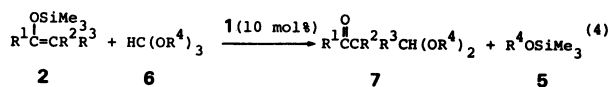
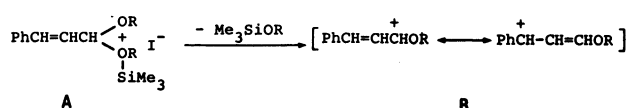


a) Yields after isolation by TLC. b) Determined by NMR. Erythro and three derivatives (**4**) were characterized by comparing the vicinal coupling constants (J_{ab}). Observations that J_{three} of *e.g.* **4b** (13 Hz) is greater than J_{erythro} (4 Hz) is in accordance with other erythro-three systems.^{8,10} c) At -35°C .

It is notable that orthoformate (**6**) reacts with **2** by catalysis of **1** to give β -keto acetal (**7**). No further reaction with the resulting β -keto acetal occurred. Apparently, the reaction of **7** with **2** is slower than the reaction of **6**.



From the mechanistic point of view, it is interesting that reactions with α,β -unsaturated acetals catalyzed by **1** proceed very selectively on the acetal carbon (see Table 1). This fact suggests strongly that a silyloxonium ion A, not a carbenium ion like B, is the most important intermediate in the reaction.



Experimental

Reactions Summarized in Table 1. The following procedure is typical. To a mixture of **2** (1.2 mmol) and **3** (or **6**) (1.0 mmol) in dry dichloromethane (2 ml) was added iodotrimethylsilane (0.02 g, 0.1 mmol) by a syringe under nitrogen at -78°C . The reaction mixture was stirred for given conditions in Table 1 and hydrolyzed with a saturated solution of hydrogen sodium carbonate at -78°C . After usual work-up, the crude product was purified by preparative thin-layer

chromatography on silica gel.⁹⁾

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