/ethyl acetate, 9:1); 18 mg (0.11 mmol, 45.7%) of 3-methoxy-1-phenylpropanone (**25**)[12] and 10 mg (0.06 mmol, 25%) of 3-methoxy-1-phenylpropanol (**27**)[13] were obtained. The mixture could be titrated with Jones reagent to afford only **25**.

**3-Methoxy-1-phenylpropan-1-one (25).**[12] To a dichloromethane solution (3 mL) of 60.3 mg (0.36 mmol) of 3-methoxy-1-phenyl-1-propanol (**27**) was added 110 mg of pyridinium chlorochromate (PCC). After 2 h the mixture was filtered through a small plug of Florisil; 46.4 mg (0.28 mmol, 78%) of 3-methoxy-1-phenylpropan-1-one (**25**) was obtained after the solvent was evaporated: IR (neat) 3061, 2893, 1685, 1597, 1449, 1118, 750, 691 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.96 (d, $J$ = 7.8 Hz, 2 H), 7.57 (m, 1 H), 7.46 (m, 2 H), 3.83 (t, $J$ = 6.4 Hz, 2 H), 3.38 (s, 3 H), 3.25 (t, $J$ = 6.4 Hz, 2 H); $^{13}C$ NMR 198.2 (C), 137.0 (C), 133.1 (CH), 129.0 (2CH), 128.1 (2CH), 67.9 ($CH_2$), 58.8 ($CH_3$), 38.6 ($CH_2$).

**3-Methoxy-1-phenyl-1-propanol (27).**[13] A methanol solution (1 mL) of 82.7 mg (0.51 mmol) of enone **9** was treated with sodium borohydride (5 mg). The mixture was stirred for 1 h at room temperature and quenched with 10% NaOH solution (3 mL). Dichloromethane (1 mL) was added and the organic layer was separated. The aqueous layer was extracted twice with 1 mL of dichloromethane. The combined organic layers were evaporated. A pure sample of alcohol **27** (60.3 mg, 0.36 mmol, 71%) was obtained by column chromatography (silica gel, hexane/ethyl acetate, 9.5:0.5): IR (neat) 3416, 3062, 2924, 1493, 1453, 1117, 758, 701 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.25 (m, 5 H), 4.9 (m, 2 H), 3.55 (m, 2 H), 3.35 (s 3 H), 1.95 (m, 2 H).

**Cinnamyl Alcohol (26).** An ether solution (2 mL) of 92.5 mg (0.57 mmol) of 3-methoxy-1-phenyl-2-propen-1-one (**9**) was treated with 43.2 mg (1.14 mmol) of $LiAlH_4$. The mixture was stirred for 2 h and quenched with 1 mL of water and then 1 mL of 10% solution of HCl. The organic layer was separated and the aqueous layer extracted with ether (2 × 1 mL). The combined organic layers were washed with 2 mL of brine solution and dried with $MgSO_4$. Evaporation of the solvent yielded 59.4 mg (0.44 mmol, 77%) of cinnamyl alcohol (**26**): IR (neat) 3356, 3026, 2926, 2862, 1598, 1494, 1449, 1217, 1093, 1012, 967, 750, 693 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.45–7.15 (m, 5 H), 6.65 (d, 1 H), 6.35 (dt, 1 H), 4.35 (d, 2 H). The oxidation of **26** to cinnamaldehyde **24** is known.[17]

**Hydrolysis of Enone 9.** A THF solution (5 mL) of 106.6 mg (0.6 mmol) of enone **9** was treated with 5 mL of 3% $HClO_4$, and the mixture was stirred for 2 h at room temperature; 5 mL of ether was added. The organic extract was washed with 2 mL of brine solution. The solution was filtered and 87.6 mg (90%) of benzoyl acetaldehyde was obtained:[14] $^1H$ NMR ($CDCl_3$) $\delta$ 8.1–7.2 (m, 5 H), 8.27 (d, $J$ = 4.4 Hz, 1 H), 6.39 (d, $J$ = 4.4 Hz, 1 H).

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**Registry No.** **1**, 111-64-8; **2**, 127618-29-5; **3**, 118452-44-1; **4**, 2719-27-9; **5**, 127618-30-8; **6**, 127618-31-9; **7**, 98-88-4; **8**, 127618-32-0; **9**, 40685-20-9; **10**, 103-80-0; **11**, 127618-33-1; **12**, 127618-34-2; **13**, 645-45-4; **14**, 127618-35-3; **15**, 127618-36-4; **16**, 1711-09-7; **17**, 127618-37-5; **18**, 127618-38-6; **19**, 127618-39-7; **20**, 127618-40-0; **21**, 60390-86-5; **22**, 127618-41-1; **23**, 23632-42-0; **24**, 14371-10-9; **25**, 55563-72-9; **26**, 4407-36-7; **27**, 13125-59-2; **28**, 18609-60-4; *p*-$ClC_6H_4COCl$, 122-01-0; *p*-$BuC_6H_4COCl$, 586-75-4; methoxyethylamine, 109-85-3; urea, 57-13-6; *N*-methoxyethyl-*N'*-nitrosourea, 127618-42-2; 1-diazo-2-methoxyethane, 59712-30-0.

