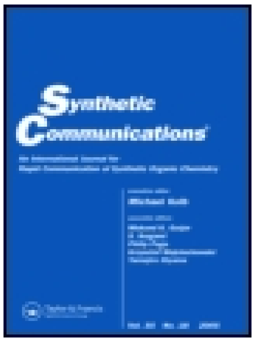

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Potassium Exchanged Layered Zirconium Phosphate as Base Catalyst for the Desilylation of Phenol Silyl Ethers.

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Abstract: Layered zirconium hydrogen phosphonate exchanged with the potassium ion was found to be an efficient heterogeneous catalyst for the hydrolysis of sterically hindered phenolic silyl ethers.

In recent years many inorganic solids have been used as catalysts in liquid phase organic synthesis.[1,2] Among them, special attention has been given to layered materials (including clays and modified clays, metal (IV) phosphates and phosphonates, layered double hydroxides) since the lamellar surface seems to be more effective than the porous or spongy surface in many catalyzed reactions. Furthermore, these layered compounds may also offer the inner layer surfaces to the reactants, as a result of intercalation processes. There are many examples of better yields, shorter reaction times, and even higher selectivities achieved as a result of reactions carried out with heterogeneous catalysts under reaction

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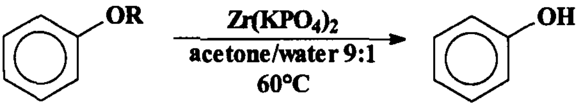
conditions milder than those employed in conventional homogeneous synthetic methods. We have previously reported that layered zirconium hydrogen phosphate exchanged with the potassium ion [$Zr(KPO_4)_2$] is an efficient basic heterogeneous catalyst in organic synthesis.[3,4,5]

In continuation of our efforts to develop new methods using $Zr(KPO_4)_2$ as base-catalyst in organic synthesis we decided to investigate its catalytic activity in the desylilation of phenolic silyl ethers.

Silylation is one of the most common methods of protecting the alcohol and phenol hydroxyl groups.[6] The use of the silyl moiety as protecting group in the case of phenols is limited by cleavage problems.

Homogeneous catalysts such as HF/NaF,[7] 48% HBr t-BuBr KF,[8,9] and DMSO/H_2O at 90°C,[10] and heterogeneous catalysts such as Al_2O_3/KF with ultrasound,[11] Al_2O_3 in a microwave,[12] $PdCl_2(CH_3)_2$[13] and K_2CO_3/H_2O[14] have been used specifically for the cleavage of phenolic silyl ethers. The reported methods have major or minor limitations depending on the nature of the protecting group, the reaction conditions and reaction the work-up.

Herein we report that $Zr(KPO_4)_2$ can be used effectively for the cleavage of hindered phenolic silyl derivatives such as t-butyldimethyl (TBDMS), triethyl (TES) and t-butyldiphenyl (TBDPS) silylethers.



The reactions were carried out at 60°C by adding silyl ether to a suspension of the catalyst in acetone/water (9:1). The reaction takes from 1 to 7 h (see table) and, after a simple work-up, affords the desilylated products in high yield. In a control experiment the reaction (e.g. entry a) was performed without $Zr(KPO_4)_2$ and the yield of desilylated product was <10% after 48h.

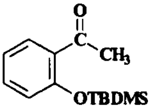
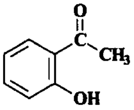
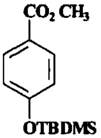
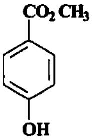
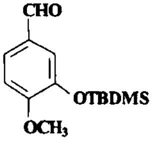
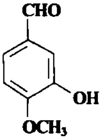
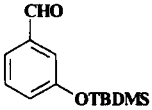
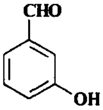
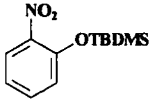
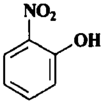
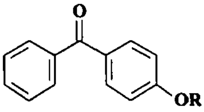
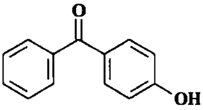
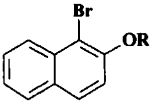
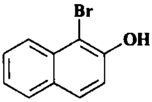
The procedure described in the present communication is effective or better than any procedure yet reported.

The important features of this method are: mild basic medium reaction conditions, simple and non acqueous work-up and recyclable nature of the catalyst,[15] the preparation of which does not require particular skill.[16] In conclusion we report an easy solid state method for cleavage of sterically hindered phenolic silyl ethers in good to excellent yields using a new catalyst $[Zr(KPO_4)_2]$. This catalytic method should be useful in synthetic organic chemistry.

