A mild and efficient method for tetrahydropyranylation and detetrahydro-
pyranylation of alcohols and phenols by BiOClO4.xH2O (or) BiONO3

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A mild and efficient method for the protection of alcohols and 
phenols as tetrahydropyrranyl ethers 3a-k and their deprotection at 
room temperature using BiOClO4.xH2O (or) BiONO3 as catalyst 
is described.

Keywords: Tetrahydropyranylation, detetrahydropyranylation, 
alcohols, phenols, BiOClO4.xH2O, BiONO3

IPC: Int.CI.7 C 07 C, C 07 D

Tetrahydropyranylation of hydroxy groups and their 
deprotection play an important role in organic 
synthesis1. Tetrahydropyranyl ethers are stable under 
variety of reaction conditions such as neutral and 
basic media, reactions involving Grignard reagents, 
lithium alkyls, redox reactions with metallic hydrides, 
oxidative alkylation, acylating agents2,3 and undergo 
easy deprotection under mild acidic conditions to 
afford corresponding alcohols.

2H-3,4-Dihydropyran 2 (DHP) is one of the useful 
reagents for the protection of hydroxy group in the 
organic synthesis4. There are several catalysts reported 
for the protection of hydroxy group as tetrahydro-
pyranyl ethers and their deprotection including protic 
acids5, Lewis acids like polystyrene supported AlCl36, 
Sc(OTf)37, In(OTf)38, I29, InCl310, ZrCl411 Lithium salts 
lke LiBr12, LiBF413, LiOTf14, LiClO415, LiPF616, 
CuCl217, NH4Cl18, and expansive graphite19, Clay 
materials20, silicasulphuric acid21 K2CoW12O40.3H2O22, 
N-bromosuccinimide23, tetrabutylammonium tribro-
mide24 etc. More recently, water is used as catalyst 
and solvent in tetrahydropyranylation of alcohols25.

Though, these methods have valuable utilities, some 
of them possess drawbacks including long reaction 
time, poor yield, high temperature, and difficulty in 
handling. Hence, still there is a need to develop mild 
and efficient method for the protection of hydroxyl 
group as tetrahydropropyranyl ethers and their 
deprotection. In this communication, we wish to 
report the use of BiOClO4.xH2O (or) BiONO3 as a 
mild, efficient, and ease of commercially available 
catalysts for the protection of hydroxyl group as 
tetrahydropropyranyl ethers 3a-k and their deprotection 
at room temperature (Scheme I).

Tetrahydropyranylation of alcohols and phenols 
was done easily in the presence of catalytic amount of 
BiOClO4.xH2O (or) BiONO3 in excellent yields at 
room temperature. Among these two bismuth salts, 
BiOClO4.xH2O is more effective catalyst. A wide 
range of alcohols such as primary, secondary, tertiary, 
benzylic and cyclic alcohols and phenols underwent 
effective tetrahydropyranylation to yield correspond-
ing tetrahydropropyranyl ethers 3a-k (Table I) and 
deprotection of tetrahydropropyranil ethers to yield 
corresponding alcohols and phenols (Table II) at 
room temperature.

Experimental Section

All the melting points were determined in open 
capillary in liquid paraffin-bath and are uncorrected. 
The purity of the compounds was checked by TLC. 
IR spectra (KBr) were recorded on Shimadzu FTIR 
Model 8010 Spectrometer; and 1H NMR spectra in 
CDCl3 on a 300 MHz NMR spectrometer using TMS 
as an internal standard. The C, H and N analysis of 
the compounds was done on a Carlo Erba Model 
EA1108 C, H and N elemental analyzer.

Note

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General procedure for tetrahydropyranylation of alcohols and phenols. BiOClO$_4$·xH$_2$O (or) BiONO$_3$ (0.1 mmole) was added to a solution of alcohol 1 (1 mmole) and DHP 2 (1 mmole) in dichloromethane (20 mL). The mixture was stirred at room temperature for a specific period of time (Table I). The progress of the reaction was monitored by TLC. After disappearance of the starting material, the catalyst was filtered and solvent was evaporated under reduced pressure. The residue was diluted with water (10 mL) and extracted twice with ether (2×20 mL). Separated organic layer was dried over Na$_2$SO$_4$. Evaporation of solvent, followed by column chromatography (ethyl acetate-petroleum ether; 2:8) furnished the desired tetrahydropyranyl ethers 3a-k.

### General procedure for depyranylation of tetrahydropyranyl ethers of alcohols and phenols.

BiOClO$_4$·xH$_2$O (or) BiONO$_3$ (0.1 mmole) was added to a solution of tetrahydropyranyl ether (1 mmole) in methanol (20 mL). The mixture was stirred at room temperature for a specific period of time (Table II). The progress of the reaction was monitored by TLC. After disappearance of the starting material, the catalyst was filtered and solvent was evaporated under reduced pressure. The residue was diluted with water (10 mL) and extracted twice with ether (2×20 mL).

### Table I — BiOClO$_4$·xH$_2$O (or) BiONO$_3$-catalysed efficient synthesis of tetrahydropyranyl ethers$^b$ 3a-k from various alcohols and phenols

<table>
<thead>
<tr>
<th>Alcohols/phenols</th>
<th>Product</th>
<th>BiOClO$_4$·xH$_2$O</th>
<th>BiONO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (min)</td>
<td>Yield (%)$^a$</td>
<td>Time (min)</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>25</td>
<td>96</td>
<td>40</td>
</tr>
<tr>
<td>4-Chlorobenzyl alcohol</td>
<td>30</td>
<td>92</td>
<td>45</td>
</tr>
<tr>
<td>4-Methoxybenzyl alcohol</td>
<td>35</td>
<td>95</td>
<td>50</td>
</tr>
<tr>
<td>Phenol</td>
<td>30</td>
<td>90</td>
<td>55</td>
</tr>
<tr>
<td>4-Methoxyphenol</td>
<td>25</td>
<td>92</td>
<td>55</td>
</tr>
<tr>
<td>4-Methylphenol</td>
<td>30</td>
<td>95</td>
<td>45</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>30</td>
<td>92</td>
<td>40</td>
</tr>
<tr>
<td>2-Methyl-2-propanol</td>
<td>40</td>
<td>95</td>
<td>45</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>25</td>
<td>94</td>
<td>45</td>
</tr>
<tr>
<td>1-Naphthol</td>
<td>28</td>
<td>92</td>
<td>50</td>
</tr>
<tr>
<td>1-Menthol</td>
<td>30</td>
<td>90</td>
<td>55</td>
</tr>
</tbody>
</table>

$^a$Yields refer to pure products and all products were characterized by comparison of their physical and spectral data with those of authentic samples.

### Table II — BiOClO$_4$·xH$_2$O (or) BiONO$_3$-catalysed efficient deprotection of tetrahydropyranyl ethers$^b$ 3a-k

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$^b$All the tetrahydropyranyl ethers are known compounds.
Evaporation of solvent, followed by column chromatography (ethyl acetate-petroleum ether; 2:8) furnished the pure alcohols.

Acknowledgement

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References