Ring-Opening Reactions of Alkanone Acetals with Iodosilane Equivalents for the Formation of Siloxyalkyl Enol Ethers

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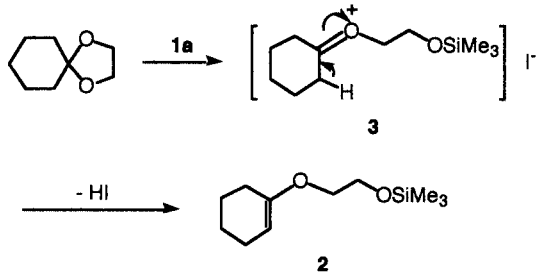
Reactions of ketone acetals with iodosilane equivalents were studied. Treatment of alkanone ethylene acetals with a 1:2 mixture of Et_2NSiMe_3 and MeI afforded 2-siloxyethyl enol ethers in good yield. Benzophenone ethylene acetal underwent deprotection with the iodosilane equivalents, giving benzophenone.

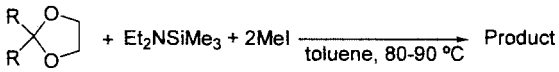
Halosilanes are widely used in the area of synthetic organic chemistry.[1,2] However, in contrast to fluoro- and chlorosilanes, the use of iodosilanes is rather limited due to their strong tendency to undergo hydrolysis even with atmospheric moisture. Recently, we have demonstrated that a 1:2 mixture of Et_2NSiMe_3 and MeI (reagent **1a**)[3–6] and a 1:1 mixture of Et_3SiH and MeI in the presence of a catalytic amount of $PdCl_2$ (reagent **1b**)[3,7] act as a synthetic equivalent of Me_3SiI and Et_3SiI, respectively.[8] They may be handled without a special care, and react readily with several organic substrates. Their reactions with cyclic ethers afford ring-opened iodosiloxyalkanes in good yield.[3,4] With reagent **1a,** alkyl esters gave trimethysilyl alkanoates with liberation of alkyl iodides.[5] It has been also reported that interaction of alkanones with **1a** gives trimethylsilyl enol ethers. [6] To explore further the scope of the synthetic utilities of the iodosilane equivalents, we studied the reactions of ketone acetals with reagent **1a**.

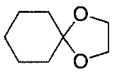
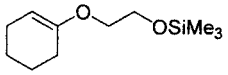
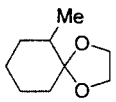
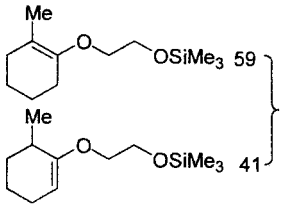
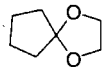
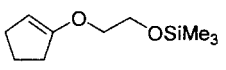
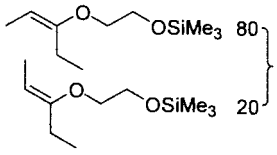
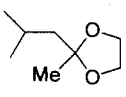
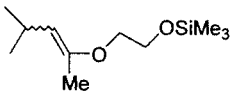
The reactions of alkanone ethylene acetals with 1 equiv of reagent **1a** proceeded smoothly to afford ring-opened siloxyethyl enol ethers as the sole volatile products, in good isolated yield, as shown in Table 1. Thus, the reaction of cyclohexanone ethylene acetal with reagent **1a** at 80–90 °C in toluene gave trimethylsiloxyethyl cyclohexen-1-yl ether (**2**) in 76% yield (run 1).[9] This is in contrast to the fact that the reactions of ketone acetals with Me_3SiI give the corresponding deprotected ketones.[10] Similar reactions have been reported for ketone dimethyl acetals, whose reactions with Me_3SiI in the presence of a slight excess of hexamethyldisilazane give methyl enol ethers by the loss of one methoxy group and an α-hydrogen.[11]



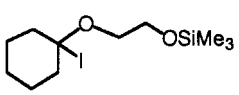
Scheme 1.

Table 1. Reactions of alkanone acetals with reagent **1a**



Run	Acetal	Product	Yield
1			76%
2		 59 / 41	75%
3			75%
4		 80 / 20	62%
5			72%

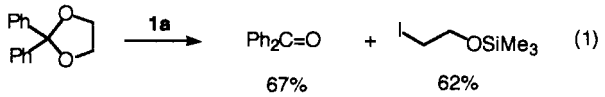
The present reaction would involve the formation of a cationic intermediate **3**, from which proton is eliminated to produce **2** (Scheme 1). It might be also possible to assume **3'** as an intermediate. However, we have not yet obtained any evidences for the formation of **3'** in this reaction.



