



## Useful methods for the synthesis of isopropylidenes and their chemoselective cleavage

Khiangte Vanlaldinpuia, Ghanashyam Bez \*

Department of Chemistry, North Eastern Hill University, Shillong 793022, India

### ARTICLE INFO

#### Article history:

Received 3 March 2011

Revised 11 May 2011

Accepted 12 May 2011

Available online 19 May 2011

#### Keywords:

Phosphotungstic acid

Isopropylidenation

Deisopropylidenation

Chemoselective

### ABSTRACT

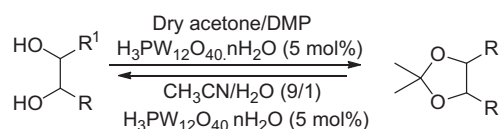
A catalytic amount of phosphotungstic acid (PTA) has been found to be a very effective catalyst for isopropylidenation of 1,2-diols and their deprotection at room temperature. The ease of handling, cost and activity of the catalyst, good to excellent yields and chemoselectivity for deprotection are some of the highlights of the reported method.

© 2011 Elsevier Ltd. All rights reserved.

The synthesis and cleavage of isopropylidene acetals are one of the most practised reaction protocols in organic synthesis due to its unflappable synonymy with manipulations in the chemistry of carbohydrates, nucleosides and alkaloids.<sup>1</sup> Due to its easy introduction and remarkable stability in alkaline pH, the chemistry of isopropylidene acetals of carbohydrates are finding importance in the field of natural product synthesis<sup>2</sup> and catalysis,<sup>3</sup> as their chiral backbone contributes to stereoselective inductions to achieve greater asymmetric molecular complexity. As a result, numerous methods using acid catalysts<sup>1b</sup> have been developed. Among the Brønsted acids, concentrated H<sub>2</sub>SO<sub>4</sub> is used very routinely as catalyst for the synthesis of *O*-isopropylidenes, *albeit* modified catalysts, such as CuSO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> and sulfuric acid immobilized on silica gel<sup>5</sup> under reflux condition in anhydrous acetone are also reported. Several in-situ generated acid catalysts, such as iodine,<sup>6</sup> triphenylphosphine polymer bound/iodine complex<sup>7</sup> and bromodimethyl sulfonium bromide (BDMS)<sup>8</sup> were also effectively employed for this transformation. Recently, Chen and co-workers<sup>9</sup> employed water tolerant vanadyl triflate (VO(OTf)<sub>2</sub>·xH<sub>2</sub>O) for isopropylidenation of 1,2- and 1,3-diols in carbohydrates in the presence of acetonide-forming solvents, such as dry acetone, 2,2-dimethoxypropane (DMP), or 2-methoxy propene (MP) to achieve significant improvement. Among the Lewis acids, anhydrous ZnCl<sub>2</sub><sup>10</sup> is commonly used as catalyst for the protection of diols in carbohydrates, *albeit* many other catalysts, such as FeCl<sub>3</sub>,<sup>11</sup> AlCl<sub>3</sub>,<sup>12</sup> and Ceric ammonium nitrate (CAN)<sup>13</sup> have been reported for similar transformation in acetone. For efficient catalyst recovery, solid catalysts, such as

Zeolite HY<sup>14</sup> and montmorillonite clay<sup>15</sup> were also employed to achieve excellent yields. There is no denying the fact that many of the reported catalysts require preparation,<sup>4,5,7,8</sup> while some of them are costly<sup>9,14</sup> and require extreme conditions.<sup>5,10,12</sup> Herein, we wish to report a reaction protocol for the protection of 1,2-diols as acetonide with a catalytic amount of phosphotungstic acid (PTA) and their deacetonation with the same catalytic system in the presence of acetonitrile and water (Scheme 1).

While working on the synthesis of Shi's ketone,<sup>16</sup> a catalyst which is finding very good applications in stereoselective epoxidation of olefins in recent years, we wanted to explore the possibility of using phosphotungstic acid (PTA) as catalyst for isopropylidenation of fructose instead of routinely used concentrated H<sub>2</sub>SO<sub>4</sub>. We reasoned that use of PTA will substantially simplify the purification process as filtration of the solid would be enough to get the pure product. To that affect, a suspension of D-fructose (1 mmol) in dry acetone (5 mL) and PTA (5 mol %) was stirred at room temperature under argon atmosphere until the sugar had dissolved. After completion of the reaction, it was observed that the catalyst forms a gummy mass to stick on the wall inside the reaction flask and could not be recovered as proposed. Therefore, the solution was

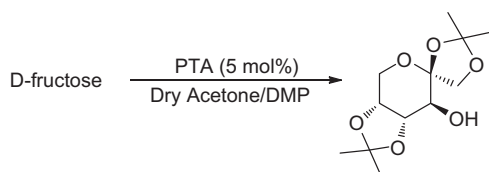


Scheme 1.

