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Gourhari Maity [a] & Subbas Chandra Roy [a]

[a] Department of Organic Chemistry , Indian Association for the Cultivation of Science , Jadavpur, Calcutta, 700 032, India

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CERIC AMMONIUM NITRATE CATALYSED PROTECTION OF ALCOHOLS BY 3,4-DIHYDRO-2H-PYRAN

Gourhari Maity and Subhas Chandra Roy*

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta - 700 032, India.

Abstract : Hydroxyl compounds readily add to dihydropyran in presence of a catalytic amount of ceric ammonium nitrate to give high yield of tetrahydropyranyl ethers.

Protection of hydroxyl groups in molecules containing multiple hydroxyl groups is an important reaction in organic chemistry, particularly during the synthesis of natural products. The protection of hydroxyl groups with 3,4-dihydro-2H-pyran (DHP) is a very useful and representative method in modern synthetic chemistry[1]. Many catalysts have already been proposed for this purpose keeping in view the sensitivity of the molecule towards acidic or basic conditions. For the tetrahydropyranylation of alcohols, acidic[2], mildly acidic[3] or even mildly basic[4] catalysts have been reported. Very recently, 2,3-dichloro-5,6-dicyano-p-

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* To whom correspondence should be addressed.

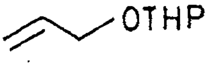
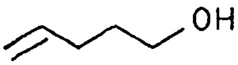
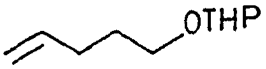
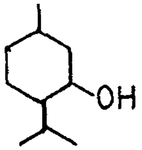
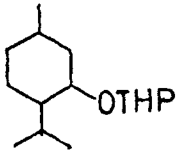
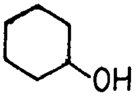
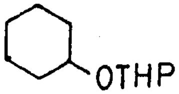
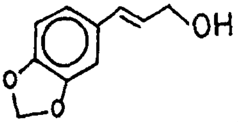
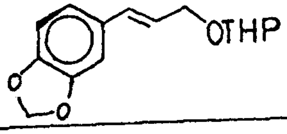
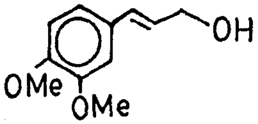
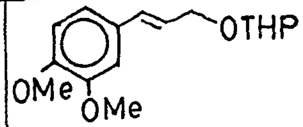
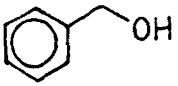
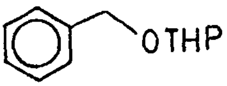
benzoquinone (DDQ) has been used as a neutral catalyst[5] for the tetrahydropyranylation of alcohols. In this paper, we wish to report that ceric ammonium nitrate (CAN) can efficiently catalyse the tetrahydropyranylation of various alcohols.

Thus, alcohols (1.0 equivalent) on treatment with DHP (1.0 equivalent) in the presence of a catalytic amount of CAN in dry acetonitrile at room temperature afforded the carresponding tetrahydropyranyl (THP) ethers in excellent yield. Usually these reactions were complete within 30 minutes. The results are summarised in Table. These reactions are quite facile with primary and secondary hydroxyl groups although secondary hydroxyls react slower than the primary ones. In a separate experiment (entry 12) with a mixture of 4-pentene-1-ol and menthol using 1.0 equivalent of DHP with respect to pentenol, ratio of protected alcohols was 65 : 35. However, a two fold excess of DHP is capable of protecting both the groups. In summary, ceric ammonium nitrate is an efficient catalyst for the protection of alcohols with dihydropyran.

Experimental : General procedure for the formation of tetrahydropyranyl-ethers from alcohols.

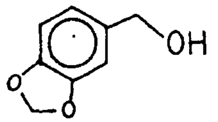
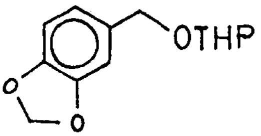
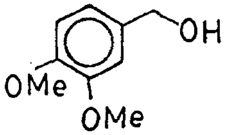
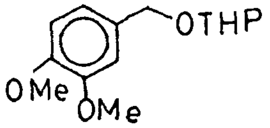
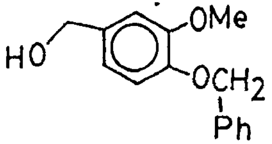
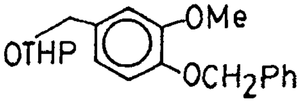
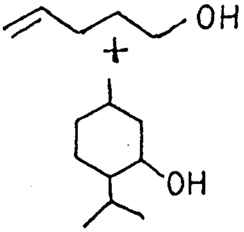
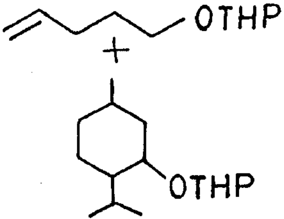
Methyl alcohol (320 mg, 10 mmol) and dihydropyran (840 mg, 10 mmol) was added to a stirred solution of ceric ammonium nitrate (20 mg) in dry acetonitrile (5 ml) and the resulting mixture was kept at room temperature for 30 min. The mixture was

Table : CAN-catalysed tetrahydropyranylation of alcohols

Entry	Alcohols	Products	Yield^{a,b}(%)
1	MeOH	Me-OTHP	81
2			90
3			91
4			89
5			90
6			85
7			85
8			86

(table continued)

(table continued)

9			87
10			89
11			87
12^c		 + *starting material*	65:35^d

(a) Yield of isolated product,(b) All the compounds were properly characterised by ^1H NMR,(c) 1.0 equivalent of DHP with respect to 4-pentene-1-ol was used.(d) Ratio of protected pentenol and menthol.

diluted with water and extracted with chloroform. The organic layer was washed with brine and dried (Na_2SO_4). Solvent was removed under reduced pressure and the residue was column chromatographed over silica gel (benzene) to yield the THP-ethers.

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