Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron Letters
Tetrahedron Letters 47 (2006) 6095–6098

Phosphomolybdic acid supported on silica gel: a mild, efficient and reusable catalyst for the synthesis of 2,3-unsaturated glycopyranosides by Ferrier rearrangement

J. S. Yadav,* M. Satyanarayana, E. Balanarsaiah and S. Raghavendra

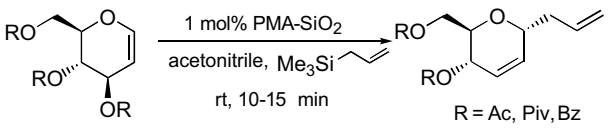
Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received 12 May 2006; revised 7 June 2006; accepted 15 June 2006

Abstract—A simple, mild, efficient and environmentally benign method for the synthesis of 2,3-unsaturated allyl C-glycosides and O- and S-glycosides is described using phosphomolybdic acid supported on silica gel as a reusable catalyst with high α-selectivity.

Phosphomolybdic acid (PMA) belongs to the class of heteropoly acids (HPA). Catalysis using HPAs and related polyoxometalate compounds is a field of growing importance.[1] HPAs are commercially cheap and environmentally friendly catalysts. They exhibit high activities and selectivities and allow cleaner processes than conventional catalysts. HPAs are promising solid acid, redox and bifunctional catalysts under homogeneous as well as in heterogeneous conditions. HPAs are very strong acids, approaching the superacid region, with a Brönsted acidity greatly exceeding that of ordinary mineral acids and solid acid catalysts. HPAs are several times more active than H_2SO_4, TsOH, $BF_3{\cdot}Et_2O$ and $ZnCl_2$.[2] It has been shown that in organic media, the molar catalytic activity of HPAs is often 100–1000 times higher than that of H_2SO_4.[3] This makes it possible to carry out a catalytic process at low concentrations and at lower temperatures. Supported HPAs are more active than typical solid acids. Acidic or neutral substances such as silica gel,[2] active carbon[4a,b] or an acidic ion-exchange resin[4c] are suitable supports, the more commonly used being silica gel.[2] Synthetically, a variety of methods have been developed and commercialized using HPAs as catalysts.[5] For example, Fries rearrangement of phenyl acetate,[6a] Friedel–Crafts acylation of phenols,[6b] oxidation of alcohols,[6c] regioselective ring opening of aziridines,[6d] chemoselective deprotection of isopropylidene acetals[6e] and chemoselective hydrolysis of *tert*-butyldimethylsilyl ethers[6f] have been reported using HPAs. The synthesis of glycosides using HPAs as catalysts is of great industrial importance.[7] Acetylated monosaccharides interact readily with alcohols in the presence of 2% HPA to yield glycosides,[8] which are used as a new, effective and biodegradable surfactants.

The acid-catalyzed allylic rearrangement of glycals in the presence of nucleophiles such as alcohols, and thiols, a process known as Ferrier rearrangement,[9] is widely employed to obtain 2,3-unsaturated glycosides. Allyl C-glycosides are attractive synthons due to the presence of terminal double bond that is amenable to easy functionalization, for instance, by hydroxylation, hydrogenation, epoxidation and aminohydroxylation. These glycosides or pseudoglycals represent versatile chiral intermediates for the synthesis of modified carbohydrates and nucleosides with important pharmacological properties.[10] This class of compounds can be transformed into 2-deoxy or 2,3-dideoxy sugars, which are building blocks for the total synthesis of many antibiotics.[11] Several strong Lewis acids[12] such as $BF_3{\cdot}Et_2O$,



Scheme 1.

Keywords: Allyl C-glycosides; Ferrier rearrangement; Phosphomolybdic acid; Silica gel.
* Corresponding author. Tel.: +91 40 2719 3030; fax: +91 40 2716 0387; e-mail: yadavpub@iict.res.in

0040-4039/$ - see front matter
doi:10.1016/j.tetlet.2006.06.084

Table 1. Synthesis of 2,3-unsaturated glycosides by PMA–SiO_2 catalyzed Ferrier rearrangement

