Rearrangement of *p*-methoxybenzyl-protected allylic alcohols to aldehydes

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Allyl *p*-methoxybenzyl ethers undergo an acid-catalysed 1,4-rearrangement to give *p*-methoxyphenylbutyraldehyde derivatives, which can be ring-closed to give substituted naphthalene derivatives.

During our work with the Lewis acid-induced carbonyl-ene reaction,[1] a key step in our studies towards the synthesis of taxanes,[2,3] we recently discovered a new type of rearrangement (Scheme 1). When a mixture of **1c** and methyl or ethyl glyoxylate was treated with zeolite β or $BF_3{\cdot}Et_2O$, the ene reaction did not occur. Instead, **1c** rearranged to give aldehyde **2c** in good yield, which also occurred in the absence of the alkyl glyoxylate. Although allylic benzyl ethers are a well known class of compounds we were surprised to find that a literature search did not reveal any similar reactions under acidic conditions. One reason for this could be the fact that the reaction does not occur when an unsubstituted benzyl group is used instead of a *p*-methoxybenzyl (PMB) group. Thus, electron rich aromatic rings seems to be necessary. Another reason is that only zeolite β and $BF_3{\cdot}OEt_2$ among fifteen Lewis acids tested effected the rearrangement. The outcome of the reaction is similar to a 1,4-Wittig rearrangement,[4,5] although the reaction conditions and the mechanisms are quite different. While the 1,4-Wittig rearrangement needs strongly basic conditions and is usually a minor side reaction, the present rearrangement proceeds under acidic conditions (zeolite β is an acidic zeolite[6]) and gives moderate to good yields.

We propose the following mechanism; the initial step is the coordination of the Lewis acid (or protic acid) to the ether oxygen (**A**). This possibly leads to increased positive charge at the benzylic carbon, which explains why the *p*-methoxy group is necessary for the charge delocalization. Next, the π-electrons in the double bond attack the benzylic position to form cation **B**, which then undergoes a 1,2-hydride shift to give the aldehyde. The hydride shift was indicated by essentially complete statistical recovery of deuterium at the carbonyl α-position of **2c** after rearrangement of **1c**, which was 50% deuteriated at the allylic methylene group.

We have performed the reaction with four different PMB-protected allylic alcohols. The reaction is very simple to carry out, and easy access to allylic ethers together with the utility of aldehydes of type **2** should make this rearrangement quite useful in organic synthesis.† As a simple demonstration of this we cyclized one of the products, **2c**, using PPA(polyphosphoric acid)[7] to give the naphthalene derivative **3** in good yield. Aromatisation *via* elimination of water followed by oxidation (presumably due to dissolved air) took place directly in the PPA reaction mixture. The scope and limitations, together with various applications, of the described rearrangement will be reported shortly.

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Footnote

† *Typical procedure*: A solution of the PMB-protected allylic alcohol (1.0 mmol) in CH_2Cl_2 (2 ml) was stirred together with zeolite β (125 mg activated at 400 °C for 4 h) overnight at room temperature. The resulting orange–red mixture was then filtered through Celite. The Celite was washed with $CHCl_3$ (2 × 5 ml) and the combined organic extracts were concentrated at reduced pressure. The crude materials were purified by column chromatography (SiO_2, heptane–ethyl acetate, 95 : 5).

References

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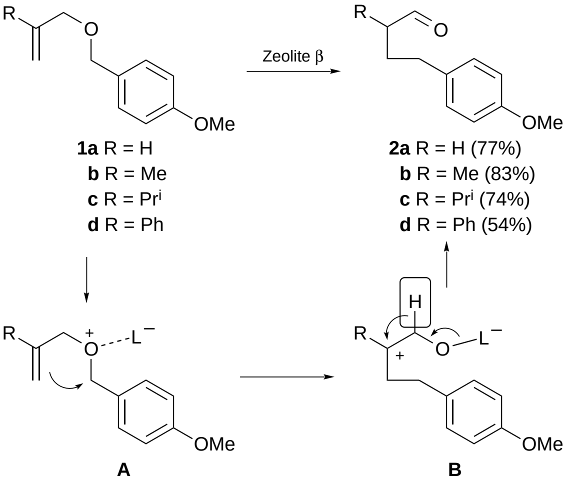

Scheme 1