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# A Novel, Mild Palladium Mediated Deprotection of O-allyl and Prop-1-enyl Ethers

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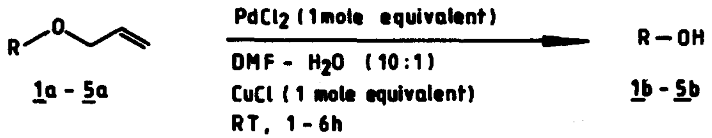
**Abstract :** A mild method for the deprotection of diverse O-allyl (**1a-5a**) and prop-1-enyl ethers (**1d-5d**) of glycosides and inositol by use of $PdCl_2/CuCl/DMF-H_2O/O_2$ is described.

Several methods of deprotection of O-allyl ethers have been described earlier. They involve a two step reaction sequence in which the O-allyl ethers were first isomerised to the prop-1-enyl ethers either with a base ($KO^tBu$)[1] or $(Ph_3P)_3RhCl$[2,3] or $[Ir(COD)(PMePh_2)_2]PF_6$[4], and then hydrolysed to the alcohols either by means of mineral acid (0.1N HCl at 60°C) or $HgCl_2/HgO/H_2O$[5] or with $I_2/H_2O$[6]. Similarly Pd/C/MeOH/TSOH or $ClSO_3H$[7] at reflux, $SeO_2$/HOAc at reflux temperature[8], $PdCl_2$/NaOAc/HOAc at 60°C[9], $Pd(Ph_3P)_4$/HOAc at 60°C[10], $SmCl_3$[11] or $AlCl_3$/N,N-dimethyl aniline/$SnCl_4$[12] were also used for the same purpose. These reaction conditions are either basic or acidic in nature for retaining the commonly used protecting groups.

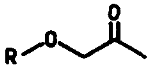
We report herein a general method where O-allyl ethers of glycosides and inositol **1a-5a** possessing sensitive protecting groups were reacted with $PdCl_2/CuCl/O_2$ in $DMF-H_2O$ to give the alcohols **1b-5b** respectively in high yields (90-92%) at room temperature (scheme 1). Thus reaction of **1a-5a** with $PdCl_2$ (1 mole equivalent) in $DMF-H_2O$ (10:1) containing CuCl (one mole equivalent) and oxygen at room temperature for 1-6 h gave the alcohols **1b-5b** respectively in 90-92% yields[13]. In order to ascertain whether enol ethers could be possible intermediates in these reactions, **1a-5a** were converted to the enol ethers **1d-5d** respectively[1]. **1d-5d** (Scheme 2) rapidly reacted (5-15 min) at room temperature with catalytic amount of $PdCl_2$ (0.2 mole equivalent) CuCl (1 mole equivalent) in $DMF:H_2O/O_2$ at room temperature to give the alcohols **1b-5b** respectively in high yields (88-93%). Mildness of the reaction conditions was clearly evident from the deprotection of **4a, 4d, 5a** and **5d** having sensitive benzylidene and isopropylidene protecting groups.

In conclusion a new and mild deprotection procedure for O-allyl and prop-1-enyl ethers has been described and the exact mechanism of this reaction is still not understood.

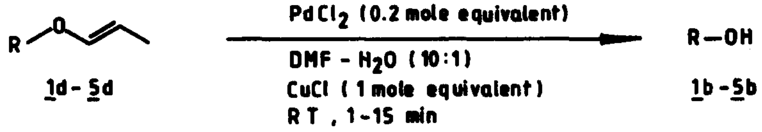
**A typical experimental procedure :** To a round bottom flask containing **1a** (1 mmol) in DMF (2 ml) and water (0.2 ml) (10:1) was added $PdCl_2$ (1 mmol) (0.2 mmol in case of **1d-5d**) and CuCl (1 mmol) and stirred for 4 h at room temperature while oxygen was continuously bubbled. The reaction mixture was diluted with solvent ether (20 ml) and filtered on a bed of celite. The filtrate was diluted with solvent ether (50 ml) and washed with water. The organic phase was dried ($Na_2SO_4$), concentrated and filtered on a bed of silica gel (60-120 mesh) to obtain **1b** in 92% yield.



(Scheme 1)

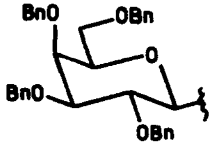


1c - 5c



(Scheme 2)

1 R =



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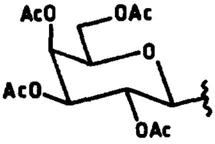

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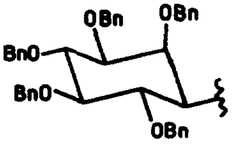

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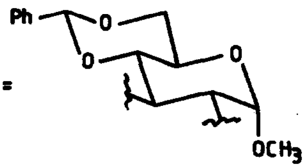

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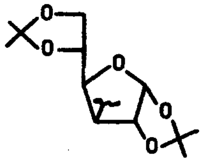

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13. Use of catalytic amount of $PdCl_2$ (0.2 mole equivalents) lead to the formation of the alcohols (**1b-5b**) in 50-60% yield along with the formation of Wacker oxidation products (**1c-5c**) in 15-18% yield.

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