JOURNAL OF CHEMICAL RESEARCH 2011 AUGUST, 477–479 **RESEARCH PAPER** 477

# Acid-washed bentonite: a new reagent for the deprotection of tetrahydropyranyl ethers

**Po.S. Poon, Ajoy K. Banerjee*, Liadis Bedoya, Jennifer Sanchez and Manuel S. Laya**

*Centro de Química, Instituto Venezolano de Investigaciones Científicas, (IVIC), Apartado-21827, Caracas-1020A, Venezuela*

Acid-washed (pH 4 and pH 6) bentonite earth cleaves the tetrahydropyranyl ethers to the corresponding alcohols in good yield under mild conditions.

**Keywords:** bentonite, dihydropyran, tetralone, dehydropyranylation

Tetrahydropyranylation is one of the most frequently used methods to protect aliphatic and aromatic hydroxyl groups. Tetrahydropyranyl ethers (THP) are usually transformed into their parent alcohols under strongly acidic conditions.[1,2] For that reason several reagents have been utilised for the deprotection of THP ethers.[3,4] However some of these reagents suffer from the disadvantages of high cost, high temperature requirement and being strongly acidic are undesirable for highly acid-sensitive alcohols. Therefore efforts have been made to accomplish dehydropyranylation under mild conditions which are highly desirable for the protection of other functional groups. Tonsil, a commercially available Mexican bentonite earth which seems to have similar behaviour as a Lewis acid, has been used for deprotection[4] of tetrahydropyranyl ethers. In the course of our studies on the synthesis of natural products related to sesquiterpenes, we attempted to deprotect the tetrahydropyranyl ethers with the commercially available (Aldrich) bentonite earth. We observed that the bentonite earth was completely ineffective for dehydropyranylation but that acid-washed bentonite earth was a suitable reagent for dehydropyranylation.

To the best of our knowledge dehydropyranylation with acid-washed bentonite has not been reported previously. We now report for the first time its utility for deprotection.

## Results and discussion

When a solution of tetrahydropyranyl ether **1** in acetone was heated with acid-washed bentonite (see experimental) at 40–50 °C, the corresponding alcohol 2 was isolated after filtration and chromatography (Scheme 1).

The experimental procedure is simple and a wide range of tetrahydropyranyl ethers (**1a–k**) afforded the corresponding alcohols (**2a–k**). The yields ranged from excellent to poor as can be observed in Table 1. The compound (**1h**) proved extremely resistant to dehydropyranylation. Dehydropyranylation of the compound (**1k**) did not afford a good yield. It can be observed that the functional groups such as methoxy, benzyl ethers, and tertiary hydroxyl group remained unaffected with this reagent. Acetone was found to be most suitable solvent for the deprotection. We also observed (Table 1) a difference in yield of the alcohol during the deprotection with acid-washed bentonite (pH=4) and (pH=6). The progress of the reaction was monitored by TLC. In conclusion, we have shown that the acid-washed bentonite is a suitable catalyst for dehydropyranylaton. To the best of our knowledge some of the tetrahydropyranyl derivatives have never been subjected to deprotection with other catalysts. We strongly believe that the present method for dehydropyranyation constitutes an important alternative for deprotection.

## Experimental

The alcohol[5] **2a** was prepared by reduction of 7-methoxy-1-tetralone with sodium borohydride following the standard procedure. The tetrahydropyranyl derivatives **1b–k** were prepared by the tetrahydropyranylation of the commercially available alcohols **2b–k**. The identity of alcohols **2a–k**, obtained by the dehydropyranylation of the tetrahydropyranyl derivatives **1a–k**, were confirmed by comparing the m.p., TLC and the spectral data of the commercially available alcohols.

### *Tetrahydropyranylation*

A mixture of alcohol **2** (**a–k**) (4.62 mmol), 3,4-dihydropyran (17–48 mL) and a catalytic amount of p-toluenesulfonic acid was stirred for 1 h at room temperature. The progress of the reaction was followed by TLC. After completion, potassium carbonate (1.2 mmol) was added, stirred for 3 min, diluted with water and extracted with ether. The organic extract was washed with water, dried and concentrated. The residue was purified over a column of silica gel (eluant hexane-ether 9:1) to obtain the tetrahydropyranyl ethers (**1a–k**) (Table 1). The identity of all the tetrahydropyranyl derivatives was confirmed by spectral data.[5–8]

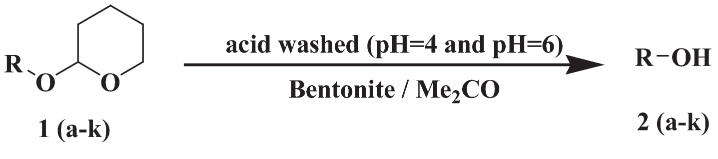
### *Preparation of activated bentonite*[9,10]

Bentonite is a commercially available (Sigma-Aldrich) colloidal clay which consists primarily of montmorillonite. The molecular formula is $H_2Al_2O_6Si$ and molecular weight 180.1 g mol$^{-1}$. The size of the bentonite was 0.3 nm.

