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Diastereoselective diallylation of various butane-2,3-diacetals by allylsilane

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Abstract—Five butane-2,3-diacetals obtained from the reaction of 1,2-diols and methanol with biacetyl have been treated with allylsilane in the presence of titanium tetrachloride to afford bis-allyldioxanes as single diastereoisomers. © 2003 Elsevier Science Ltd. All rights reserved.

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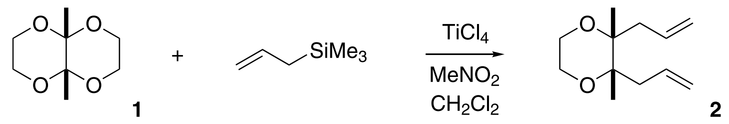
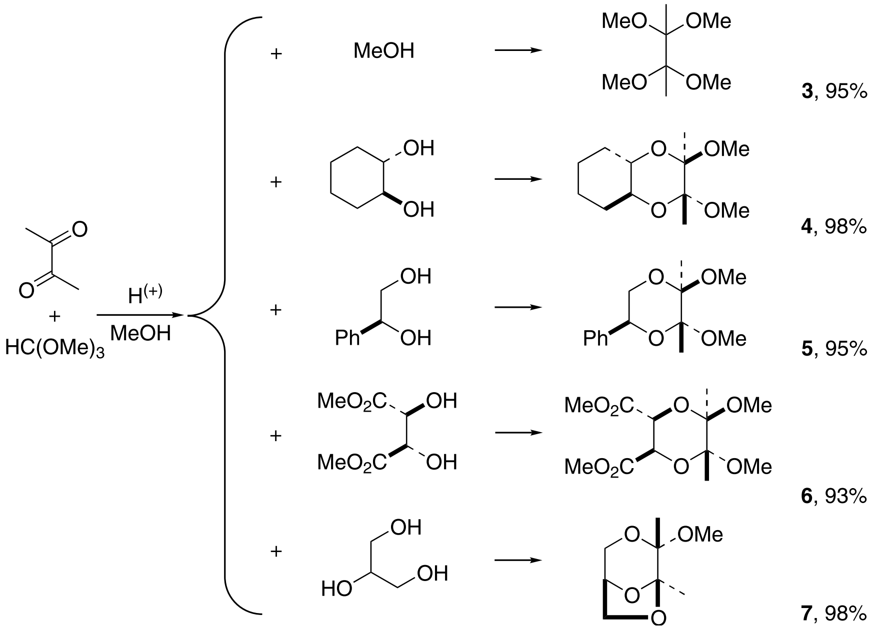
1. Introduction

Extensive efforts have been devoted to the carbon–carbon bond formation of acetals with silylated nucleophiles promoted by various reagents.[1] In particular, the reaction between acetals or less often cetals and allylsilanes is a mild and general method for the formation of homoallylic ethers.[2] In 1995, we have shown that the *cis*-tetraoxadecaline **1** (resulting from the acetalisation of biacetyl with glycol) treated with allyltrimethylsilane in the presence of titanium tetrachloride leads to the selective formation of *meso*-2,3-diallyl-2,3-dimethyl-1,4-dioxane **2**.[3] Clearly, double addition of the allyl moiety is occurring according a stepwise process.





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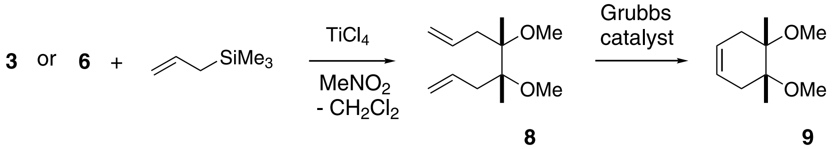
Recently, Ley and co-workers have described the preparation from biacetyl of some 1,2-diacetals bearing a dioxane ring and a *trans*-diaxial 1,2-dimethoxy moiety.[4] Moreover, compounds **4**–**6** could constitute remarkable chiral building blocks.

Then, we studied the $TiCl_4$-mediated addition of allylsilane and, for each case, we observed a very clean reaction. So, from **3** and **6** and using 3 equivalents of allylsilane in the presence of 4 equivalents of nitromethane, we obtained only *meso*-4,5-dimethyl-4,5-dimethoxyocta-1,7-diene **8** (43% yield from **3**, 60% yield from **6**).[5] The structure of **8** was established by its ring closure metathesis using the Grubbs catalyst,[6] into *meso*-1,2-dimethyl-1,2-dimethoxycyclohex-4-ene **9** (90% yield).



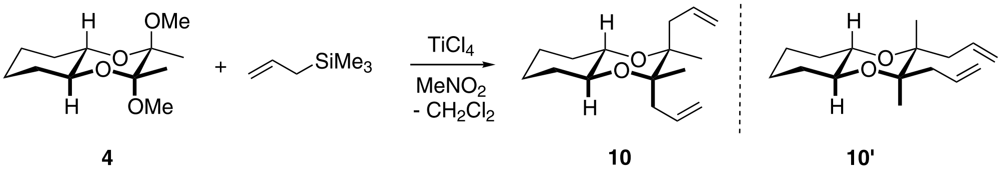
In the case of **4**, the substitution of methoxy groups was observed and the dioxadecaline **10** was obtained in 68% yield as the sole product. The NMR spectra prove that the C_2-axis is maintained. Only two structures **10** and **10′** having a C_2-axis can be obtained. Nevertheless and in spite of various procedures, all attempts of ring closure metathesis applied on **10** failed, leading us to propose the structure **10** resulting from a substitution with retention of configuration.[7]