**Supplementary Material Available:** $^1H$ NMR spectra of the diazo ketones and methoxy enones shown in Table I (12 pages). Ordering information is given on any current masthead page.

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# Activation and Synthetic Applications of Thiostannanes. Deprotection and Transformations of Tetrahydropyranyl Ethers

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Protection of functional groups is encountered quite frequently in organic synthesis, and new, more effective methodologies are still highly desired.[1] Another important synthetic operation is functional group transformation. In particular, direct transformations from the protected forms into other functionalities are extremely useful.[2-11] It, therefore, would meet a variety of synthetic demands if deprotection and chemical transformation are achievable from a common protecting form. To realize this idea, however, one must overcome the contradiction that the protection is a process which *deactivates* functional groups while the transformation requires *activation* of these groups. In this paper, we disclose that tetrahydropyranyl (THP) ethers **1** serve this purpose quite well when treated with thiostannanes **2** in the presence of $BF_3{\cdot}OEt_2$ (**3**). Thus, alcohols are regenerated under extremely mild conditions, and various functionalities are produced in one-pot from **1** without passing through the free alcohols.[12]

In general, THP ethers are deblocked under acidic conditions. To improve this disadvantage, dimethylaluminum chloride (2 equiv)[13] and magnesium bromide (3 equiv)[14] were found to be effective even in the presence of a *tert*-butyldimethylsiloxy group. We reported that distannoxanes[15] and organotin phosphate condensates[16] catalyzed deprotection of **1** compatible with various acid-labile groups. On the other hand, a THP group was replaced by an acyl group on treatment with acid chlorides

(1) *Protective Groups in Organic Chemistry*; McOmie, J. F. W., Ed.; Plenum Press: London, 1973. Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981.

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(12) For a preliminary report of this study, see: Sato, T.; Tada, T.; Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1989**, *30*, 1665.

(13) Ogawa, Y.; Shibasaki, M. *Tetrahedron Lett.* **1984**, *25*, 663.

(14) Kim, S.; Park, J. H. *Tetrahedron Lett.* **1987**, *28*, 439.

(15) Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 5743.

(16) Otera, J.; Niibo, Y.; Chikada, S.; Nozaki, H. *Synthesis* **1988**, 328.

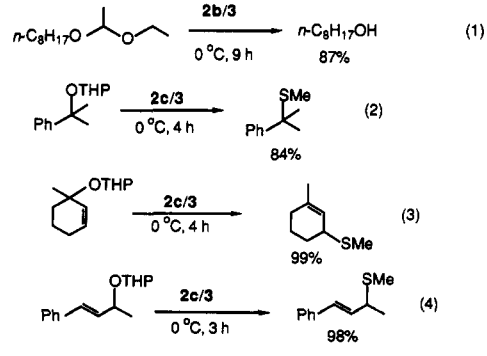
0022-3263/90/1955-4770$02.50/0 

in the presence of zinc chloride.[2a] More recently, THP ethers were converted into alkyl halides with 1,2-bis(diphenylphosphino)ethane tetrabromide[2b] or triphenylphosphine/carbon tetrabromide.[2c]

The present study has its foundation on our previous finding that thiostannanes combined with $BF_3{\cdot}OEt_2$ effect thioalkoxylation of acetals giving monothioacetals exclusively.[17] If we turn our attention to the organotin components in this reaction, we can reasonably assume alkoxystannanes to be formed as the counterpart product. In situ utilization of the alkoxystannanes thus formed has led us to novel modifications of THP ethers (Scheme I).

**Deprotection.** The deprotection of 1 was achieved by hydrolysis of the intermediary alkoxystannanes. A toluene solution of 1 (1 equiv), **2** (1.1–1.6 equiv), and **3** (1 equiv) was stirred at −20 to 0 °C for 1.5–25 h. Usual aqueous workup provided good yields of parent alcohols along with 2-(alkylthio)tetrahydropyrans. Table I summarizes our results. Although both trialkyl- and dialkyltin compounds are effective (entries 1–3), the dimethyltin derivative **2c** is most conveniently employed. The resulting dimethyltin oxide is insoluble in organic solvents, and the other product, 2-(methylthio)tetrahydropyran, is relatively volatile. Consequently, almost pure alcohols are recovered simply by filtrating off the oxide followed by concentrating the extracted organic layer without recourse to further purification. That the reaction proceeds in an aprotic solvents is also of synthetic value. THP ethers derived from primary, secondary, and tertiary alcohols may be employed (entries 3–5). Primary and secondary benzylic and allylic alcohols are also deprotected smoothly (entries 6–9) while tertiary derivatives cannot be used (vide infra). Acid-sensitive geraniol and nerol give rise to neither isomerization nor cyclization (entries 10, 11). Moreover, *tert*-butyldimethylsilyl, acetyl, mesyl, and methoxymethyl (MOM) groups are completely tolerated, and thus the THP group is readily unmasked exclusively from unsymmetrically protected diols (entries 12–15). No Michael addition of the methylthio group to an $\alpha,\beta$-unsaturated ester occurs under the present reaction conditions (entry 16). These results clearly indicate the mildness and the versatility of this method.

