Deprotection of Tetrahydropyranyl and Silyl Ethers Catalyzed by Organotin Phosphate Condensates

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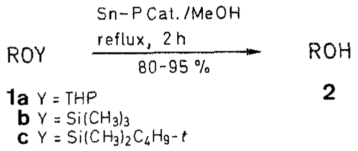
A new method for deprotecting tetrahydropyranyl and silyl ethers has been established by using organotin phosphate condensates as a catalyst. The reaction proceeds selectively under mild conditions. The heterogenous reaction enables easy separation of the catalyst, which can be reused for further reactions without purification.

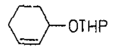
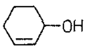
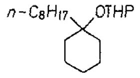
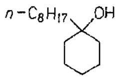
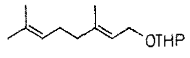
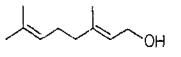
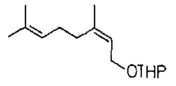
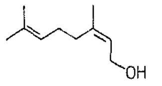
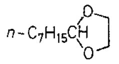
Organotin phosphate condensates, Sn-P Cat, which are pyrolysis products of organotin oxides or chlorides in the presence of trialkyl phosphates, are effective catalysts for polymerization[1] and ring-opening[2-4] of oxiranes. This indicates the unusual Lewis acidity of Sn-P Cat as compared with other organotin compounds, since high polymers of oxiranes are generally obtained with organoaluminum[5] and -zinc[6] catalysts.[7]

Tetrahydropyranyl (THP) ethers, which are the most common protected form of alcohols, are usually transformed into their parent alcohols under acidic conditions.[8,9] Many efforts have been made to overcome this drawback.[10] Silylation is another useful means of protecting the hydroxyl group and the cleavage proceeds under neutral conditions with the aid of fluoride ion.[8,9] Herein we wish to report a new effective method for deprotection of both groups with Sn–P Cat.



Of practical importance is that the reaction mixture in the present method is virtually heterogeneous. Despite the insolubility of the Sn-P Cat in methanol, the reaction proceeds quite

Table. Conversion of Tetrahydropyranyl and Silyl Ethers **1** into Alcohols **2**

Entry	**1**	**2**	Yield (%)[a]
1	$n\text{-}C_8H_{17}OTHP$	$n\text{-}C_8H_{17}OH$	99
2	$n\text{-}C_{12}H_{25}OTHP$	$n\text{-}C_{12}H_{25}OH$	99 (90)
3	$n\text{-}C_{11}H_{23}CH(OTHP)CH_3$	$n\text{-}C_{11}H_{23}CH(OH)CH_3$	100
4			86
5			100
6	$C_6H_5CH_2OTHP$	$C_6H_5CH_2OH$	100 (95)
7	$C_6H_5CH(CH_3)OTHP$	$C_6H_5CH(CH_3)OH$	99 (82)
8			98
9			98
10	$C_6H_5CH{=}CHCH_2OTHP$	$C_6H_5CH{=}CHCH_2OH$	86 (80)
11	$n\text{-}C_8H_{17}OSiMe_3$	$n\text{-}C_8H_{17}OH$	98 (90)
12	$n\text{-}C_8H_{17}OSiMe_2Bu\text{-}t$	$n\text{-}C_8H_{17}OH$	91
13[b]	$n\text{-}C_8H_{17}OCH_2OMe$	–	–
	$n\text{-}C_{12}H_{25}OTHP$	$n\text{-}C_{12}H_{25}OH$	97
14[c]	$n\text{-}C_8H_{17}OCH_2OCH_2CH_2OMe$	–	–
	$n\text{-}C_{12}H_{25}OTHP$	$n\text{-}C_{12}H_{25}OH$	98
15[d]		–	–
	$n\text{-}C_{12}H_{25}OTHP$	$n\text{-}C_{12}H_{25}OH$	98

[a] Based on GLC analysis. Isolated yields are given in parentheses. All products were fully confirmed by comparison with authentic samples.

[b] An equimolar mixture of the MOM and THP ethers were subjected to the reaction; the former component was recovered unchanged, while the THP ether was completely cleaved.

[c] An equimolar mixture of the MEM and THP ethers were subjected to the reaction; the former component was recovered unchanged, while the THP ether was completely cleaved.

[d] An equimolar mixture of the acetal and the THP ether were subjected to the reaction; the former component was recovered unchanged, while the THP ether was completely cleaved.

smoothly. The catalyst is easily removed from the reaction mixture by filtration. The repeated use of the recovered catalyst causes no decrease in the activity.

Table 1 illustrates the features of the present method. The reaction is universally applicable to primary (entries 1, 2, 11, and 12), secondary (entries 3 and 4), tertiary (entry 5), benzylic (entries 6 and 7), and allylic alcohols (entries 8–10).

Of special interest is that acid-sensitive geraniol and nerol are recovered without any isomerization or cyclization. Methoxymethyl (MOM) and 2-methoxyethoxymethyl (MEM) ethers as well as 1,3-dioxolanes remain unchanged under the present reaction conditions so that THP ethers are exclusively deprotected in the presence of these functionalities (entries 13–15).

Preparation of Sn-P Cat:

Into a glass reaction tube connected to a distillation apparatus and a gas holder are added dibutyltin oxide (24.0 g, 0.1 mol) and tributyl phosphate (53.2 g, 0.2 mol). The reaction tube is heated by using a cylindrical aluminum oven, containing a cavity in the center to accommodate the tube. When the temperature of the oven reaches 200 °C, the reaction tube containing the reactants is inserted into the cavity. The oven is heated at 250 °C for 30 min, during which time gases are evolved vigourously. Then, the reaction tube is heated at 80 °C *in vacuo* for 15 min to remove volatile products. The residue thus obtained is pulverized to a white powder (24 g).

Conversion of (2-Tetrahydropyranyl)oxyalkanes and Silyloxyalkanes 1 into Alcohols 2; Typical Procedure:

A reaction flask containing Sn-P Cat (200 mg) is heated at 150 °C *in vacuo* for 1 h, charged with nitrogen, and cooled to room temperature. In this flask are added methanol (7 mL) and dodecyl tetrahydropyranyl ether (270 mg, 1 mmol). The reaction mixture is heated under reflux while being stirred. After 2 h, GLC analysis indicates the complete consumption of the THP ether and the formation of dodecanol in 99 % yield (Silicon OV-17, dodecane as an internal standard). The reaction mixture is filtered and the filtrate is concentrated. Column chromatography (silica gel, hexane/ethyl acetate, 10:1) of the residue provides pure dodecanol (identical with authentic specimen on the basis of GLC analysis); yield: 168 mg (90 %).

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