\* Corresponding author.

E-mail addresses: [ghanashyambez@yahoo.com](mailto:ghanashyambez@yahoo.com), [bez@nehu.ac.in](mailto:bez@nehu.ac.in) (G. Bez).

**Table 1**  
Acetonide protection of D-fructose<sup>a</sup>



| Entry | Catalyst                                                                            | Solvent              | Time (h)          | Yield <sup>b</sup> (%) |
|-------|-------------------------------------------------------------------------------------|----------------------|-------------------|------------------------|
| 1     | H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> ·xH <sub>2</sub> O                  | Acetone              | 2                 | 31                     |
| 2     |                                                                                     | Acetone              | 5                 | 56                     |
| 3     |                                                                                     | Acetone <sup>c</sup> | 5                 | 55                     |
| 4     |                                                                                     | Acetone              | 10                | 55                     |
| 5     |                                                                                     | Acetone              | 15                | 52                     |
| 6     | H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> ·xH <sub>2</sub> O-SiO <sub>2</sub> | DMP                  | 4                 | 67                     |
| 7     |                                                                                     | DMP <sup>c</sup>     | 4                 | 66                     |
| 8     |                                                                                     | DMP <sup>d</sup>     | 4                 | 71                     |
| 9     |                                                                                     | DMP                  | 5                 | 45                     |
| 10    |                                                                                     | Acetone              | 5                 | 15                     |
| 11    |                                                                                     | Acetone              | 15 <sup>e</sup>   | 26                     |
| 12    |                                                                                     | Acetone              | 15 <sup>c,e</sup> | 31                     |

<sup>a</sup> Unless otherwise stated typical reaction conditions: substrate (1 mmol), dry acetone (5 mL), catalyst (5 mol %).

<sup>b</sup> Isolated yields.

<sup>c</sup> 10 mol % of the catalyst was used.

<sup>d</sup> Substrate (1 mmol), DMP (2 mmol), Acetone (5 mL), catalyst (5 mol %).

<sup>e</sup> Reaction stops automatically after the substrate got dissolved completely.

decanted, dried under reduced pressure, and redissolved in CH<sub>2</sub>Cl<sub>2</sub>. The dichloromethane solution was washed with water, dried with Na<sub>2</sub>SO<sub>4</sub>, and evaporated to get the crude product, which was recrystallized by dissolving in boiling ether (5 mL/g), cooling, and then adding hexane (5 mL/g) to give the pure product in 31% yield. As the reaction protocol was very simple, we decided to optimize some parameters, viz. temperature, solvent, catalyst ratio to enhance the yields of the said reaction. When the solvent was changed to 2, 2-dimethoxypropane (DMP) keeping the other parameters constant, we found substantial increase in the reaction yield (67%). Our findings are summarized in Table 1.

It is quite evident from the Table 1 that reaction yields are better, when DMP was used as a solvent and PTA was used as catalyst, while in acetone yields are around 55% in all the cases. While keeping the catalyst concentration constant (5 mol %), the increase in reaction time from 5 h to 10 h did not help both in anhydrous acetone and DMP. Interestingly, the reaction worked even better (entry 8, Table 1), when DMP (2 equiv) in dry acetone was used as solvent. When the catalyst was adsorbed on silica to enhance the surface area of the catalyst, we encountered rather an unexpected observation, wherein the reaction yields drop considerably (Table 1, entry 9–12). As the yields found in acetone and DMP-acetone differ considerably in D-fructose, we decided to test the isopropylidenation of various diols in both the solvents.<sup>17</sup> It is observed that for carbohydrates, the extent of isopropylidenation is much better in DMP-acetone than in anhydrous acetone alone (entry 1–5, Table 2). All the carbohydrates were undergoing isopropylidenation at room temperature within reasonable time (5–10 h) in anhydrous acetone, while the reaction took comparatively shorter time in DMP-acetone. Protection of D-mannose (entry 1) with acetone gave 2,3:5,6-di-O-isopropylidene-D-mannofuranose in good yield (62%) but D-glucose (entry 2) and D-galactose (entry 3) gave only 48% and 46% yield, respectively, which may be due to the low solubility of the starting materials in acetone. Likewise D-fructose gave 1,2:4,5-di-O-isopropylidene-β-D-fructopyranose, **4a** in 57% when the reaction was stopped after 7 h. Among the carbohydrates tested, D-mannitol (entry 5) gave the best result with 75% yield in acetone and D-mannose (entry 1) gave the best yield (89%) in DMP-acetone when other parameters are similar. When this

