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Dodecatungestophosphoric acid (H$_3$PW$_{12}$O$_{40}$) as a solid green Brønsted acid catalyzes high yielding and efficient trimethylcyanosylilation reactions of aldehydes and ketones by trimethylsilyl cyanide

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Abstract

An efficient solvent-free method is described for the addition of TMSCN to carbonyl groups employing dodecatungestophosphoric acid (H$_3$PW$_{12}$O$_{40}$) as a heterogeneous and environmentally benign catalyst. By this method, aromatic, aliphatic, cyclic and heterocyclic aldehydes and ketones are converted into their corresponding cyanotrimethylsilyl ethers in excellent yields (89–98%) in short reaction times (<10 min).
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Keywords: Dodecatungestophosphoric acid; Aldehyde; Ketone; Cyanotrimethylsilyl ethers

1. Introduction

The development of practical protocol for the preparation of α-hydroxy-, α-substituted acids, ketones, aldehydes, and α-hydroxy amines from readily available carbonyl compounds is an important achievement in organic synthesis. One of the most straightforward entries to this important goal is through their cyanohydrin preparations [1]. They are also components of commercially important compounds such as the pyrethroid insecticides, cypermetrin and fluvaliate [2]. Preparation of cyanohydrins by the addition of highly toxic HCN to carbonyl group is not a straightforward process and the procedure should be undertaken with caution. The other problem which affects the yields of the products stems from the existence of inevitable equilibrium condi-

tion between the reactants and the adduct product. In order to surmount this problem, the reaction of TMSCN with carbonyl groups in the presence of Lewis acid or Lewis base catalysts has been under attention in the last decade [3]. Very recently new catalysts such as; indium tribromide [4a], layered zirconium hydrogen phosphate [4b], and several *N*-oxide compounds [4c–h] have been reported for this purpose. However, general, mild, and high-yielding processes for cyanation of hindered carbonyl groups are still very limited in the literature.

Development of methods using heteropolyacids (HPAs) as catalysts for fine organic synthetic processes related to fine chemicals, such as flavors, pharmaceuticals and food industries [5] have been under attention in the last decade. Heteropolyacids are more active catalysts than conventional inorganic and organic acids for various reactions in solution [6]. They are used as industrial catalysts for several liquid-phase

reactions [7–10], such as alcohol dehydration [11], alkylation [12], or esterification [13] reactions. Among heteropolyacids, polytungstic acids are the most widely used catalysts owing to their high acid strengths, thermal stabilities, and low reducibilities. The catalysts based on heteropolyacids have many advantages over liquid acid catalysts. They are non-corrosive and environmentally benign, presenting fewer disposal problems. Solid heteropolyacids have attracted much attention in organic synthesis owing to easy workup procedures, easy filtration, and mini-mization of cost and waste generation due to reuse and recycling of the catalysts [14].

On the other hand, due to the current challenges for developing solvent-free and environmentally benign syn-thetic systems [15] and in continuation of our interests in the applications of $H_3PW_{12}O_{40}$ for various organic transformations [16,17], we here report another catalytic activity of $H_3PW_{12}O_{40}$ for the high yielding cyanation of carbonyl compounds with TMSCN in the absence of solvent. When an aldehyde or a ketone was allowed to react with TMSCN in the presence of catalytic amounts (0.1–0.15 mol%) of $H_3PW_{12}O_{40}$, the cyanation of the carbonyl compounds proceeds well to give the corre-sponding trimethylcyanation adduct in excellent yields within few minutes (Scheme 1, Table 1).

Acetophenone was chosen to optimize the reaction conditions, such as temperature, time, and molar ratio of $H_3PW_{12}O_{40}$ to the substrate. We found that 0.1 mol% of $H_3PW_{12}O_{40}$ was sufficient to obtain the de-sired cyanohydrin trimethylsilyl ether in 96% yield with-in 5 min at room temperature. In Table 1, we have compared the catalytic activity of $H_3PW_{12}O_{40}$ for the reaction of acetophenone with trimethylsilyl cyanide with those reported for other catalysts.
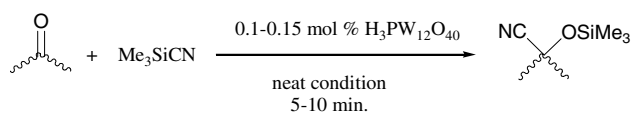
We then applied our reaction conditions for addi-tion of trimethylsilyl cyanide to structurally different carbonyl compounds. The results are shown in Table 2.