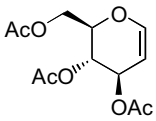
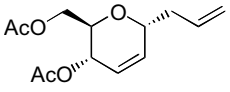
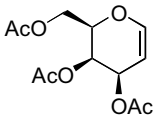
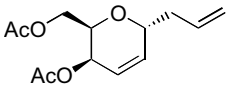
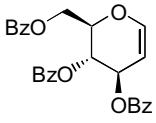
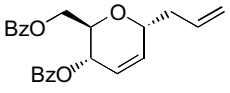
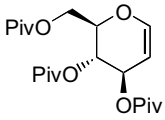
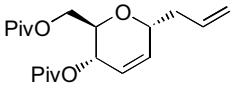
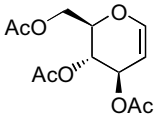
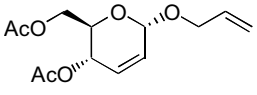
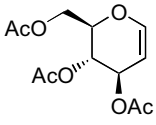
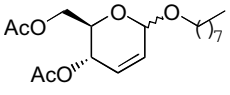
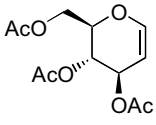
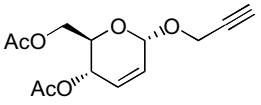
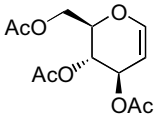
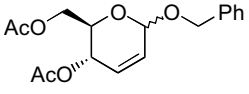
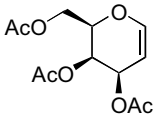
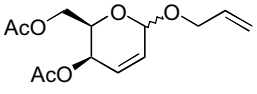
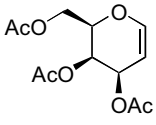
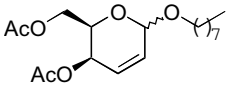
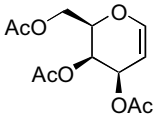
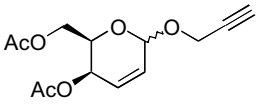
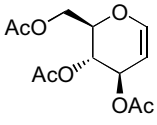
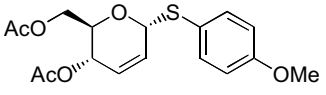
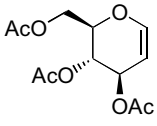
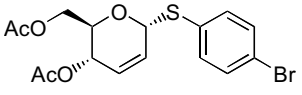
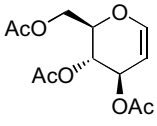
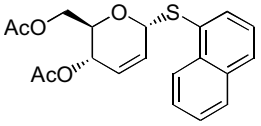
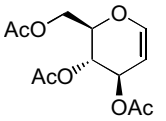
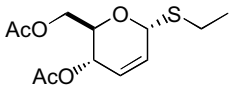
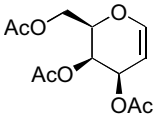
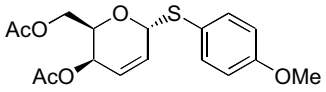
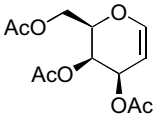
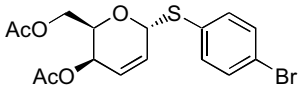
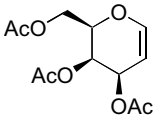
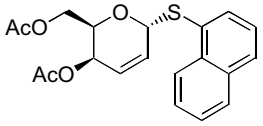
Entry	Substrate (**1**)	Product (**2**)	Time (min)	Yield[a] (%)	(α/β)[b]	Ref.
a			10	89	α	15c
b			15	90	α	15c
c			10	85	α	13e
d			15	87	α	13e
e			10	90	α	16e
f			15	93	19:1	16e
g			10	92	α	16e
h			10	89	19:1	16e
i			15	85	19:1	16e
j			15	84	19:1	16e
k			15	90	19:1	—
l			10	90	α	16e
m			10	92	α	—
n			10	90	α	—

Table 1 (*continued*)

Entry	Substrate (**1**)	Product (**2**)	Time (min)	Yield[a] (%)	(α/β)[b]	Ref.
o			10	94	α	—
p			10	88	α	—
q			10	94	α	—
r			10	90	α	—

[a] Isolated yields as pure anomeric mixtures after purification.
[b] Anomeric ratio was determined on the basis of the integrated ratios of the anomeric hydrogens in the ^{1}H NMR spectra.