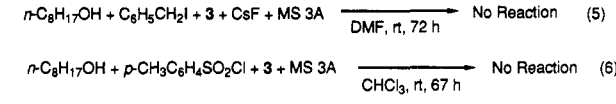
It seems of interest to note a reaction with an $\alpha$-ethoxyethyl (EE) ether (eq 1). In sharp contrast to the inert MOM ether, the EE ether was cleaved smoothly. Apparently, the substituent on the acetal carbon facilitates the deprotection, suggestive of an oxonium intermediate in the thiostannane-mediated procedure. In accordance with this, THP ethers involving a teriary benzyl or an allylic moiety and a secondary cinnamyl group, which are highly susceptible to cation formation, provided benzylic or allylic sulfides (eqs 2–4)




(17) Sato, T.; Kobayashi, T.; Gojo, T.; Yoshida, E.; Otera, J.; Nozaki, H. *Chem. Lett.* **1987**, 1661. Sato, T.; Otera, J.; Nozaki, H. *Tetrahedron* **1989**, *45*, 1209.

**Chemical Transformations.** Since alkoxystannanes have found a number of synthetically useful reactions,[18] our next goal was to make use of the alkoxystannane intermediates for chemical transformations other than the simple deprotection. We succeeded in benzylation,[19] 2-methoxyethoxymethylation, benzoylation, tosylation, and oxidation to an aldehyde (Scheme II). The initial step for the alkoxystannane formation was best conducted in toluene. Then, it should be replaced by the solvents for the next reactions as shown in Scheme II. The choice of the solvent is important for obtaining good yields of the final products. In the reactions with benzyl iodide and (2-methoxyethoxy)methyl (MEM) chloride, CsF was required to induce cleavage of the Sn–O bond. This reagent was also helpful in purification of the products since the organotin component is converted to tributyltin fluoride, which is easily separated from the reaction mixture.[20] In benzoylation for which CsF was not necessary, we encountered the difficulty that chromatographic separation of octyl benzoate and tributyltin chloride was rather troublesome. However, use of benzoyl fluoride overcame the problem. Tosylation proceeded smoothly without CsF. Finally, conversion to an aldehyde was achieved through oxidation with pyridinium chlorochromate (PCC).[21]

The crucial role of the alkoxystannane intermediate was confirmed by the control experiments. Benzylation and tosylation were attempted in the absence of thiostannanes under the otherwise same reaction conditions (eqs 5 and 6). No desired products were detected even after prolonged reaction time.




**Conclusion.** On exposure to thiostannanes in the presence of $BF_3{\cdot}OEt_2$, THP ethers behave as either stabilized or activated forms of the hydroxyl function. The character is switched depending on the reagents to which the alkoxystannane intermediates are exposed. The hydrolytic procedure results in deprotection while electrophiles or PCC leads to functional group modifications. In addition to the novelty of the concept, the present method is synthetically useful. THP ethers are deblocked, leaving a variety of other functional groups intact. The one-pot conversion of THP ethers to other functionalities is promising since isolation of parent alcohols is unnecessary.

## Experimental Section

NMR spectra were recorded at 100 and 25 MHz for $^1H$ and $^{13}C$ NMR spectra, respectively. Mass spectra were obtained using electron impact ionization. GLC analysis was performed with a column of 2% Silicon OV 17 on Chromosorb W (3.2 $\phi$ × 2000). Column chromatography was performed on Kieselgel 60 (70–230 mesh). Organotin thioalkoxides were prepared according to the literature methods.[22] All the reaction products were confirmed by comparison with authentic samples.

**Deprotection of THP Ethers (General Procedure).** To a toluene solution (3.5 mL) of dodecyl THP ether (270 mg, 1 mmol) and **2b** (202 mg, 0.55 mmol) was added **3** (1.0 M toluene solution, 1 mL, 1 mmol) at −20 °C. The mixture was stirred for 1.5 h at

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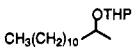
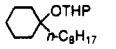
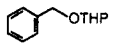
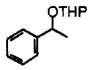
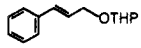
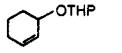
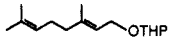
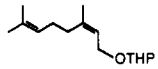
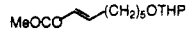
(19) CsF-promoted alkylation of alkoxystannanes: Nagashima, N.; Ohno, M. *Chem. Lett.* **1987**, 141.

