One Pot Deprotective Oxidation of *O*-Allyl Ethers Using 70% tert-Butyl Hydroperoxide and Catalytic CrO_3[#]

S. Chandrasekhar*, Pradyumna K. Mohanty, T. Ramachander
Indian Institute of Chemical Technology, Hyderabad - 500 007, India
Fax +91 (91) 407173387; E-mail: srivaric@iict.ap.nic.in

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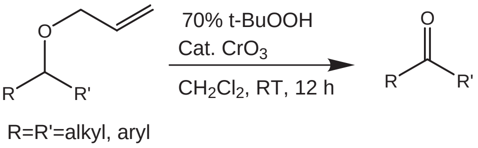
Abstract: Deprotection of *O*-allyl ether and in situ oxidation of the liberated free hydroxy group to carbonyl functionality is achieved in one pot using 70% tert-Butyl Hydroperoxide and catalytic CrO_3. Other sensitive groups viz., -OTHP, -OTBDMS and –OMOM ethers survive under the reaction conditions.

Key words: protecting groups, allylation, oxidation, catalyst, one pot reaction

Chromium based oxidations have been widely explored since becoming available to organic chemists, which is exemplified by plethora of literature.[1] This is primarily due to chemoselectivities achieved using these reagents in oxidation. The various oxidations carried out using chromium reagents includes, benzylic and allylic oxidations,[2] conversion of alcohols to carbonyl compounds[3] and acids[4] besides others.[5] However, the environmental hazards caused by chromium metal prompted the use of this class of reagents to be restricted totally or at least minimized. Towards this end, various catalytic variations have been developed wherein CrO_3 or CrO_3-amines are used in catalytic amounts and peroxide/peracids are used as stoichiometric oxidants. This combination of Cr-Peroxide is substantially studied in these transformations.[6] As part of an ongoing programme, new reagents and procedures for selective deprotective oxidation of 1^{o}-*O*-silyl ethers[7] and deprotection of allyl ethers[8] have been addressed by us. It was further envisaged that allyl ethers would be cleaved oxidatively[8] and that proper choice of reagents would allow further oxidation of liberated free alcohol to carbonyl compounds, thus allowing us to achieve two transformations in one pot namely, deprotection and oxidation. Herein, we report our latest findings for the conversion of *o*-allyl ethers to carbonyl compounds using catalytic amounts of CrO_3 and excess of 70% TBHP. It is interesting to note that CrO_3, even though known for over several years as a oxidant, is never used in deprotection of organic functional groups.



Scheme

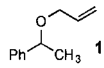
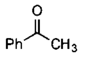
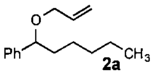
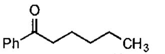
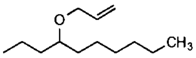
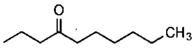
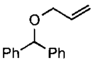
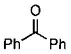
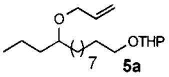
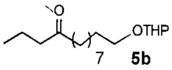
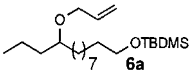
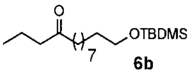
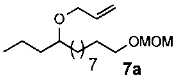
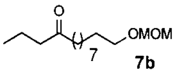
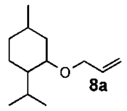
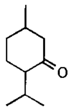
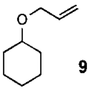
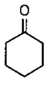
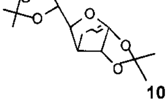
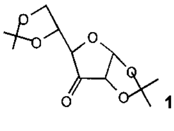
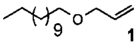
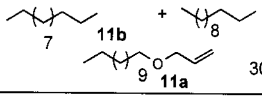
In the first instance, readily available α-phenyl ethanol was protected as its allyl ether under standard reaction conditions[9] and subjected to the CrO_3-TBHP oxidation in CH_2Cl_2 (entry 1, Table). As anticipated, clean formation of acetophenone was observed after 12 h in 77% isolated yield. Similarly α-phenyl hexan-1-ol-o-allyl ether furnished the corresponding keto compound (entry 2) in 74% isolated yield. To check the capability of the reaction protocol, a few substrates containing *o*-allyl group on one end and other protective groups *viz*., OTHP ether (entry 5), OTBDMS (entry 6), and OMOM (entry 7) ethers on the other end were exposed to CrO_3-TBHP and good yields of *o*-allyl deprotection-oxidation products were obtained without affecting the other protective groups. Similarly, the menthol allyl ether (entry 8) was deprotectively oxidised uneventfully. To check the efficacy of the CrO_3-TBHP on sugar substrates, where the allyl group is extensively used as a protective group, the furanose substrate (entry 10) was reacted with CrO_3-TBHP and ulose derivative (**10b**) was isolated in good yield without any damage at the 1,2,5,6-di-*O*-isopropylidene site. However, when 1^0-o-allyl ether (entry 11) was exposed, a mixture of aldehyde, alcohol and starting material were recovered in 30:40:30 ratio, this being a limitation to the present protocol.

In summary, a new and efficient reagent system comprising of 70% tbhp and catalytic amount of CrO_3 (10 mol%) has been developed for the first time for one pot deprotection of *o*-allyl ethers and in situ oxidation.[10]

Typical Procedure for the Chromium-Catalysed Allyl Ether Oxidation by 70% TBHP:

To a stirred solution of CrO_3 (10 mol%, 24 mg) in methylene chloride (15 mL) was added successively 70% of TBHP (888 mg, 9.87 mmol, 0.95 mL) and 1-(1-allyloxyethyl)benzene **1a** (400 mg, 2.46 mmol) in 5 mL of methylene chloride. The resulting mixture was stirred at ambient temperature for 12 h. The mixture was filtered through a plug of alumina, then washed successively with aqueous $NaHCO_3$ and brine solution. Evaporation of the volatiles followed by chromatography using silica gel (2% EtOAc in hexane as eluent) furnished 227 mg of pure acetophenone (**1b**, 77%).

Table Deprotective Oxidation of O-allyl ethers

Entry	Substrate	Product	Yield^{a} (%)
1	 **1a**	 **1b**	77
2	 **2a**	 **2b**	74
3	 **3a**	 **3b**	62
4	 **4a**	 **4b**	74
5	 **5a**	 **5b**	70
6	 **6a**	 **6b**	72
7	 **7a**	 **7b**	65
8	 **8a**	 **8b**	58
9	 **9a**	 **9b**	60
10	 **10a**	 **10b**	55
11	 **11a**	 **11b** + **11c** **11a**	30 : 40 : 30

^{a}Yields calculated after column chromatography of the products

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References and Notes

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(10) All new compounds are characterized by ^{1}H NMR and mass spectroscopy.

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