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Novel Silylating Agents Employing 4-Pentenyl Silyl Ethers‡

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Abstract: Nonsymmetrical silaketals R'OSiR_2OR" other than R = Me were efficiently prepared by the activation of 4-pentenyl silyl ethers with IDCP in the presence of an alcohol. In addition, trialkylsilyl ethers could be prepared from the corresponding trialkylsilyl pentenyl ether.

In a program centered on the use of the temporary silicon connection in intramolecular glycosylations[1,2] we were recently confronted with the problem of having to construct a nonsymmetrical silaketal, R'OSiR_2OR", other than the usually employed dimethylsilaketal (R = Me) owing to, in certain circumstances, the acidic instability of the latter. The usual protocol for dimethylsilaketal formation, however, could not be applied as this calls for the silylation of one alcohol with excess Me_2SiCl_2, subsequent removal of the volatile dichlorosilane and the eventual addition of the second alcohol. The higher boiling points of other dialkyldichlorosilanes make this procedure incompatible for the preparation of analogous silaketals. Complications of this sort have already been encountered by Craig for the preparation of nonsymmetrical diphenylsilaketals.[3] Gillard *et al.* introduced *t*-Bu_2Si(OTf)Cl for the preparation of di-*t*-butylsilaketals although the second silylation step proved sometimes difficult due to the sterically demanding *t*-butyl group.[4,5]

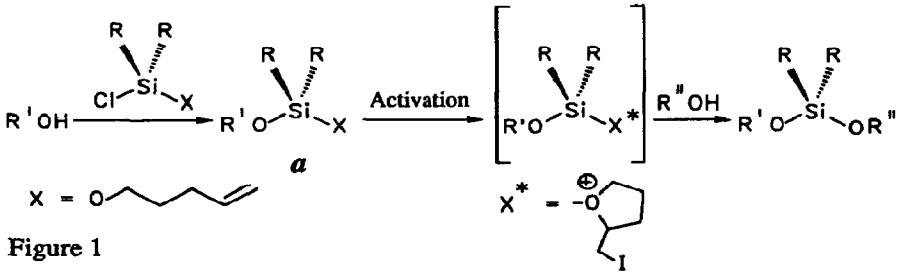
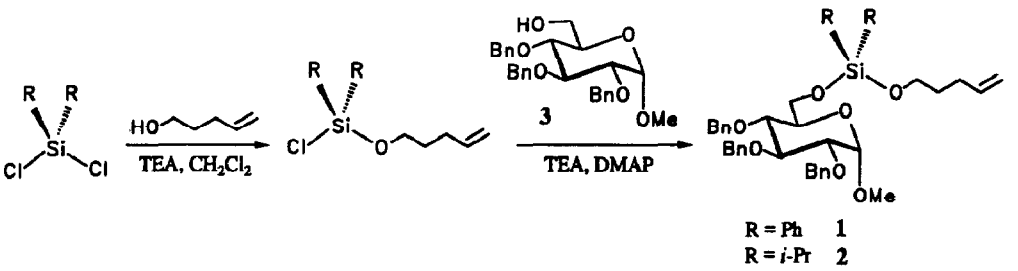


Figure 1

We conceived that a two-step sequence might be feasible as shown in Figure 1 whereby the intermediate product ***a*** would be sufficiently stable to undergo purification. Activation of ***a*** and hence silylation with the second alcohol would lead to the derived silaketal. As an activating group, we chose the 4-pentenyl silyl ether; its activation was anticipated to proceed upon addition of iodonium dicollidine perchlorate (IDCP) as described by Fraser-Reid for glycosylation with *O*-pentenyl glycosides.[6]

‡ This paper is dedicated to Professor Anders Kjær on the occasion of his 75th birthday.



