CHEMISTRY LETTERS, pp. 385-388, 1987.

Directing Effects of a Silyl Group on Cationic Rearrangement Reactions[†]

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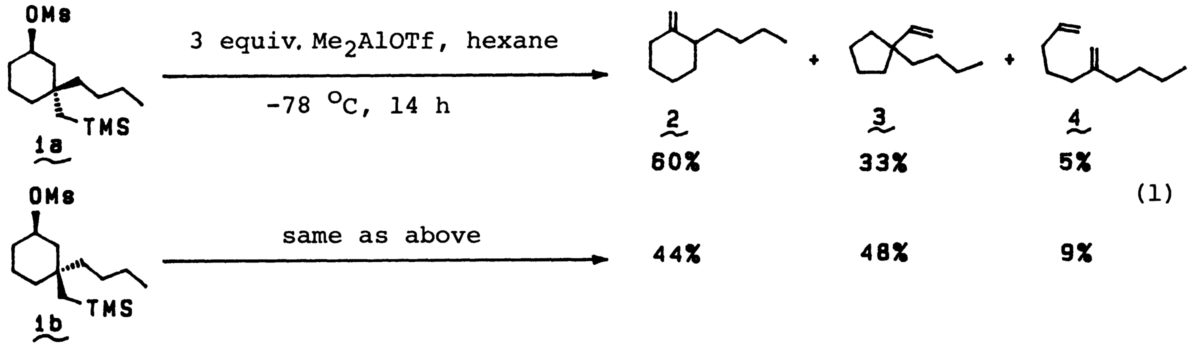
In the reaction of 3-(trimethylsilyl)methylcyclohexyl mesylates with dimethylaluminium triflate, the silyl group has a remarkable effect to induce successive rearrangements of a hydride and an alkyl group so as to form a stable β-silyl cationic species which finally afford the corresponding olefins.

A β-cation stabilizing effect of a silyl group has been utilized in a wide range of synthetic organic chemistry.[1)] Behaviors of homoallylsilanes[2)] have suggested that such effect also works efficiently on γ-position.[3)] We describe herein an effect of a silyl group to attract a cationic site from δ-position and to control the direction of cationic rearrangement reactions.

Treatment of 3-substituted 3-(trimethylsilyl)methylcyclohexyl mesylates **1a** or **1b** with dimethylaluminium triflate in hexane at -78 °C led to the formation of two types of rearrangement products, a methylenecyclohexane **2** and a vinylcyclopentane **3**, along with a small amount of a fragmentation product **4** (Eq. 1).



These results indicate that the silyl group has an effect to attract a cationic site from δ-position to γ- and finally β-position, which induces a selective hydride shift followed by rearrangement of an alkyl group.

However, since **5**, which generates a common cationic intermediate **A**, gave **2** exclusively under similar conditions (Eq. 2), steric factors of TMS-methyl and/or the leaving groups appear to play also important roles for determining the reaction course.

Results of the reactions with conformationally rigid substrates **1c**-**1f** have

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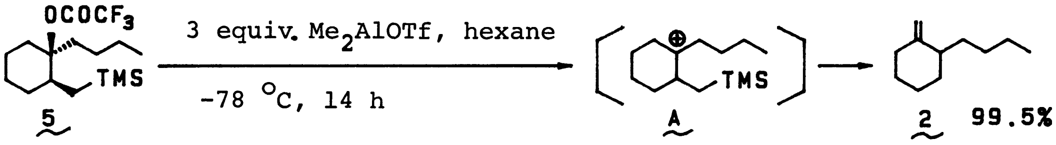
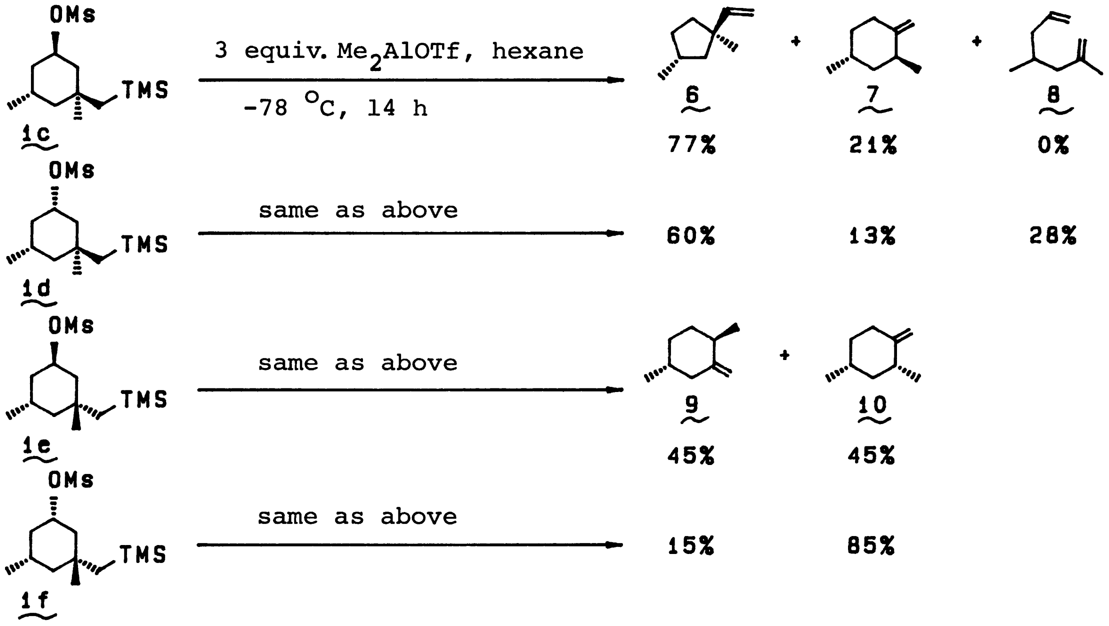
[†] Dedicated to Professor T. Mukaiyama on the occasion of his 60th birthday