To the bentonite (5 g) in distilled water (20 mL), heated at 80 °C, was added dropwise sulfuric acid (0.1 mL) and maintained at this temperature for 12 h. The reaction mixture was cooled and then filtered. Bentonite was washed several times with distilled water until it reached pH=4. By similar treatment bentonite pH=6 was prepared. Acid-washed bentonite was heated at reduced pressure in a furnace at 100 °C for 8 h, then cooled and crushed.

### *Dehydropyranylation*

Tetrahydropyranyl ether (0.37 mmol) in acetone (2 mL) and bentonite (pH=4 or pH=6) were heated gently (40–50 °C) for 5–90 min. The progress of the reaction was monitored by TLC. The reaction mixture was cooled and filtered. The filtrate was chromatographed (eluant hexane: ether 7: 3) over silica gel to obtain the respective alcohol whose identity was confirmed by comparing its spectroscopic data with alcohol commercially available.

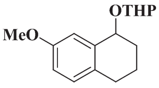
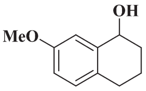
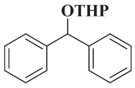
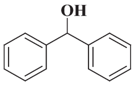
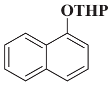
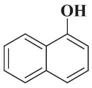
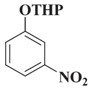
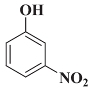
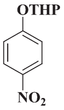
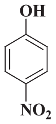
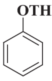
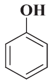
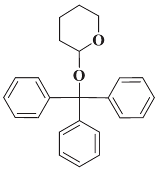
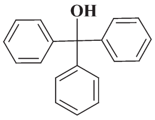
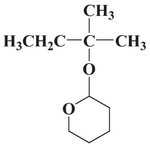
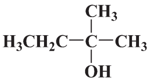
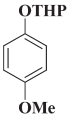
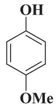
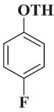
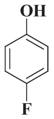
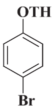
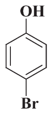


**Scheme 1** Deprotection of tetrahydropyranyl ethers with acid-washed bentonite.

---

* Correspondent. E-mail: abanerje@ivic.gob.ve

**Table 1** Deprotection of tetrahydropyronyl ethers using acid-washed bentonite[a,b,c]

| Entry | THP (**1**) | Alcohol (**2**) M.p. (lit.) | Time period /min pH=6 | yield | Time period /min pH=4 | Yield/% |
|---|---|---|---|---|---|---|
| **a** |  | <br>Low melting solid | 90 | 100 | 5 | 65 |
| **b** |  | <br>m.p. 64–67°C (65–67°C) | 70 | 73 | 30 | 42.6 |
| **c** |  | <br>m.p. 94–97°C (95–96°C) | 20 | 95 | 10 | 100 |
| **d** |  | <br>m.p. 95–98°C (96–98°C) | 70 | 53 | 50 | 97 |
| **e** |  | <br>m.p. 114–116°C (112–115°C) | 20 | 39 | 20 | 86.7 |
| **f** |  | <br>m.p. 42–45°C (40–42°C) | 10 | 91 | 5 | 65 |
| **g** |  | <br>m.p. 159–162°C (159–162) | 90 | 39 | 10 | 100 |
| **h** |  |  $\mathrm{H_3CH_2C{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_3}$<br>Oil (b.p.102°C) | 60 | – | 40–50 | 10 |
| **i** |  | <br>m.p. 54–57°C (55–57°) | 20–60 | – | 10 | 92 |
| **j** |  | <br>m.p. 44–47°C (46–48°C) | 42 | 30 | 20 | 100 |
| **k** |  | <br>m.p. 63–66°C (64–68°) | 20 | 32 | 60 | 2 |

[a] The products were characterised by comparison with known samples.
[b] Yields refer to isolated products.
[c] m.p. and b.p. of the commercially available alcohols are noted in parentheses.

*Received 14 June 2011; accepted 11 August 2011*
*Paper 1100751 doi: 10.3184/174751911X13133127427965*

## References

1 P.J. Kocienski, *Protecting groups*, eds D. Ender, R. Nayori and B. Trost, Georg Thieme Verlag, Strttgart, 1994.
2 T.W. Greene and P.G.M. Wutts, *Protective groups in organic synthesis*, 3rd edn, John Wiley and Sons: New York, 1991.
3 I. Mohammadpoor-Baltork, B. Kharmesh and S. Kolagar, *Synth.Commun.*, 2002, **32**, 1633.
4 R. Cruz-Almanza, F.J. Perez-Flores and M. Avila, *Synth.Commun.*, 1990, **20**, 1125.
5 P.S. Poon, A.K. Banerjee, L. Bedoya, M.S. Laya, E.V. Cabrera and K. Albornoz, *Synth. Commun*., 2009, **39**, 3369.
6 D.B.G. Williams, S.B. Simelane, M. Lawton, H.H. Knife, *Tetrahedron*, 2010, **66**, 4573.
7 A. Semwal, S.K. Nayak, *Synthesis*, 2005, **1**, 71.
8 L. Tong-Shuang, Z. Zhan-Hui, J. Tong-Shou, *Synth. Commun*., 1999, **29**, 181.
9 B. Makhoukhi, M.A. Didi, D. Villlemin and A. Azzouz, *Grasas Aceites*, 2009, **60**, 343.
10 M.A. Didi, B. Makhoukhi, A. Azzouz and D. Villemin, *Appl.Clay Sci.*, 2009, **42**, 336.