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High Pressure Reaction of 1-Methoxy-3-trialkylsiloxybuta-1,3-diene with Aldehydes. [4 + 2] Cycloaddition or Silicon Migration Reaction[1)]§

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The high pressure reaction of Danishefsky's diene with aromatic aldehydes produces the [4 + 2] cycloadduct, while with an aliphatic aldehyde such as 2-phenylpropionaldehyde the intermolecular silicon migration from oxygen to oxygen takes place.

A recent publication by Jurczak, Golebiowski, and Rahm2) on high pressure [4 + 2] cycloaddition of 1-methoxy-3-trialkylsiloxybuta-1,3-diene (**1**) to butyl glyoxylate has prompted me to report my own findings in this area. They reported that Danishefsky's diene (**1**) underwent [4 + 2] cycloaddition with butyl glyoxylate at 10 kbar in ethyl ether. I have also found that the cycloaddition between **1** and arylaldehydes proceeds quite smoothly under high pressure3) (10 kbar, CH_2Cl_2, 20 °C, 24 h) to produce **2** in 90% yield (Eq. 1).

However, the cycloaddition with aliphatic enolizable aldehydes, such as isobutyraldehyde, butyraldehyde, and 2-phenylpropionaldehyde did not occur under the same conditions. Treatment of **1** with 2-phenylpropionaldehyde (**3**) under higher temperature and a prolonged reaction time (10 kbar, CH_2Cl_2, 50 °C, 7 d) took a completely different reaction course (Eq. 2). The migration of $SiMe_3$ group from **1** to the aldehyde was observed; **4** and **5** were produced in 70% and 83% yield, respectively. The isomer ratio of **4** was 4 : 1. Presumably, the migration proceeds through an eight membered cyclic transition state (**6**). The high pressure induced intermolecular silicon migration from oxygen to carbon via an eight membered transition state has been reported previously.1) To the best of my knowledge, this is the first example of the high pressure induced intermolecular silicon migration from oxygen to oxygen.

In order to investigate whether this type of silicon migration takes place readily in other silyl enol ethers, the high pressure reactions of **3** with **7** or with **8** were examined. Here again, **4** was produced under the similar conditions. On the other hand, the similar reaction of **3** with **9** resulted in recovery of the starting materials, indicating that the intermolecular silicon migration from carbon to oxygen does not take place even under high pressure.

In conclusion, the high pressure promoted silicon migration reaction of silyl enol ethers or ketene silyl acetals are classified into three categories (Scheme 1); aldol reaction via six membered transition state (Type I);5)

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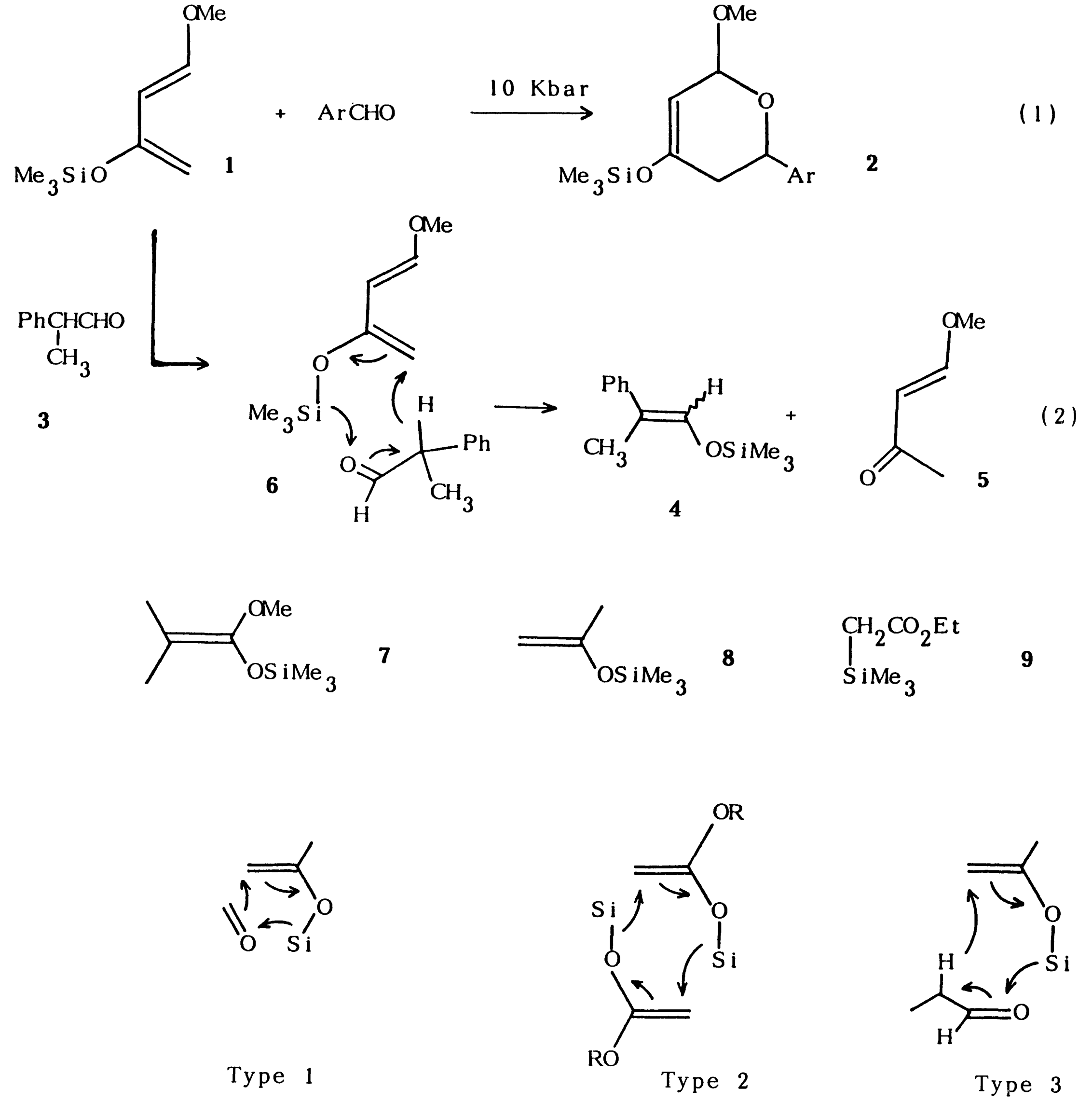
§ This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.

migration from oxygen to carbon (Type 2);[1)] migration from oxygen to oxygen (Type 3).



Type 1 Type 2 Type 3

Scheme 1.

References

1) For Part 5 in the series "Organometallic High Pressure Reactions," see: Y.Yamamoto, K.Maruyama, and K.Matsumoto, Organometallics, 3, 1583 (1984).

2) J.Jurczak, A.Golebiowski, and A.Rahm, Tetrahedron Lett., 27, 853 (1986).

3) For an excellent review on high pressure reactions, see K.Matsumoto, A.Sera, and T.Uchida, Synthesis, 1985, 1; K.Matsumoto and A.Sera, ibid., 1985, 999.

4) The isomer ratio of **2**-cis : **2**-trans was 5:1. For Lewis acid catalyzed cyclocondensation of **1** with aldehydes see: S.Danishefsky, J.F.Kerwin, and S. Kobayashi, J.Am.Chem.Soc., 104, 358 (1982).

5) Y.Yamamoto, K.Maruyama, and K.Matsumoto, J.Am.Chem.Soc., 105, 6963 (1983).

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