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Reductive Deprotection of Aryl Allyl Ethers With $Pd(Ph_3)_4/NaBH_4$

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Abstract: Treatment of aryl allyl ethers with catalytic amounts of $Pd(PPh_3)_4$ and $NaBH_4$ at room temperature afforded the parent phenol in high yield under non-hydrolytic conditions.

The allyl group has been frequently used in organic synthesis as a protecting group for alcohols and amines due to its stability under basic and acidic conditions.[1] Removal of this protecting group is usually effected by two step sequence involving isomerization of the allyl ether to the corresponding 1-propenyl ether followed by H^+ or Hg^{2+} catalyzed hydrolysis or oxidative cleavage. Strong bases (KO^{t}Bu-DMSO) or transition metal catalysts such as Wilkinson's reagent have been used for the isomerization purpose, usually at high temperature.

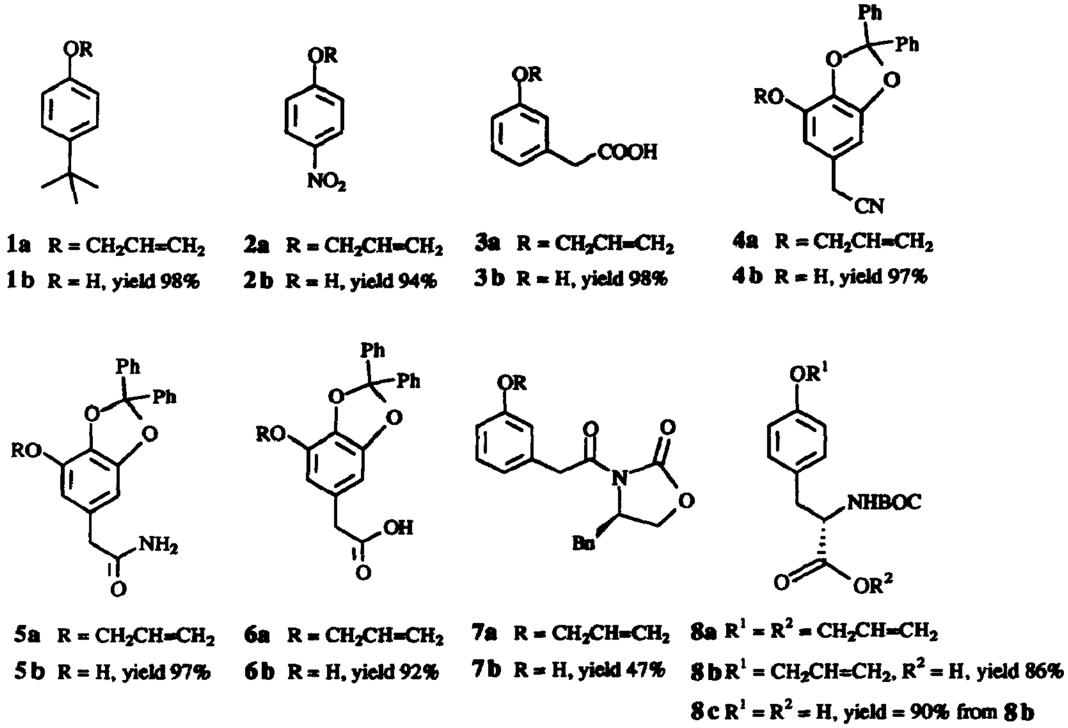
Recently, various one pot deprotection procedures have been reported.[2] In connection with ongoing research, we encountered a deallylation problem and we found, as a solution, that the combination of a catalytic amount of $Pd(PPh_3)_4$ and $NaBH_4$ can smoothly cleave the allylic ethers. The results are summarized in figure 1.[3]

A range of reducible functional groups: nitro, acetals, carboxylic acids, amides, nitriles, carbamates and imides are compatible with our reaction conditions. This method is applicable to amino acids as shown for compound **8a** whose chiral center is not affected (**8c**: $[\alpha]_D = +5$, *c* 0.24, AcOH. lit[4] $[\alpha]_D = +4$, AcOH). An allyl ester was also cleaved and moreover, selectively in the presence of allyl ether (compound **8b**). $Pd(PPh_3)_2Cl_2$ could also be used as catalyst and in this case, the reaction was found to be instantaneous after addition of $NaBH_4$, probably due to the high reactivity of the $Pd(PPh_3)_2$ generated *in situ*.

A typical experimental procedure is as follows. To a solution of compound **4a** (70.5 mg, 0.19 mmol) in THF (2 ml) was added a catalytic amount of $Pd(PPh_3)_4$ (4.4 mg, 0.02 eq). The slightly yellow solution was stirred for 5 min and $NaBH_4$ (11 mg, 0.287 mmol) was introduced. After 1 h, the excess of $NaBH_4$ was destroyed by addition of 1N HCl. The solvent was removed and the aqueous solution was extracted with CH_2Cl_2, the combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. The crude mixture was purified by flash chromatography (SiO_2, Heptane/EtOAc = 3/1) to afford product **4b** (61 mg, 97%).

While no detailed mechanistic study has yet been undertaken, we assumed that the reaction proceeded *via* the formation of π-complex rather than the commonly accepted propenyl intermediate and that hydride transfer[5] from $NaBH_4$ to this π-complex afforded propene and phenol after aqueous work-up.

Mild conditions, compatibility of the functional groups and easy handling of the reagent constitute the particular advantages of the present system.



1a $R = CH_2CH{=}CH_2$
1b $R = H$, yield 98%
2a $R = CH_2CH{=}CH_2$
2b $R = H$, yield 94%
3a $R = CH_2CH{=}CH_2$
3b $R = H$, yield 98%
4a $R = CH_2CH{=}CH_2$
4b $R = H$, yield 97%
5a $R = CH_2CH{=}CH_2$
5b $R = H$, yield 97%
6a $R = CH_2CH{=}CH_2$
6b $R = H$, yield 92%
7a $R = CH_2CH{=}CH_2$
7b $R = H$, yield 47%
8a $R^1 = R^2 = CH_2CH{=}CH_2$
8b $R^1 = CH_2CH{=}CH_2$, $R^2 = H$, yield 86%
8c $R^1 = R^2 = H$, yield = 90% from **8b**

Figure 1

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