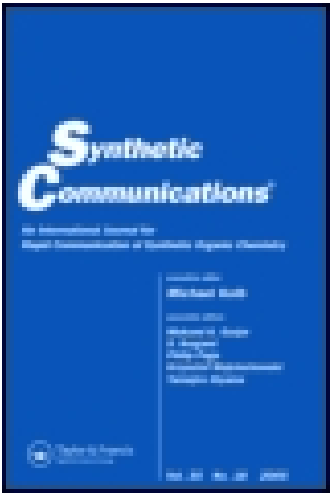

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Poly(4-Vinylpyridinium P-Toluenesulfonate) as a Polymer-Supported Catalyst for Hydrolysis of Tetrahydropyranyl Ethers

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POLY(4-VINYLPYRIDINIUM *P*-TOLUENESULFONATE) AS A POLYMER-SUPPORTED CATALYST FOR HYDROLYSIS OF TETRAHYDROPYRANYL ETHERS

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Abstract: Poly(4-vinylpyridinium) *p*-toluenesulfonate is used as an immobilized catalyst for the hydrolysis of tetrahydropyranyl ethers. This method is mild, efficient and convenient, giving the corresponding products in good to excellent yields and purity.

The tetrahydropyranyl (THP) ether is one of the most widely used protecting groups[1] for alcohols and phenols in multi-step organic synthesis because of its remarkable stability[2] towards strongly basic media, organometallic reagents, reductive and oxidative reagents etc. Many reagents have been developed[1] for the formation and cleavage of THP ethers. Pyridinium *p*-toluenesulfonate (PPTS)[3] is among the most popular catalysts for tetrahydropyranulation as well as hydrolysis of THP ethers because of its mildness and efficiency. A number of solid-supported catalysts were also reported for tetrahydropyranylation.[4]

During the course of a recent project to develop an organoselenium linker[5] for solid phase organic synthesis, there was a need to prepare a large quantity of

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Table 1. Hydrolysis of THP ethers Using PolyPPTS as Catalyst[a]

Entry	R	Reaction Time (min)	Yield(%)[b]
1	$(-CH_2CH_2-p-C_6H_4-)_2Se_2$[5]	30	99[c,8]
2	benzyl	30	99[c]
3	2-naphthyl	20	99[c]
4	cholesteryl	40	100[c]
5	5,6-α-epoxy-cholesteryl	60	86[d]
6	menthyl	45	98[c]
7	1-adamantyl	50	99[c]
8	1-methoxy-2-indanyl	40	89[d]
9	n-octadecanyl	60	99[d]

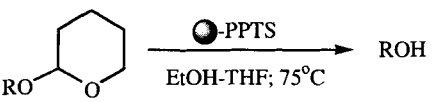
[a]0.05-0.1 M solution of the THP ether in ethanol/THF (1:1) heated at 75°C using 0.5 g catalyst per g substrate; [b]All products showed satisfactory spectroscopic data compared to authentic samples; [c]Essentially pure products by filtration and removal of solvents; [d] isolated yield after column chromatography.

diselenide (entry 1, Table 1) from the corresponding bis-THP ether. It was desirable to use a solid-supported catalyst to effect the hydrolysis as the workup is simply filtration and evaporation of solvent.[6] A survey of the literature revealed that heterogeneous catalysts for the hydrolysis of THP ethers seem to be limited to ion-exchange resins, Amberlyst H-15 and Dowex-50W-X8.[7] These resins can have limitations when applied to compounds containing other acid sensitive funtionalities.[4d]

We found that poly(4-vinylpyridinium) *p*-toluenesulfonate** (PolyPPTS) is an excellent catalyst for our hydrolysis (entry 1, table). Menger et al reported the catalytic activity of this polymer for tetrahydropyranylation.[4a] Nonetheless, the

** Purchased from Aldrich Chemical Company

hydrolysis of THP ethers using this polymer does not appear to have been reported to the best of our knowledge. We then examined the hydrolysis of a number of THP ethers using PolyPPTS, the results are summarized in Table 1.



Entry 5 illustrates the mildness of PolyPPTS for THP cleavage, when Dowex-50W-X8 or Amberlyst H-15 were used instead, the epoxide was also hydrolyzed under the reaction conditions. Finally, the polymer showed no loss of catalytic activity and can be reused. In conclusion, poly(4-vinylpyridinium) *p*-toluenesulfonate is a mild and efficient polymer-supported catalyst for hydrolysis of THP ethers, giving the corresponding alcohols and phenols in good to excellent yields and purity.

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8. ^{1}H NMR (300 MHz, $CDCl_3$) 7.55(d, 2H, J = 8.2 Hz), 7.13(d, 2H, J = 8.2 Hz), 3.85(t, 2H, J = 6.4 Hz), 2.85(t, 2H, J = 6.4 Hz), 1.50 (s, 1H, D_2O exchangeable); ^{13}C NMR (90 MHz, $CDCl_3$) 138.52, 133.47, 133.29, 132.06, 129.93, 128.82, 63.50, 38.73; MS: M^+ + Na, 423; Anal. Calcd. for $C_{16}H_{18}O_2Se_2$: C, 48.01; H, 4.53. Found: C, 47.67; H, 4.43.

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