In order to test this approach, the pentenyl silyl ethers **1** and **2** were prepared. Treatment of commercially available diphenyl- or diisopropyldichlorosilane with 4-pentenol at 0°C as described by Gillard[5] *et al.* and purification by distillation furnished the corresponding 4-pentenyl chlorosilyl ethers. Simple silylation of alcohol **3** gave the required precursors **1** and **2** in an approximately 75% yield, easily purified by chromatography. Subjecting a dichloromethane solution of **1** or **2** and an alcohol (1.0 equiv.) to 1.5 equiv. of IDCP at 20°C led to a quick conversion of the pentenyl ethers affording the desired silaketals in good yields. The results are shown in Table 1. The reactions were usually completed within 15 min and were easily performed on an approximately 0.1 mmol scale.[7] Again, the silaketals could be purified by chromatography showing no sign of decomposition.

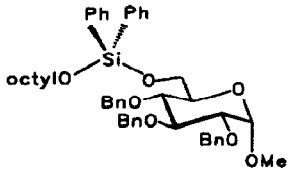
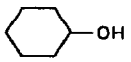
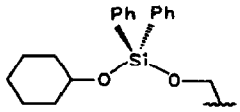
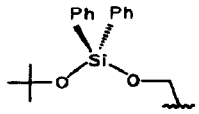
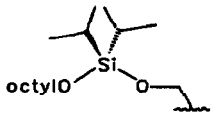
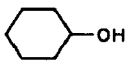
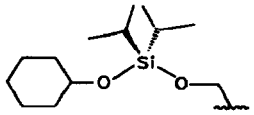
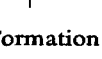
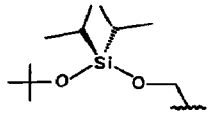
Precursor	Alcohol	Product	Yield
1	Octanol		90%
1			81%
2			80%
2	Octanol		82%
2			89%
2			86%

Table 1: Silaketal Formation

For the high yields obtained, it was necessary that the alcohol be present before adding IDCP. Introduction of the alcohol after IDCP activation led to a significant decrease in the nonsymmetrical silaketal yield as well as the formation of the symmetrical silaketal $(R'O)_2SiR_2$. Attempts to proceed via a two-step procedure by conversion of **1** to the corresponding silyl bromide or chloride upon activation with Br_2, Bu_4NBr_3 or ICl and subsequent treatment with the alcohol and TEA also led to substantial amounts of the symmetrical silaketal. A possible scenario rationalizing these results is presented in Figure 2. Activation with IDCP gives the silyloxonium intermediate which may be transformed into the silyl perchlorate.[8,9] Which of the two responsible for the actual silylation was not determined, but in the absence of an alcohol these potentially reactive intermediates may react with either the original silaketal[10] or collidine,[9a] to give a symmetrical silaketal and a silyl perchlorate or an *N*-silyl collidinium perchlorate, respectively.