Table 2 clearly shows that aliphatic and aromatic aldehydes with electron-donating or electron-withdraw-ing groups give their corresponding cyanotrimethylsilyl ethers in excellent yields. Cyclic and acyclic carbonyl compounds (Table 2, entries 8, 15–20) are also con-verted into their corresponding cyanotrimethylsilyl ethers with excellent yields in less than 5 min. Further-more, the reaction of acid sensitive substrates such as furfuraldehyde, methylfuril ketone, cinnamaldehyde in the presence of 0.1 mol% of the catalyst proceeds smoothly in high yields and the lack of polymerization is observed.

This catalyst is exceptionally effective for the cyano-trimethylsilylation of conformationally constrained camphor to produce the desired product in 95% yield at room temperature within 10 min in the absence of sol-vent (Scheme 2).

In order to show the effectiveness of this catalyst, the results obtained by some other catalysts used for the similar reaction are as follows:

$P(MeNMCH_2CH_2)_3N$ (15 mol%, 5 h, 33% yield), [3p]

ZnI_2 (5 mol%, 24 h, 98% yield), [4h]

$LiOCH_2CH_2(OCH_2CH_2)_2OCH_3$
(50 mol%, 1 h, 96% yield). [4h]

The catalyst is also used effectively for the cyanation of other hindered ketones such as 9-fluorenone, and benzophenone (Table 2, entries 21, 22) to give their
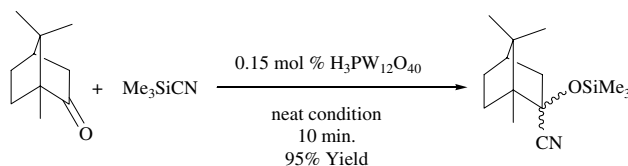
Scheme 1.

Scheme 2.

Table 1
Reaction of acetophenone with trimethylsilyl cyanide in the presence of different catalysts

Entry	Catalyst[ref.]	(mol%)	Time (h)	Yield
1	$H_3PW_{12}O_{40}$	0.1	5 min	96
2	$Cu(OTf)_2$ [3e]	5	3	84
3	$Yb(OTf)_3$ [3m]	20	20	0
4	Solid $LiClO_4$ [3n,3o]	100	3	86
5	$LiOCH_2CH_2(OCH_2CH_2)_2OCH_3$ [4g]	1	12 min	96
6	$Zr(KPO_4)_2$ [4b]	0.2 g	24	98
7	*N*-methylmorpholine *N*-oxide [4f]	30	8	98
8	*N*-oxide–Ti(O^{i}Pr)$_4$ [2/1] [4d]	10	62	82
9	*N*-oxide-quaternary ammonium bromide [1/1] [4h]	2.5	15	95

Table 2
$H_3PW_{12}O_{40}$ (0.1–0.15 mol%) mediated TMSCN addition to carbonyl groups under neat conditions at room temperature

Entry	Substrate	Product	Yield[a]
1.			92
2.			90
3.			95
4.			91
5.			93
6.			90
7.			94
8.			93
9.			96
10.			95
11.			96
12.			98[b]
13.			93
14.			97
15.			89
16.			91
17.			94
18.			92
19.			95
20.			96
21.			97
22.			98
23.			95

[a] Yields refer to the isolated products.

corresponding cynanotrimethylsilyl ethers in excellent yields in very short reaction times (10 min).

2. Conclusion

$H_3PW_{12}O_{40}$ can be considered as a mild and suitable Brønsted acid catalyst for promoting high yielding cyanosilylation of carbonyl compounds even hindered ketones under mild and solvent-less condition. The availability, low cost, environmentally benign and the effectiveness of the catalyst are worthy to be mentioned.

3. Experimental

Chemicals were purchased from Merck and Fluka Chemical Companies. IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250. The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV$_{254}$ plates or GC. All products are known compounds.

