. Commun., **1978**, 176.
7) This aluminum reagent could be easily prepared by treating methylaluminum dichloride with an equimolar amount of phenol in methylene chloride.
8) On alkylation of lithiated 2-methylcyclohexanecarbonitrile with iodomethyltrimethylsilane, *cis*-carbonitrile (97:3) was obtained almost exclusively, and its stereochemistry was confirmed by comparison with the authentic sample. On predominant equatorial alkylation of cyclohexanecarbonitriles, see: H. O. House and T. M. Bare, J. Org. Chem., **33**, 943 (1968).

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