$SnCl_4$, $TiCl_4$ and I_2,[13a] montmorillonite K10,[13b] DDQ,[13c] *N*-iodosuccinamide,[13d] $LiBF_4$,[13e] TMSOTf,[14a] $Sc(OTf)_3$,[14b,c] $Yb(OTf)_3$,[14d,e] indium halides,[15] $BiCl_3$,[16a] $FeCl_3$,[16b] CAN,[16c] $CeCl_3{\cdot}7H_2O$,[16d] $HClO_4$–SiO_2[16e,f] are also known to promote glycosylation of glycals. However, many of the above methods suffer from disadvantages in terms of yields, stoichiometric amounts of catalysts to be used, harsh reaction conditions, high cost of the catalysts, low stereoselectivities and in reusability of the catalysts. Therefore, there is still a need to find a potentially general method for this transformation.

In continuation of our efforts[6e] to explore the synthetic utility of phosphomolybdic acid supported on silica gel (PMA–SiO_2), herein we report the synthesis of 2,3-unsaturated allyl C-glycosides and O- and S-glycosides with PMA–SiO_2. The reaction proceeds smoothly with 1 mol % of PMA–SiO_2 at room temperature with allyltrimethylsilane. When alcohols and thiols were used instead of allyltrimethylsilane, the corresponding O- and S-glycosides were obtained in excellent yields within 10–15 min (Scheme 1 and Table 1).

In a typical experiment, a solution of triacetyl glucal and allyltrimethylsilane in acetonitrile was stirred with 1 mol % PMA–SiO_2 at room temperature. The reaction was completed within 10 min to produce exclusively the corresponding α-4,6-di-*O*-acetyl-2,3-unsaturated *C*-allyl glycoside in high yield. After the reaction was complete, the catalyst was filtered and could be reused five times without any appreciable loss in catalytic activity and yields. In all the cases studied, we obtained exclusively the α-anomer, as confirmed by spectroscopic data. Although no reaction was observed with nucleophiles such as trimethylsilyl cyanide, trimethylsilylacetylene, silyl enol ethers and β-ketoesters, 2,3-unsaturated glycopyranosides were successfully prepared with nucleophiles such as alcohols and thiols. A mixture of two anomers of 2,3-unsaturated glycopyranosides (α and β) was obtained in the case of glucal and galactal where an alcohol was the nucleophile, while exclusively α-anomers were obtained with thiols. The predominant formation of this α-anomer may arise from a thermodynamic anomeric effect.

There are several advantages to the use of PMA–SiO_2 as catalyst for this transformation, which include high α-selectivity, high yields of the products, the very small quantity of the catalyst required and its reusability.

In summary, we have shown[17] that PMA–SiO_2 is as an efficient and reusable catalyst for the synthesis of allyl C-glycosides, *O*- and *S*-glycopyranosides with high α-selectivity and high yields. The simplicity in operation, low cost of the catalyst, reusability and environmental considerations make this procedure reliable and useful.

Acknowledgements

The authors M.S.N., E.B. and S.R. thank CSIR, New Delhi, for the award of research fellowships.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.06.084.

References and notes

1. (a) Kozhevnikow, I. V. *Chem. Rev.* **1998**, *98*, 171–198; (b) Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, *98*, 199–217.