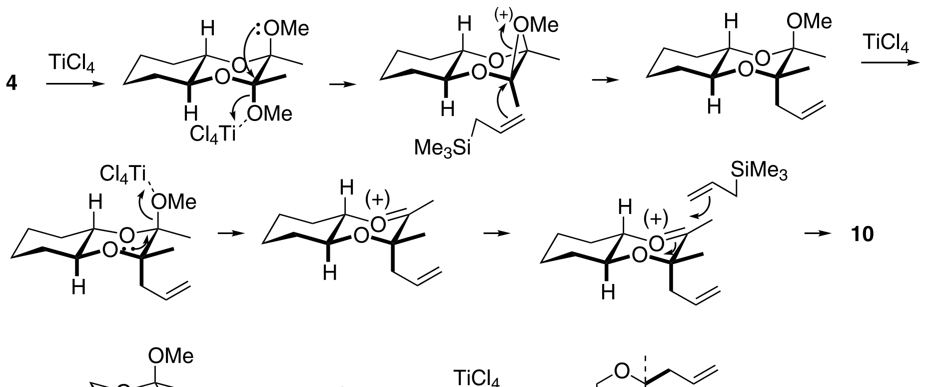
The twice retention of configuration observed in the case of **4**, can result from a participation of one methoxy group providing the departure of the other. As described below, the first substitution occurs with retention. Then, the anomeric assisted ionisation[8] of the last methoxy group leads to an oxocarbenium ion which is attacked by allylsilane on the axial position.

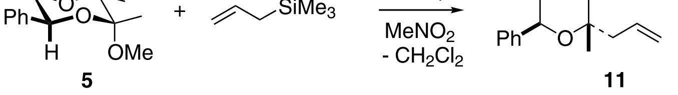
Similarly, the dioxane **11** has been obtained from **5** and here too, no ring closure metathesis using the Grubbs reagent was observed. NOESY data allowed us to confirm the identity of the structure **11**.

For the asymmetric dioxane **7**, with one equivalent of allylsilane, the first reaction is a substitution of the methoxy group with overall retention followed by an invertive ('S_N2-like') substitution on the mixed ketal moiety. Again, the stereochemistry of **13** has been checked by a ring closure metathesis using the Grubbs catalyst giving rise to a *cis*-ring junction dioxadecaline **14**. Moreover, NOESY experiments are in agreement with the proposed structure.[9]

For the substitution with retention, the most reasonable interpretation is that, after coordination of titanium

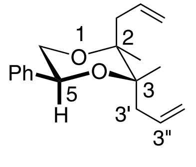


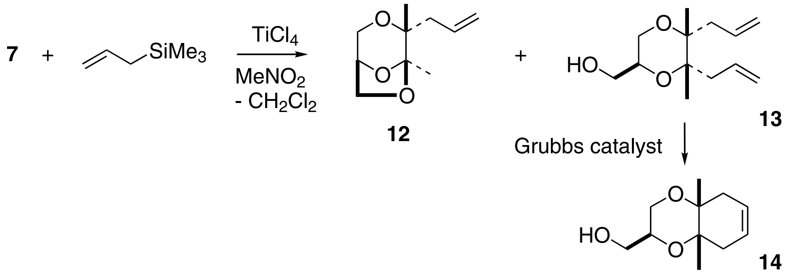


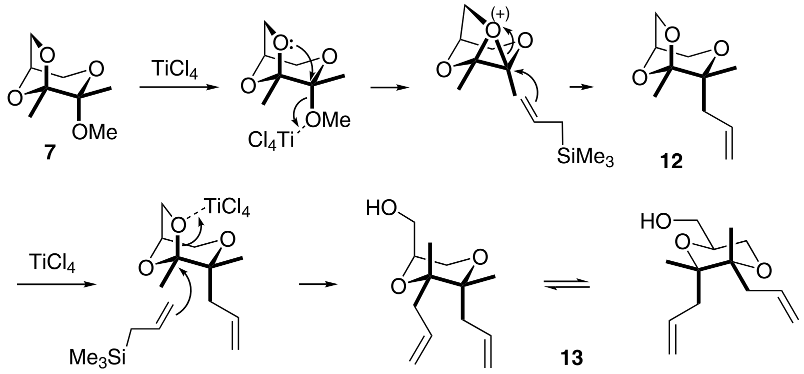


NOESY observed: H(5) - H(3'); H(5) - H(3")

no NOESY observed: Me(2) - H(5); Me(3) - H(5)







tetrachloride with the oxygen atom of the methoxy group, an oxygen participation occurred to give an oxonium ion which is attacked by allylsilane with an overall retention. Then, the coordination of titanium tetrachloride with the oxygen atom of the bridge provokes the substitution with inversion. In each case, the more C–O reactive bond is in axial position.

2. Conclusion

We have shown that allylsilane can react with 1,2-diacetals with an high stereoselectivity consistent with a substitution mechanism controlled by the anomeric effect.

Acknowledgements

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5. Oil with about 4% of *dl*-isomers (chiral VPC). **9**, ^{1}H ($CDCl_3$, 300 MHz) δ 5.53 (2H, br s), 3.23 (6H, s), 2.44 (2H, 0.5AB, d, $J=16.3$ Hz), 1.96 (2H, 0.5AB, d, $J=16.3$ Hz), 1.13 (6H, s); ^{13}C ($CDCl_3$, 75 MHz) δ 124.8 (d), 78.0 (s), 49.8 (q), 33.8 (t), 17.8 (q).
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7. **10**, oil; structure confirmed by NOESY experiments: we observed that only the allyl methylene gives cross peaks with axial hydrogen geminated with oxygen.
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9. **12**, **13** and **14** are oils. For **13** and **14**, in the NOESY experiments, we note cross peaks between the two methyl groups and the hydroxymethyl group.