3.1. General procedure

A mixture of a carbonyl compound (5 mmol), TMSCN (6 mmol, 0.6 g) and solid $H_3PW_{12}O_{40}$ (0.005–0.0075 mmol, 0.015–0.022 g) was magnetically stirred at room temperature in 5–10 min. EtOAc or any other appropriate organic solvent (10 mL) was added to the reaction mixture and the solid $H_3PW_{12}O_{40}$ was filtered and washed the solid residue with organic solvent (5 mL). The filtrate was evaporated on a rotary evaporator and the crude product was purified by a short column chromatography on silica gel (eluted with petroleum ether (40–60 °C)/EtOAc (95:5)) to afford the pure product(s) in 89–98% yields (Table 1). All isolated products gave satisfactory spectral data (IR, ^{1}H NMR, and ^{13}C NMR, GC) and compared with those reported in the literature [3n,3o,4d,f,g].

Selected analytical data for 2-methyl-2-trimethylsilyloxy-4-phenylbut-3-enenitrile (Table 2, Entry 14): IR (neat): 2355 cm^{-1} (CN). ^{1}H NMR (CDCl$_3$, 250 MHz): $\delta = 0.24$ (s, 9 H), 1.65 (s, 3 H), 6.12 (d, 1 H, $J = 15.9$ Hz), 6.88 (d, 1 H, $J = 15.9$ Hz), 7.24–7.41 (m, 5H). ^{13}C NMR (CDCl3, 63 MHz): $\delta = 1.30$, 30.77, 69.85, 120.50, 126.72, 128.43, 128.62, 129.47, 130.80, 135.00 [4h].

References

[1] (a) B.R. Matthews, H. Gountzos, W.R. Jackson, K.G. Watson, Tetrahedron Lett. 30 (1989) 5157;
(b) W.R. Jackson, H.A. Jacobs, G.S. Jayatilake, B.R. Matthews, K.G. Watson, Aust. J. Chem. 43 (1990) 2045;
(c) W.R. Jackson, H.A. Jacobs, B.R. Matthews, G.S. Jayatilake, K.G. Watson, Tetrahedron Lett. 31 (1990) 1447;
(d) T. Ziegler, B. Horsch, F. Effenberger, Synthesis (1990) 575;
(e) F. Effenberger, U. Stelzer, Angew. Chem., Int. Ed. Engl. 30 (1991) 873;
(f) P. Zandbergen, J. Brussee, A. Van der Gen, C.G. Kruse, Tetrahedron-Asymmetr. 3 (1992) 769;
(g) M. North, Synlett (1993) 807.

[2] (a) R.J.H. Gregory, Chem. Rev. 99 (1999) 3649;
(b) G.M. Shan, R.P. Hammer, J.A. Ottea, J. Agric. Food Chem. 45 (1997) 4466;
(c) F.Z. Galin, R.H. Rakhimov, G.A. Tolstikov, Russ. Chem. Bull. 47 (1998) 530.

[3] (a) D.A. Evans, L.K. Truesdale, G.L. Carroll, J. Chem. Soc., Chem. Commun. (1973) 55;
(b) P.G. Gassman, J.J. Talley, Tetrahedron Lett. 19 (1978) 3773;
(c) R. Noyori, S. Murato, M. Suzuki, Tetrahedron 37 (1981) 3899;
(d) M.T. Reetz, M.W. Drewes, K. Harms, W. Reif, Tetrahedron Lett. 29 (1988) 3295;
(e) V.K. Singh, P. Saravanan, R.V. Anand, Tetrahedron Lett. 39 (1998) 3823;
(f) M. North, Synlett (1993) 807;
(g) H. Deng, M.P. Ister, M.L. Snapper, A.H. Hoveyda, Angew. Chem., Int. Ed. 41 (2002) 1009;
(h) K. Tanaka, A. Mori, S. Inoue, J. Org. Chem. 55 (1990) 181;
(i) M. Hayashi, Y. Miyamoto, T. Inoue, N. Oguni, J. Org. Chem. 58 (1993) 1515;
(j) S. Kobayashi, Y. Tsuchiya, T. Mukaiyama, Chem. Lett. (1991) 537;
(k) Y. Hanashima, D. Sawada, H. Nogami, M. Kanai, M. Shibasaki, Tetrahedron 57 (2001) 805;
(l) S.K. Tian, R. Hong, L. Deng, J. Am. Chem. Soc. 125 (2003) 9900;
(m) J.K. Whitesell, R.A. Podaca, Tetrahedron Lett. 37 (1996) 2525;
(n) Y. Yang, D. Wang, Synlett (1997) 1379;
(o) N. Azizi, M.R. Saidi, J. Organomet. Chem. 688 (2003) 283;
(p) Z. Wang, B. Fetterly, J.G. Verkade, J. Organomet. Chem. 646 (2002) 161.