(2)

disclosed the following features (see Eq. 3). Thus, for determining the reaction course, the stereochemistry of TMS-methyl group is much more important than that of the leaving group: An axial TMS-methyl group on 1c and **1d** exhibits an essentially similar effect which favors the ring contraction irrespective of stereochemistry of the leaving group except the formation of a fragmentation product **8**. On the other hand, in the reaction of substrates bearing an equatorial TMS-methyl (**1e** and **1f**), the stereochemistry of the leaving group has also a great influence on the direction of rearrangement, and the formation of **6** was completely excluded. Further, three types of methylenecyclohexanes are formed in these reactions, but their structural features are strictly dependent on the stereochemistry of TMS-methyl group of the starting materials.



(3)

In a similar manner with usual cationic 1,2-rearrangement processes, successive migrations of two antiperiplanar substituents on axial positions may be greatly favored in these silicon-directed rearrangements too. However, it appears to be necessary to take additional factors into account to explain these puzzling results. We would like to propose such an assumption that two successive 1,2-rearrangement steps may involve conformational transformation of a cyclohexane ring, and most of sp^3 character may be still retained$^{4)}$ in the cationic species generated through such processes. Thus, in the reaction of **1c** or **1d**, preferential rearrangements of an axial hydrogen and TMS-methyl accompany conformational transformation to give the intermediate **B** bearing a vacant orbital antiperiplanar to a ring carbon, which leads to the formation of the ring contraction product **6** via a carbon skeleton rearrangement so as to yield a stable β-silyl cationic species (Fig. 1). Formation of **7** may be attributable to a less favored synclinal hydride shift from **B**.

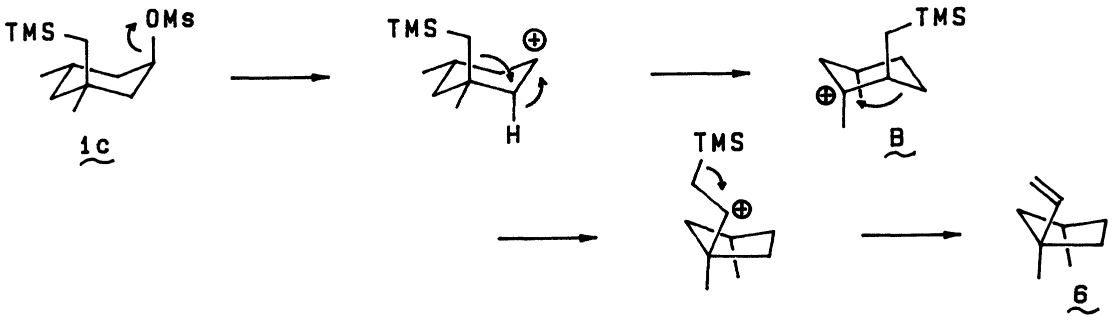


Fig. 1.

Similarly, successive hydride and methyl rearrangements from the substrates bearing an equatorial TMS-methyl group produce a β-silicon-stabilized intermediate **C**, which gives **9** exclusively. However, TMS-methyl seems to have a much greater tendency for migration over methyl,[5] and its 1,2-synperiplanar rearrangement may form an intermediate **D** bearing an axial vacant orbital, which undergoes an antiperiplanar axial hydride shift to afford **10** (Fig. 2).