Experimental

^1H NMR spectra of $CDCl_3$ solutions were recorded on a Bruker AC 200 spectrometer operating at 200.1 MHz in the Fourier transform mode. GC analyses and MS spectra were carried out with an HP 5890 gaschromatograph (dimetyl silicone column 12.5 m) equipped with an HP 5971 Mass Selective Detector. Flash column chromatography was performed on 0.040-0.063 mm (230-400 mesh ASTM) Merck silica gel.

Typical procedure: $Zr(KPO_4)_2$[16] (60 mg) was added to a stirred solution of TBDMS-ether[17] (1 mmol) in acetone/water (9:1, 3 ml) at 60°C. The progress of

Entry	Starting material	Product[1]	Time (h)	Yield (%)[a]
a			4	93
b			7	79
c			8	83
d			7	78
e			3.5	76
f				
	R=TBDMS		4	90
	R=TES		1	85
	R=TBDPS		4	87
g				
	R=TBDMS		6	90
	R=TES		1	88
	R=TBDPS		5	84

[a] Yields of isolated products.

the reaction was monitored by TLC. Stirring was continued for the appropriate time (see Table). The catalyst was then filtered and washed with acetone and the organic layer was evaporated at reduced pressure. The residue was diluted with dichloromethane, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by flash chromatography (eluent dichloromethane).

1-(2-hydroxyphenyl)-1-ethanone (a1): colourless oil; ^{1}H NMR δ 2.6 (s, 3H, C<u>H</u>$_3$), 6.90 (m, 1H, PhH), 6.98 (m, 1H, PhH), 7.48 (m, 1H, PhH), 7.74 (m, 1H, PhH); MS m/z 136, 121, 107, 93. Anal. Calcd for $C_8H_8O_2$;C, 70.57; H, 5.92. Found: C, 70.55; H, 5.94.

methyl 4-hydroxybenzoate (b1): solid m.p.125-128°C; ^{1}H-NMR δ 3.98 (s, 3H, C<u>H</u>$_3$), 7.08 (m, 2H, Ph-H), 8.07 (m, 2H, Ph-H); MS m/z 152, 136, 121, 93. Anal. Calcd for $C_8H_8O_3$;C, 63.15; H, 5.30. Found: C, 63.16; H, 5.28.

3-hydroxy-4-methoxybenzaldehyde (c1): solid m.p.113-116°C; ^{1}H NMR δ 3.97 (s, 3H, C<u>H</u>$_3$), 6.95 (m, 1H, PhH),743 (m, 2H, PhH), 9.82 (s,1H, CHO); MS m/z 152, 136, 122, 93. Anal. Calcd for $C_8H_8O_3$;C, 63.15; H, 5.30. Found: C, 63.13; H, 5.32.

3-hydroxybenzaldehyde (d1): solid m.p.112-114°C; ^{1}H NMR δ 7.16 (m, 1H, PhH), 7.38-7.47 (m, 3H, PhH)9.92 (s, 1H, CHO); MS m/z 122, 121, 93. Anal. Calcd for $C_7H_6O_2$;C, 68.85; H, 4.95. Found: C, 68.82; H, 4.97.

2-nitrophenol (e1): solid m.p.43-46°C; ^{1}H NMR δ 6.99(m, 1H, PhH), 7.70 (m, 1H, PhH), 7.59 (m, 1H, PhH), 8.12 (m, 1H, PhH); MS m/z 139, 122, 109, 93. Anal. Calcd for $C_6H_5NO_3$;C, 51.80; H, 3.62; N, 10.07. Found: C, 51.78; H, 3.60; N, 10.09.

(4-hydroxyphenyl)(phenyl)methanone (f1): solid m.p.132-134°C; ^{1}H NMR δ 6.94 (m, 2H, PhH), 7.42-7.59 (m, 3H, PhH), 7.77 (m, 4H, PhH); MS m/z 198, 169, 121, 105. Anal. Calcd for $C_{13}H_{10}O_2$;C, 78.77; H, 5.08. Found: C, 78.79; H, 5.05.

1-bromo-2-naphthol (g1): solid m.p.77-80°C; ^{1}H NMR δ 7.28 (d, 1H, *j=8.87Hz*, PhH), 7.39 (m, 1H, PhH), 7.58 (m, 1H, PhH), 7.78 (m, 2H, PhH), 8.04 (m, 1H, PhH); MS m/z 223, 193, 143, 114. Anal. Calcd for $C_{10}H_7BrO$;C, 53.84; H, 3.16; Br, 35.82. Found: C, 53.82; H, 3.18; Br, 35.81.

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15 The catalyst, washed with CH_2Cl_2 and dried at 180°C for one days may be used for several experiments without decrease of yield.

16 For the preparation and charateristic of the catalyst see ref.3 and 4.

17 For the preparation of silyl derivatives see ref.6.

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