[4] (a) M. Bandini, P.G. Cozzi, P. Melchiorre, A.V. Ronchi, Tetrahedron Lett. 42 (2001) 3041;
(b) M. Curini, F. Epifano, M.C. Marcotullio, O. Rosati, M. Rossi, Synlett (2002) 315;
(c) F. Chen, X. Feng, B. Qin, G. Zhang, Y. Jiang, Synlett (2003) 558;
(d) Y. Shen, X. Feng, Y. Li, G. Zhang, Y. Jiang, Tetrahedron 59 (2003) 5667;
(e) Y. Shen, X. Feng, Y. Li, G. Zhang, Y. Jiang, Synlett (2002) 793;
(f) S.S. Kim, D.W. Kim, G. Rajagopal, Synthesis 2 (2004) 213;
(g) H.S. Wilkinson, P.T. Grover, C.P. Vandenbossche, R.P. Bakale, N.N. Bhongle, S.A. Wald, C.H. Senanayake, Org. Lett. 3 (2001) 553;
(h) H. Zhou, Fu-X Chen, B. Qin, X. Feng, G. Zhang, Synlett (2004) 6, eFirst.

[5] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 221.

[6] (a) M.N. Tiofeeva, A.V. Dimidov, I.V. Kozhevnikov, J. Mol. Catal. 79 (1993) 21;
(b) R.S. Drago, J.A. Dias, T. Maier, J. Am. Chem. Soc. 119 (1997) 7702.

[7] Y. Ono, J.M. Thomas, K.I. Zamaraev (Eds.), Perspectives in Catalysis, Blackwell, London, 1992, p. 341.

[8] I.V. Kozhevnikov, K.I. Matveev, Appl. Catal. 5 (1983) 135.

[9] Y. Izumi, K. Urabe, A. Onaka, Zeolite, Clay and Heteropolyacids in Organic Chemistry, VCH, Weinheim, Kodansha, Tokyo, 1992, p. 99.

[10] I.V. Kozhevnikov, Catal. Rev.-Sci. Eng. 37 (1995) 311.

[11] M. Misono, N. Noriji, Appl. Catal. 64 (1990) 1.

[12] Y. Izumi, R. Hasebe, K. Urabe, J. Catal. 84 (1983) 402.

[13] H. Soeda, T. Okuhara, M. Misono, Chem. Lett. (1994) 909.

[14] M.A. Schwegler, H. van Bekkum, N. Munck, Appl. Catal. 74 (1991) 191.

[15] (a) K. Tanaka, F. Toda, Chem. Rev. 100 (2000) 1025;
(b) R.S. Varma, Green Chem. (1999) 43.

[16] (a) H. Firouzabadi, N. Iranpoor, K. Amani, Green Chem. 3 (2001) 131;
(b) H. Firouzabadi, N. Iranpoor, K. Amani, Synthesis (2002) 59;
(c) H. Firouzabadi, N. Iranpoor, K. Amani, J. Mol. Catal. 195 (2003) 289;
(d) H. Firouzabadi, N. Iranpoor, K. Amani, F. Nowrouzi, J. Chem. Soc., Perkin Trans. 1 (2002) 2601;
(e) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, K. Amani, Synthesis 60 (2003) 408.

[17] (a) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, K. Amani, Chem. Commun. (2003) 764;
(b) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, K. Amani, Tetrahedron Lett. 44 (2003) 3951;
(c) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, Tetrahedron Lett. 44 (2003) 5343.