method was extrapolated beyond carbohydrates, the diols (entry 6–12, Table 2) gave excellent yields in both anhydrous acetone and in DMP-acetone. More importantly, several acid sensitive functional groups, such as THP, Bn, and OC<sub>3</sub>H<sub>7</sub> were not affected at all under our reaction conditions, as reflected in the yields of the reactions. For open chain 1,2-diols, all the reactions complete within 1 h. Keeping the reaction longer than 2 h in acetone medium resulted in decreased yield due to possible hydrolysis of the product, while in DMP-acetone no such observation was made.

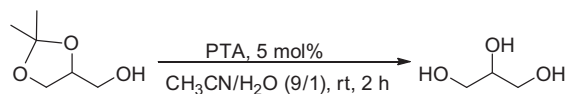
As stated earlier, deprotection of acetonide is also another very important aspect in organic synthesis. In fact, many chiral natural products have been synthesized using monoisopropylidene derivatives of D-mannose and D-glucose.<sup>18</sup> Given the fact that many isopropylidene acetals are remarkably stable in comparison to other functional groups that cannot withstand drastic hydrolysis conditions,<sup>19</sup> many methods had been reported for the deprotection of acetonides in order to develop efficient and chemoselective protocols.<sup>1b</sup> Some of the reagents frequently used include protic conditions<sup>20</sup>, such as aq HCl, aq HBr, 60% aq acetic acid, 0.8% H<sub>2</sub>SO<sub>4</sub> in MeOH, TFA, Nafion-H, Dowex 50 W-X8, and p-TsOH. Lewis acids<sup>21</sup> such as CuCl<sub>2</sub>·2H<sub>2</sub>O in ethanol, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, CeCl<sub>3</sub>·7H<sub>2</sub>O/(COOH)<sub>2</sub>, BiCl<sub>3</sub>, InCl<sub>3</sub>, Er(OTf)<sub>3</sub>, Yb(OTf)<sub>3</sub>·H<sub>2</sub>O, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, VCl<sub>3</sub> and Iodine were also employed and a few supported reagents<sup>22</sup>, such as FeCl<sub>3</sub>·6H<sub>2</sub>O/SiO<sub>2</sub>, NaHSO<sub>4</sub>/SiO<sub>2</sub>, PMA/SiO<sub>2</sub>, polymer supported FeCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>·SiO<sub>2</sub>, and HClO<sub>4</sub>/SiO<sub>2</sub> were also reported. But, as always, some of them require high catalyst loading, long reaction time, and high temperature. Recently, Gregg and co-workers<sup>23</sup> reported the use of In(OTf)<sub>3</sub> as catalyst for chemoselective deprotection of terminal acetonide in the presence of internal acetonides under microwave irradiation. But use of costly In(OTf)<sub>3</sub> and high temperature necessarily negates the usefulness of the method, especially when such deprotection can be carried out at room temperature. Here, we report our findings in the deprotection of acetonides using phosphotungstic acid as a catalyst in acetonitrile-water medium.