3'

Similar treatment of 2-methylcyclohexanone ethylene acetal with **1a** gave a mixture of regioisomers, 2- and 6-methylcyclohexen-1-yl ether, in a ratio of 59/41 in 75% combined yield (run 2). Cyclopentanone and acyclic alkanone ethylene acetals also underwent ring opening with **1a** to give the corresponding siloxyethyl enol ethers in good yields (runs 3–5).

In contrast to the cases of alkanone ethylene acetals described above, similar reaction of benzophenone ethylene acetal with **1a** under the same conditions gave deprotected benzophenone and 1-iodo-2-(trimethylsiloxy)ethane [eq (1)].



In conclusion, we demonstrated that the iodosilane equivalent **1a** reacted readily with ketone acetals. Of these, the reactions of alkanone ethylene acetals with **1a** seem to be of importance which led to the one step synthesis of 2-siloxyethyl enol ethers.[12] The products may be useful as a novel class of enol ethers bearing a silyl-protected hydroxy group.

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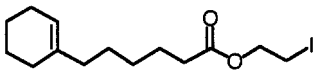
References and Notes

1 G. L. Larson, "The Chemistry of Organic Silicon Compounds," ed. by S. Patai and Z. Rappoport, Wiley, New York (1989), Part 1, Chap. 11.
2 E. W. Colvin, "Silicon Reagents in Organic Synthesis", Academic Press, London (1988).
3 J. Ohshita, A. Iwata, F. Kanetani, A. Kunai, Y. Yamamoto, and C. Matui, *J. Org. Chem.*, **64**, 8024 (1999).
4 Y. Yamamoto, H. Shimizu, C. Matui, and M. Chinda, *Main Group Chemistry* , **1**, 409 (1996).
5 Y. Yamamoto, H. Shimizu, and Y. Hamada, *J. Organomet. Chem.*, **509**, 119 (1996).
6 Y. Yamamoto and C. Matui, *Organometallics*, **16**, 2204 (1997).
7 A. Kunai, T. Sakurai, E. Toyoda, and M. Ishikawa, *Organometallics*, **13**, 3233 (1994).
8 It has been reported that mixtures of chlorosilanes and NaI in acetonitrile work as synthetic equivalents of iodosilanes. See, a) T. Morita, Y. Okamoto, and H. Sakurai, *J. Syn. Org. Chem.*, **39**, 973 (1981). b) H. Sakurai and Y. Okamoto, *J. Syn. Org. Chem.*, **40**, 525 (1982).
9 A mixture of 5.95 g (41.0 mmol) of Et_2NSiMe_3, 5.79 g (40.8 mmol) of cyclohexanone ethylene acetal, 12.2 g (86.1 mmol) of MeI in 20 mL of toluene was stirred at 80–90 °C for 12 h. The resulting ammonium salts were filtered and the solvent was evaporated. Distillation of the residue under reduced pressure gave 6.63 g (76% yield) of compound **2**: bp 73–75 °C (1 mmHg); ^{1}H NMR (δ in $CDCl_3$) 4.58 (br s, 1H), 3.81 (t, J = 5.1 Hz, 2H), 3.69 (t, J = 5.1 Hz, 2H), 2.15–2.02 (m, 4H), 1.68–1.62 (m, 2H), 1.55–1.49 (m, 2H), 0.12 (s, 9H); ^{13}C NMR (δ in $CDCl_3$) 154.5, 93.9, 61.5, 67.4, 27.8, 23.5, 22.9, 22.7, –0.4; MS *m/z* 214 (M^+). Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34%. Found: C, 61.51; H, 10.49%.
10 M. E. Jung, W. A. Andrus, P. L. Ornstein, *Tetrahedron Lett.*, **1977**, 4175.
11 R. D. Miller and D. R. McKean, *Tetrahedron Lett.*, **1982**, 323.
12 The reaction of alkanone acetals with reagent **1b** proceeded in a different fashion from those with **1a**, producing iodides arising from coupling of two units of the acetals. For example, compound **4** was obtained from the reaction of cyclohexanone ethylene acetal with **1b** in 63% isolated yield. The details will be reported elsewhere.



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