2. Izumi, Y.; Hasebe, R.; Urabe, K. *J. Catal.* **1983**, *84*, 402–409.
3. (a) Kozhevnikov, I. V. *Russ. Chem. Rev.* **1987**, *56*, 811–825; (b) Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113.
4. (a) Izumi, Y.; Urabe, K. *Chem. Lett.* **1981**, 663–666; (b) Schwegler, M. A.; van Bekkum, H.; de Munck, N. A. *Appl. Catal.* **1991**, *74*, 191–204; (c) Baba, T.; Ono, Y. *Appl. Catal.* **1986**, *22*, 321.
5. Izumi, Y.; Urabe, K.; Onaka, M. *Zeolite, Clay and Heteropoly Acid in Organic Reactions*; Kodansha/VCH: Tokyo, 1992, 99.
6. (a) Kozhevnikova, E. F.; Derouane, E. G.; Kozhevnikov, I. V. *Chem. Commun.* **2002**, 1178–1179; (b) Kaur, J.; Griffin, K.; Harrison, B.; Kozhevnikov, I. V. *J. Catal.* **2002**, *208*, 448–455; (c) Firouzabadi, H.; Iranpoor, N.; Amani, K. *Synthesis* **2003**, 408–412; (d) Kishore Kumar, G. D.; Baskaran, S. *Synlett* **2004**, *10*, 1719–1722; (e) Yadav, J. S.; Raghavendra, S.; Satyanarayana, M.; Balanarsaiah, E. *Synlett* **2005**, *16*, 2461–2464; (f) Kishore Kumar, G. D.; Baskaran, S. *J. Org. Chem.* **2005**, *70*, 4520–4523.
7. Misono, M.; Nojiri, N. *Appl. Catal.* **1990**, *64*, 1–30.
8. Kiromura, K.; Kitazawa, S.; Takata, Y.; Sakakibara, T. U.S. Patent 4,874,852, 1988. *Chem. Abstr*. **1989**, *111*:154289y.
9. (a) Ferrier, R. J. *J. Chem. Soc. (C)* **1964**, 5443; (b) Ferrier, R. J.; Ciment, D. M. *J. Chem. Soc. (C)* **1966**, 441–445; (c) Ferrier, R. J.; Prasad, N. *J. Chem. Soc. (C)* **1969**, 570–575; (d) Ferrier, R. J.; Prasad, N. *J. Chem. Soc. (C)* **1969**, 581–586; (e) Danishefsky, S.; Keerwin, J. F. *J. Org. Chem.* **1982**, *47*, 3803–3805.
10. (a) Schmidt, R. R.; Angerbauer, R. *Carbohydr. Res.* **1979**, *72*, 272–275; (b) Danishefsky, S. J.; Bilodeau, M. T. *Angew. Chem., Int. Ed.* **1996**, *35*, 1380–1419; (c) Fraser-Reid, B. *Acc. Chem. Res.* **1985**, *18*, 347–354; (d) Bussolo, V. D.; Kim, Y.-J.; Gin, D. Y. *J. Am. Chem. Soc.* **1998**, *120*, 13515–13516; (e) Srivastava, R. M.; Oliceira, F. J. S.; Silva, L. P.; de Freitas Filho, J. R.; Oliveira, S. P.; Lima, V. L. M. *Carbohydr. Res.* **2001**, *332*, 335–340.
11. (a) Holder, N. *Chem. Rev.* **1982**, *82*, 287–332; (b) Liu, Z. J.; Zhou, M.; Min, J. M.; Zhang, L. H. *Tetrahedron: Asymmetry*. **1999**, *10*, 2119–2127; (c) Brito, T. M. B.; Silva, L. P.; Siqueira, V. L.; Srivastava, R. M. *J. Carbohydr. Chem.* **1999**, *18*, 609–616; (d) Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976–4978; (e) Paterson, L.; Keown, L. E. *Tetrahedron Lett.* **1997**, *38*, 5727–5730; (f) Horita, K.; Sakurai, Y.; Nagasawa, M.; Hachiya, S.; Tonemistu, O. *Synlett* **1994**, 43–45.
12. (a) Sutherlin, D. P.; Stark, T. M.; Hughes, R.; Armstrong, R. W. *J. Org. Chem.* **1996**, *61*, 8350–8354; (b) Grynkiewicz, G.; BeMiller, J. N. *J. Carbohydr. Chem.* **1982**, *1*, 121; (c) Grynkiewicz, G.; BeMiller, J. N. *Carbohydr. Res.* **1982**, *108*, C1; (d) Ichikawa, Y.; Isobe, M.; Konobe, M.; Goto, T. *Carbohydr. Res.* **1987**, *171*, 193–199; (e) Grynkiewicz, G.; Priebe, W.; Zamojski, A. *Carbohydr. Res.* **1979**, *68*, 33–41; (f) Bhate, P.; Horton, D.; Priebe, W. *Carbohydr. Res.* **1985**, *144*, 331–337.