Initially, dl-1,2-isopropylideneglycerol (1 mmol) was dissolved in CH<sub>3</sub>CN:H<sub>2</sub>O (9:1) and to it 5 mol % of phosphotungstic acid was added (Scheme 2). The reaction mixture was allowed to stir at room temperature and the progress of the reaction was monitored using TLC. It was found that the starting material was completely converted after 2 h of stirring. As for the catalyst, 5 mol % PTA was found optimum, while reduction of catalyst ratio enhances the reaction time. Use of PTA/SiO<sub>2</sub> as catalyst while keeping other parameters unchanged, hydrolysis of dl-1,2-isopropylideneglycerol completes within 5 min. As for di-O-isopropylidenes, very clear chemoselective pattern was observed wherein all terminal isopropylidenes are preferentially deprotected. Deprotection of 1,2:5,6-di-O-isopropylidene-α-D-glucopyranose (entry 7) and its derivatives (entry 8 and 9, Table 3) resulted in deprotection of terminal acetonides<sup>24</sup> in excellent yield. Interestingly, increase in reaction time to 24 h resulted in complete hydrolysis of the isopropylidenes. As **1a** reportedly undergoes hydrolysis to form an inseparable mixture<sup>25</sup> of 2,3-O-isopropylidene-D-mannofuranose and 2,3-O-isopropylidene-D-mannopyranose, we carried out deisopropylidenation of 1-O-benzyl derivative of 2,3:5,6-di-O-isopropylidene-D-mannofuranose (entry 11, Table 3) in our reaction condition,<sup>26</sup> to find that the terminal 5,6-O-isopropylidene ring cleaves in preference to the 2,3-O-isopropylidene moiety in excellent yields (94%) within 2 h. On the other hand, the 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**3a**) undergoes complete hydrolysis under the reaction conditions and gave the starting D-galactose quantitatively. Interestingly, for Shi's ketone (entry 13, Table 3), upon hydrolysis in our reaction conditions generated the 4,5-deprotected mono-O-isopropylidene derivative, **13b**<sup>27</sup> suggesting that spiro-fused isopropylidene moiety is more stable than the internal isopropylidene acetal ring. When we tried to see the

**Table 2**Preparation of acetonides using PTA as a catalyst<sup>a</sup>

| Entry | Substrate  | Product <sup>b</sup> | Solvent <sup>c</sup> | Time (h) | Yield <sup>d</sup> (%) | Ref. (reported yield %) |
|-------|------------|----------------------|----------------------|----------|------------------------|-------------------------|
| 1     |            |                      | Acetone<br>DMP       | 5<br>5   | 62<br>89               | 8 (95)                  |
| 2     |            |                      | Acetone<br>DMP       | 10<br>7  | 48<br>86               | 14 (50)                 |
| 3     |            |                      | Acetone<br>DMP       | 10<br>7  | 46<br>85               | 14 (20)                 |
| 4     | D-Fructose |                      | Acetone<br>DMP       | 7<br>4   | 57<br>71               | 30 (58)                 |
| 5     |            |                      | Acetone<br>DMP       | 7<br>5   | 75<br>88               | 8 (89)                  |
| 6     |            |                      | Acetone<br>DMP       | 1<br>0.5 | 89 <sup>e</sup><br>92  |                         |
| 7     |            |                      | Acetone<br>DMP       | 1<br>0.5 | 81<br>86               |                         |
| 8     |            |                      | Acetone<br>DMP       | 1<br>0.5 | 91<br>94               |                         |
| 9     |            |                      | Acetone<br>DMP       | 1<br>0.5 | 91<br>92               | 31 (78)                 |
| 10    |            |                      | Acetone<br>DMP       | 1<br>1   | 78<br>82               |                         |
| 11    |            |                      | Acetone<br>DMP       | 1<br>1   | 94<br>92               |                         |
| 12    |            |                      | Acetone<br>DMP       | 1<br>1   | 89<br>87               |                         |

<sup>a</sup> Typical reaction conditions: substrate (1.0 mmol), solvent (5 mL) and PTA (5 mol %).<sup>b</sup> All products were characterized by <sup>1</sup>H and <sup>13</sup>C NMR and mass spectroscopy.<sup>c</sup> DMP refers to 2 equiv DMP in dry acetone.<sup>d</sup> Isolated yields.<sup>e</sup> Confirmed by comparing with commercially available authentic sample.



Scheme 2.

deisopropylidenation of 1,2: 3,5-di-*O*-isopropylidene-*D*-xylose (entry 14, Table 3) under our reaction condition, we observed that 3,5-*O*-isopropylidene moiety cleaves selectively, making clear indication that 1,3-dioxane moiety is comparatively labile<sup>28</sup> to this acid catalyst than the corresponding 1,3-dioxolane moiety.