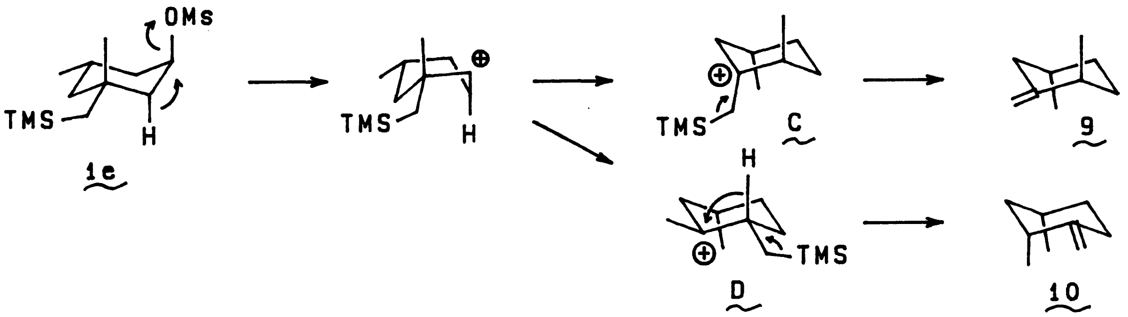
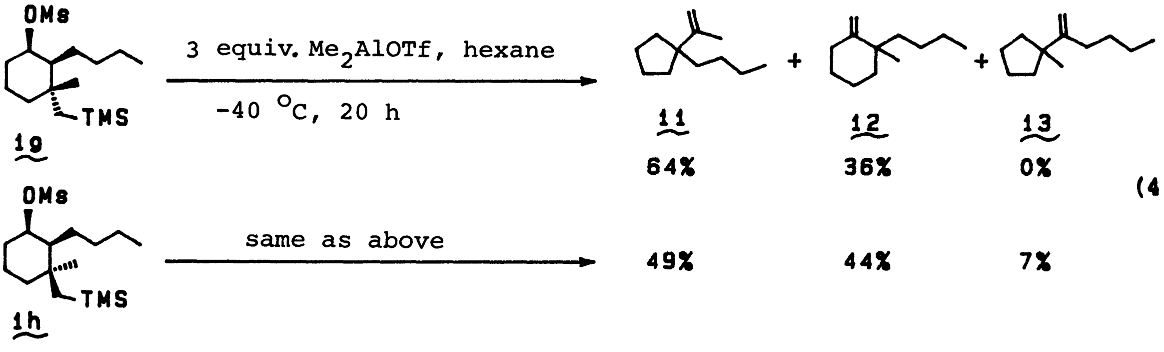


Fig. 2.

In contrast to such larger migration aptitude of TMS-methyl, a ring carbon or methyl migration follows an initial hydride shift in the reaction of 2-substituted ones **1g** or **1h** to afford **11** or **12**, respectively (Eq. 4). In these cases, such a second alkyl group migration as above allows a direct generation of a stable β-silyl tertiary cationic intermediate, whereas TMS-methyl rearrangement apparently brings little stabilization to the resulting species.

Similar effects have also worked on bicyclic compounds. As predicted from the above results, the substrate **1i** gave methylenedecalin **14** through rearrangements of a hydride and TMS-methyl, whereas **1j** selectively afforded <u>trans</u>-fused hydroazulene **16** via a ring carbon migration (Eq. 5).



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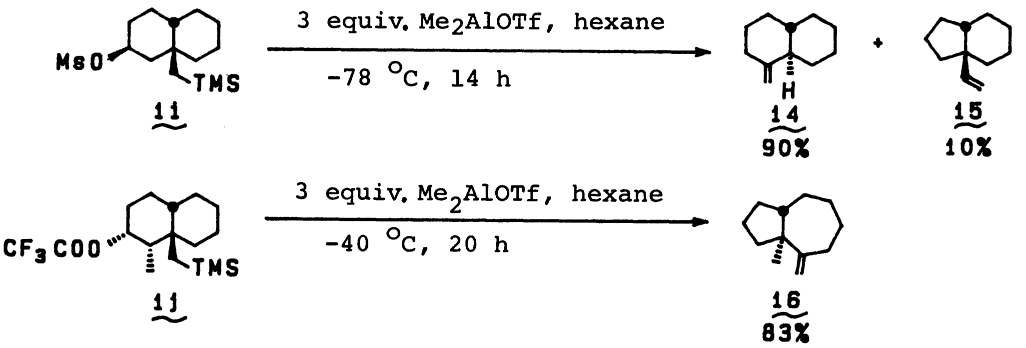

(5)

This work is partially supported by a Grant-in-Aid for Special Research from the Ministry of Education, Science, and Culture of Japanese Government.

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5) A larger migration aptitude of substituents bearing a silyl group has also been observed in the Baeyer-Villiger oxidation: P. F. Hudrlik, A. M. Hudrlik, G. Nagendrappa, T. Yimenu, E. T. Zellers, and E. Chin, J. Am. Chem. Soc., 102, 6894 (1980).

(Received October 28, 1986)