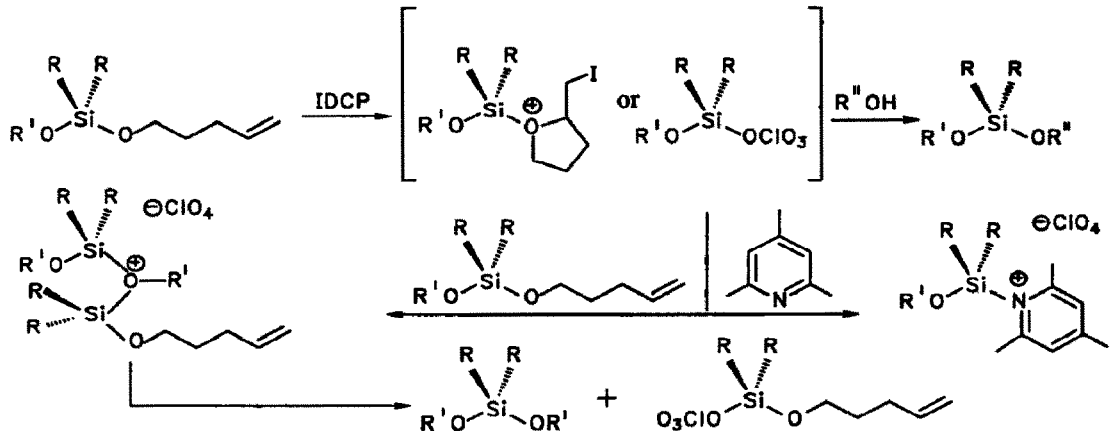
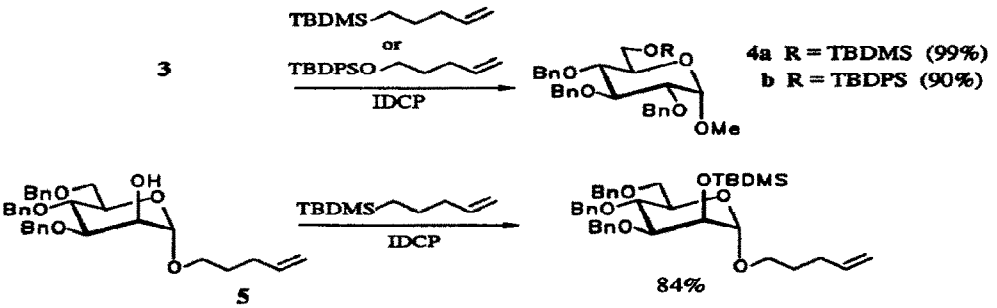


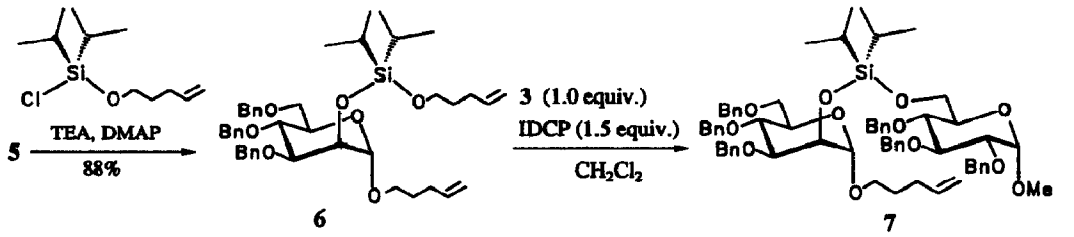
Figure 2

That the other etheral oxygen is not required for efficient silylation was shown from the silylation of **3** with either *t*-butyldimethylsilyl (TBDMS) or *t*-butyldiphenylsilyl (TBDPS) pentenyl ethers to give **4a** or **b** in excellent yields. Noteworthy is the silylation of the pentenyl mannoside **5** in 84% yield, where the 4-pentenyl silyl ether was selectively activated.



Another notable example of regioselective iodination was demonstrated with compound **6**, easily prepared from **5** and displaying two potentially reactive 4-pentenyl ether functionalities in the same compound. Nevertheless, upon treatment with alcohol **3** (1 equiv.) and IDCP (1.5 equiv.) a 78% yield of the

silaketal **7** was obtained in which the 4-pentenyl silyl ether had selectively been activated. This successful kinetic differentiation suggests the interesting possibility of performing a two-step silylation and intramolecular glycosylation *in situ* with excess IDCP, hence avoiding the isolation of the intermediate silaketal as reported earlier.[1] This approach is currently being pursued in our laboratory.



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7. *Typical procedure:* A solution of **1** (82 mg, 0.11 mmol) and octanol (15 mg, 0.11 mmol) in DCM (2 mL) was stirred for 30 min in the presence of 3 Å molecular sieves (~200 mg). IDCP (68 mg, 0.145 mmol) was added and the mixture was stirred for 1 h. The molecular sieves were filtered off and the organic phase was washed with a $Na_2S_2O_3$ solution, dried, and evaporated to dryness. Flash chromatography (hexane:ethyl acetate, 8:1) gave the corresponding octyl silaketal (78 mg, 90% yield).
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