**Table 3**  
Deprotection of acetonides using PTA as a catalyst<sup>a</sup>

| Entry | Substrate | Product        | Time (h)       | Isolated yield (%) <sup>b</sup> | Ref. (reported yield %) |
|-------|-----------|----------------|----------------|---------------------------------|-------------------------|
| 1     |           | <br><b>1b</b>  | 2              | 99 <sup>c</sup>                 |                         |
| 2     |           | <br><b>2b</b>  | 5              | 89 <sup>c</sup>                 |                         |
| 3     |           | <br><b>3b</b>  | 1              | 87                              |                         |
| 4     |           | <br><b>4b</b>  | 1              | 79                              |                         |
| 5     |           | <br><b>5b</b>  | 1              | 89                              |                         |
| 6     |           | <br><b>6b</b>  | 1              | 82                              |                         |
| 7     |           | <br><b>7b</b>  | 4              | 95                              | 24a (81)                |
| 8     |           | <br><b>8b</b>  | 5              | 93                              | 24c (87)                |
| 9     |           | <br><b>9b</b>  | 5              | 88                              | 32 (70)                 |
| 10    |           | <br><b>10b</b> | 5              | 90                              | 21b (97)                |
| 11    |           | <br><b>11b</b> | 2              | 94                              | 21h (92)                |
| 12    |           | <br><b>12b</b> | 3 <sup>c</sup> | -                               | —                       |

Table 3 (continued)

| Entry | Substrate | Product | Time (h)       | Isolated yield (%) <sup>b</sup> | Ref. (reported yield %) |
|-------|-----------|---------|----------------|---------------------------------|-------------------------|
| 13    |           |         | 2 <sup>d</sup> | 83                              | 27 (79)                 |
| 14    |           |         | 2              | 93                              | 24a (91)                |

<sup>a</sup> Typical reaction conditions: substrate (1 mmol), acetonitrile/water (2 mL, 9:1 v/v), PTA (5 mol %), room temperature unless otherwise stated.

<sup>b</sup> The products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, Mass and IR spectroscopy and compared with the literature data.

<sup>c</sup> Complete hydrolysis led to generation of D-galactose.

<sup>d</sup> 10 mol % catalyst was used.

<sup>e</sup> Confirmed by comparing with commercially available authentic sample.

Nevertheless, for most of the carbohydrate derived isopropylidenes, the spiro-fused isopropylidene moiety was very stable toward our reaction conditions than both the internal and terminal isopropylidenes. It has also been observed that the reaction condition is very much compatible toward acid labile functionalities, such as OTHP (entry 3, Table 3), OBn (entry 4, 8, Table 3), OAc (entry 9, Table 3) and OBz (entry 10, Table 3). It is interesting to note that the OTBS group, *albeit* being more labile than isopropylidenes under acidic conditions<sup>29</sup> was not hydrolyzed in our reaction conditions and gave considerably good yield of the deisopropylidene product (entry 6, Table 3).

In summary, we have developed a simple, efficient, and catalytic method for preparation and removal of *O*-isopropylidenes from 1,2-diols using a catalytic amount of phosphotungstic acid (PTA) as a new catalyst. The same catalyst system was found to be extremely efficient for chemoselective deacetonation of terminal isopropylidenes in the presence of internal isopropylidenes upon changing the solvent to acetonitrile–water. Non-toxicity, availability and low cost of the catalyst; easy handling, purification and high yields of this protocol are expected to attract attention of the wider synthetic community.

## Acknowledgments

Thanks are due to UGC, New Delhi [(Grant No. 31-54/2005 (SR))], CSIR, New Delhi [Grant No. 01(1992)/05/EMR-II] and DST, New Delhi [Grant No. SR/S1/OC-25/2007] for providing financial support to carry out this work. SAIF, NEHU is acknowledged for the analytical data.

## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.05.050.