13. (a) Koreeda, M.; Houston, T. A.; Shull, B. K.; Klemke, E.; Tuinman, R. J. *Synlett* **1995**, 90–92; (b) Toshima, K.; Ishizuka, T.; Matsuo, G.; Nakata, M. *Synlett* **1995**, 306–308; (c) Toshima, K.; Ishizuka, T.; Matsuo, G.; Nakata, M. *Chem. Lett.* **1993**, 2013–2016; (d) Lopez, J. C.; Gomez, A. M.; Valverdi, S.; Fraser-Reid, B. *J. Org. Chem.* **1995**, *60*, 3851–3858; (e) Yadav, J. S.; Reddy, B. V. S.; Chandraiah, L.; Reddy, K. S. *Carbohydr. Res.* **2001**, *332*, 221–224.
14. (a) Dawe, R. D.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1981**, 1180–1181; (b) Yadav, J. S.; Reddy, B. V. S.; Murthy, C. V. S. R.; Kumar, G. M. *Synlett* **2000**, 1450–1451; (c) Yadav, J. S.; Reddy, B. V. S.; Chand, P. K. *Tetrahedron Lett.* **2001**, *42*, 4057–4059; (d) Takhi, M.; Abdel-Rahman, A. A.-H.; Schmidt, R. R. *Synlett* **2001**, 427–429; (e) Takhi, M.; Abdel-Rahman, A. A.-H.; Schmidt, R. R. *Tetrahedron Lett.* **2001**, *42*, 4053–4056.
15. (a) Ghosh, R.; De, D.; Shown, B.; Maiti, S. B. *Carbohydr. Res.* **1999**, *321*, 1–3; (b) Yadav, J. S.; Reddy, B. V. S.; Raman, J. V.; Niranjan, N.; Kumar, S. K.; Kunwar, A. C. *Tetrahedron Lett.* **2002**, *43*, 2095–2098; (c) Yadav, J. S.; Reddy, B. V. S. *Synthesis* **2002**, 511–514; (d) Yadav, J. S.; Reddy, B. V. S.; Raju, A. K.; Rao, C. V. *Tetrahedron Lett.* **2002**, *43*, 5437–5440; (e) Babu, B. S.; Balasubramanian, K. K. *Tetrahedron Lett.* **2000**, *41*, 1271–1274; (f) Das, S. K.; Reddy, K. A.; Roy, J. *Synlett* **2003**, *11*, 1607–1610.
16. (a) Swamy, N. R.; Venkateswarlu, A. *Synthesis* **2002**, 598–600; (b) Masson, C.; Soto, J.; Bessodes, M. *Synlett* **2000**, 1281–1282; (c) Pachamuthu, K.; Vankar, Y. D. *J. Org. Chem.* **2001**, *66*, 7511–7513; (d) Yadav, J. S.; Reddy, B. V. S.; Reddy, K. B.; Satyanarayana, M. *Tetrahedron Lett.* **2002**, *43*, 7009–7012; (e) Misra, A. K.; Tiwari, P.; Agnihotri, G. *Synthesis* **2005**, *2*, 260–266; (f) Tiwari, P.; Agnihotri, G.; Misra, A. K. *Carbohydr. Res.* **2005**, *340*, 749–752.
17. *Experimental procedure*: PMA/SiO_2 catalyst was prepared following the published procedure.[6d] *Preparation of glycosides*: To a solution of tri-*O*-acetyl glucal (272 mg, 1.0 mmol) and alcohol or allyl trimethylsilane (2.0 mmol) in acetonitrile was added 1 mol % PMA/SiO_2 (0.01 mmol, based on PMA), and the mixture stirred at r.t. for 10–15 min. After completion of the reaction as indicated by TLC, the solvent was removed under reduced pressure and the residue was dissolved in THF (2 mL) and filtered. The filtrate was concentrated under reduced pressure and purified by column chromatography (100–200 silica gel mesh) using hexane and EtOAc to afford pure glycosides. The filtered catalyst was reused without drying. Spectral data for **2a**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ ppm: 2.08 (s, 6H), 2.35–2.45 (m, 2H), 3.95 (dt, 1H, $J = 6.5$ and 3.7 Hz), 4.10–4.20 (m, 2H), 4.25–4.30 (m, 1H), 5.05–5.20 (m, 3H), 5.75–5.95 (m, 3H). Compound **2g**: 2.08, 2.10 (2 × s, 6H), 2.4 (t, $J = 2.2$ Hz, 1H), 4.0–4.08 (m, 1H), 4.20–4.28 (m, 2H), 4.30 (m, 2H), 5.2 (br s, 1H), 5.32–5.36 (dd, $J = 9.6$, 1.2 Hz, 1H), 5.8–5.9 (m, 2H). Compound **2m**: 2.06 (s, 3H), 2.10 (s, 3H), 4.19–4.22 (m, 2H), 4.34–4.40 (m, 1H), 5.30–5.35 (m, 1H), 5.66–5.68 (m, 1H), 5.83–5.88 (m, 1H), 5.98–6.04 (m, 1H), 7.39–7.42 (m, 4H).