## References and notes

- (a) Green, T. W.; Wuts, P. G. M. *Protecting Groups in Organic Synthesis*, fourth ed.; Wiley & Sons: New York, 2007. pp 306; (b) Kocienski, P. J. *Protecting Groups*, first ed.; Georg Thieme Verlag: Stuttgart, 2003. pp 120.
- (a) Lichtenthaler, F. W. Carbohydrate Synthons in Natural Products Chemistry, ACS Symposium Series, 2002, Volume 841, Chapter 4, pp 47; (b) Yeung, K.-S.; Paterson, I. *Chem. Rev.* **2005**, *105*, 4237; (c) Sengoku, T.; Satoh, Y.; Takahashi, M.; Yoda, H. *Tetrahedron Lett.* **2009**, *50*, 4937.
- Diéguez, M.; Pámies, O.; Claver, C. *Chem. Rev.* **2004**, *104*, 3189–3215.
- Hering, K. W.; Karaveg, K.; Moremen, K. W.; Pearson, W. H. *J. Org. Chem.* **2005**, *70*, 9892.
- Rajput, V. K.; Mukhopadhyay, B. *Tetrahedron Lett.* **2006**, *47*, 5939.
- Kartha, K. P. R. *Tetrahedron Lett.* **1986**, *27*, 3415.
- Silvana, P.; Annalisa, G.; Daniele, D.; Mauro, D. N.; Giovanni, P. *Synthesis* **2006**, 305.
- Khan, A. T.; Khan, M. M. *Carbohydr. Res.* **2010**, *345*, 154.
- Lin, C.-C.; Jan, M.-D.; Weng, S.-S.; Lin, C.-C.; Chen, C.-T. *Carbohydr. Res.* **2006**, *341*, 1948.
- Schmidt, O. *Th. Methods Carbohydr. Chem.* **1963**, *2*, 318.
- Singh, P. P.; Gharia, M. M.; Dasgupta, F.; Srivastava, H. C. *Tetrahedron Lett.* **1977**, *5*, 439.
- Lal, B.; Gidwani, R. M.; Rupp, R. H. *Synthesis* **1989**, 711.
- Manzo, E.; Barone, G.; Parrilli, M. *Synlett* **2000**, 887.
- Rauter, A. P.; Ramôa-Ribeiro, F.; Fernandes, A. C.; Figueiredo, J. A. *Tetrahedron* **1995**, *51*, 6529.
- Asakura, J.-I.; Matsubara, Y.; Yoshihara, M. *J. Carbohydr. Chem.* **1996**, *15*, 231.
- Tu, Y.; Wang, Z.-X.; Shi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9806.
- Typical procedure for isopropylidenation of 1, 2-diols: A suspension of the substrate (1 mmol) in dry acetone (5 mL)/2,2-dimethoxypropane (2 mmol) in dry acetone (5 mL) was added 5 mol % of phosphotungstic acid and was stirred at room temperature under nitrogen atmosphere for the specific time given in Table 2. After completion of the reaction, the solvent was removed under reduced pressure. The residue was extracted with dichloromethane (3 × 20 mL) and water and the combined organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum to give the crude product. The crude product was purified by column chromatography on Silica gel (60–120 mesh) with 15–30% ethylacetate in hexane as eluent.
- Szabo, W. A.; Lee, H. T. *Aldrichimica Acta* **1980**, *13*, 13.
- (a) Barone, G.; Bedini, E.; Iadonisi, A.; Manzo, E.; Parrilli, M. *Synlett* **2002**, 1645; (b) Chen, M.-Y.; Lu, K. C.; Lee, A. S.-Y.; Lin, C.-C. *Tetrahedron Lett.* **2002**, *43*, 2777; (c) Chen, M.-Y.; Patkar, L. N.; Lu, K. C.; Lee, A. S.-Y.; Lin, C.-C. *Tetrahedron* **2004**, *60*, 11465.
- (a) Fleet, G. W. J.; Smith, P. W. *Tetrahedron Lett.* **1985**, *26*, 1469; (b) Gerspacher, M.; Rapoport, H. *J. Org. Chem.* **1991**, *56*, 3700; (c) Yadav, J. S.; Chander, M. C.; Reddy, K. K. *Tetrahedron Lett.* **1992**, *33*, 135; (d) Sukumar, M.; Jacques, V.; Pendri, Y.; Falck, J. R. *Tetrahedron Lett.* **1986**, *27*, 2679; (e) Lablance, Y.; Fitzsimmons, J.; Adams, E. P.; Rokacha, J. *J. Org. Chem.* **1986**, *51*, 789; (f) Rawal, G. K.; Rani, S.; Kumar, A.; Vankar, Y. D. *Tetrahedron Lett.* **2006**, *47*, 9117; (g) Park, K. H.; Yoon, Y. J.; Lee, S. G. *Tetrahedron Lett.* **1994**, *35*, 9737; (h) Ichihara, M. U.; Sakamura, S. *Tetrahedron Lett.* **1977**, *18*, 3473.
- (a) Iwata, M.; Ohnui, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2837; (b) Vijayasaradhi, S.; Singh, J.; Aidhen, I. S. *Synlett* **2000**, 110; (c) Xiao, X.; Bai, D. *Synlett* **2001**, 535; (d) Swamy, N. R.; Venkateswarlu, Y. *Tetrahedron Lett.* **2002**, *43*, 7549; (e) Pfengle, F.; Dekaris, V.; Schefzig, L.; Zimmer, R.; Reissig, H.-U. *Synlett* **2008**, *19*, 2965; (f) Procopio, A.; Gaspari, M.; Nardi, M.; Oliverio, M.; Romeo, R. *Tetrahedron Lett.* **2008**, *49*, 1961; (g) Yadav, J. S.; Reddy, B. V. S.; Reddy, S. K. *Chem. Lett.* **2001**, 430; (h) Reddy, S. M.; Reddy, V.; Venkateswarlu, Y. *Tetrahedron Lett.* **2005**, *46*, 7439; (i) Sabitha, G.; Reddy, G. S. K. K.; Reddy, K. B.; Reddy, N. M.; Yadav, J. S. *J. Mol. Catal.* **2005**, *238*, 229; (j) Yadav, J. S.; Satyanarayana, M.; Raghavendra, S.; Balanarsaiah, E. *Tetrahedron Lett.* **2005**, *46*, 8745.
- (a) Kim, K. S.; Song, Y. H.; Lee, B. H.; Hahn, C. S. *J. Org. Chem.* **1986**, *51*, 404; (b) Mahender, G.; Ramu, R.; Ramesh, C.; Das, B. *Chem. Lett.* **2003**, 734; (c) Yadav, J. S.; Raghavendra, S.; Satyanarayana, M.; Balanarsaiah, E. *Synlett* **2005**, 2461; (d) Chari, M. A.; Syamasundar, K. *Synthesis* **2005**, 708; (e) Agarwal, A.; Vankar, Y. D. *Carbohydr. Res.* **2005**, *340*, 1661.
- Golden, K. C.; Gregg, B. T.; Quinn, J. F. *Tetrahedron Lett.* **2010**, *51*, 4010.
- (a) Ates, A.; Gautier, A.; Leroy, B.; Plancher, J.-M.; Yannick, Q.; Vanherck, J.-C.; Marko, I. E. *Tetrahedron* **2003**, *59*, 8989; (b) Meyer, A. S.; Reichstein, T. *Helv. Chim. Acta* **1946**, *29*, 152; (c) Fleet, G. W.; Witty, D. R. *Tetrahedron: Asymmetry* **1990**, *1*, 119; (d) Czernecki, S.; Georgoulis, C.; Stevens, C. L.; Vijaykumaran, R. *Tetrahedron Lett.* **1985**, *26*, 1699.

25. Bhaskar, P. M.; Mathiselvam, M.; Loganathan, D. *Carbohydr. Res.* **2008**, 343, 1801.
26. *Typical procedure for deprotection of isopropylidenes*: The substrate (1 mmol) was dissolved in acetonitrile/water mixture (2 mL, 9:1 v/v) and to it was added phosphotungstic acid (5 mol %). The mixture was stirred at room temperature for the appropriate time. After completion of the reaction, the solvent was removed under reduced pressure. The residue was directly purified by using column chromatography on silica gel (60–120 mesh) with 50–100% ethylacetate in hexane as eluent to get the product.
27. Wu, X.-Y.; She, X.; Shi, Y. *J. Am. Chem. Soc.* **2002**, 124, 8792.
28. Diner, U. E.; Brown, R. K. *Canadian J. Chem.* **1967**, 45, 1297.
29. Kishore Kumar, G. D.; Baskaran, S. *J. Org. Chem.* **2005**, 70, 4520.
30. Mio, S.; Kumagawa, Y.; Sugai, S. *Tetrahedron* **1991**, 47, 2133.
31. Kitchin, J.; Borthwick, A. D.; Brodie, A. C.; Cherry, P. C.; Crame, A. J.; Pipe, A. J.; Procopiou, P. A.; Seaman, M. A.; Turnbull, J. P. *Bioorg. Med. Chem.* **1995**, 3, 1595.
32. Smanathan, R.; Hellberg, L. H. *Org. Prep. Proced. Int.* **1984**, 16, 388.