(20) This method may find wide applications in other cases since separation of organotin compounds is often difficult, especially when a stoichiometric amount of these reagents is employed.

(21) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(22) Abel, E. W.; Armitage, D. A.; Brady, D. B. *J. Organomet. Chem.* **1966**, *5*, 130. Bamberg, P.; Ekstroem, B.; Sjoeberg, B. *Acta Chem. Scand.* **1968**, *22*, 367.

**Table I. Thiostannane-Promoted Deprotection of THP Ethers**

| entry | 1 | 2 (equiv) | reaction temp, °C | reaction time, h | alcohol yield,[a] % |
|---|---|---|---|---|---|
| 1 | $n$-$C_{12}H_{25}$OTHP | **2a** (1.1) | -20 | 3 | (97) |
| 2 | $n$-$C_{12}H_{25}$OTHP | **2b** (0.55) | -20 | 1.5 | 97 (100) |
| 3 | $n$-$C_{12}H_{25}$OTHP | **2c** (0.6) | 0 | 16 | (100) |
| 4 |  | **2c** (0.6) | 0 | 16 | 84 (100) |
| 5 |  | **2c** (0.6) | 0 | 9 | 80 (86) |
| 6 |  | **2c** (0.8) | 0 | 16 | (70) |
| 7 |  | **2c** (0.8) | 0 | 16 | (82) |
| 8 |  | **2c** (0.8) | 0 | 16 | 90 |
| 9 |  | **2c** (0.6) | 0 | 18 | (81) |
| 10 |  | **2c** (0.8) | -20 to 0 | 12 | 70 (85) |
| 11 |  | **2c** (0.8) | -20 to 0 | 12 | (82) |
| 12 | $^t$BuMe$_2$SiO-$(CH_2)_6$OTHF | **2c** (0.8) | 0 | 16 | 88 |
| 13 | AcO$(CH_2)_6$OTHP | **2c** (0.8) | 0 | 16 | 97 |
| 14 | $CH_3SO_3$-$(CH_2)_6$OTHP | **2c** (0.8) | 0 | 16 | 90 |
| 15 | MOMO-$(CH_2)_6$OTHP | **2c** (0.8) | 0 | 25 | 89 |
| 16 |  | **2c** (0.8) | 0 | 11 | 80 |

[a] Isolated yields. GLC yields are given in parentheses.

this temperature. GLC analysis of the solution indicated formation of 1-dodecanol in 100% yield. The reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was dried ($Na_2SO_4$) and evaporated. Column chromatography of the residue on silica gel (hexane–ethyl acetate, 97:3 to 70:30) afforded 1-docecanol (180 mg, 97%) and 2-(phenylthio)-tetrahydropyran (190 mg, 98%).[17]

**Deprotection of EE Octyl Ether.** To a toluene solution (4 mL) of EE octyl ether (203 mg, 1 mmol) and **2b** (204 mg, 0.56 mmol) was added **3** (1.0 M toluene solution, 1 mL, 1 mmol) at 0 °C. The mixture was stirred for 9 h at this temperature. Aqueous workup provided octanol in 87% based on GLC.

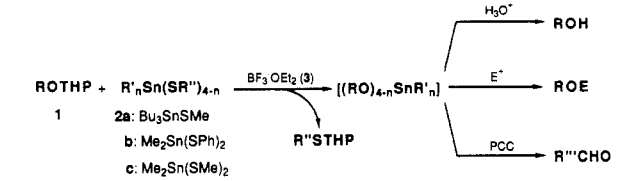
**Attempted Deprotection of 2-Phenyl-2-(tetrahydropyran-2-yloxy)propane.** To a toluene solution (3 mL) of 2-phenyl-2-(tetrahydropyran-2-yloxy)propane (220 mg, 1 mmol) and **2c** (136 mg, 0.56 mmol) was added **3** (1.0 M toluene solution, 1 mL, 1 mmol) at 0 °C. The mixture was stirred for 4 h at this temperature and poured into aqueous $NaHCO_3$. The mixture was extracted with benzene. Drying ($Na_2SO_4$), evaporation, and column chromatography (hexane) afforded 2-(methylthio)-2-phenylpropane (141 mg, 84%): $^1$H NMR ($CDCl_3$) $\delta$ 1.69 (s, 6 H), 1.76 (s, 3 H), 7.20–7.60 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 12.3, 29.4, 46.6, 126.3, 126.4, 128.0, 146.1; HRMS calcd for $C_{10}H_{14}S$ 166.0816, found 166.0771.

1-Methyl-1-(tetrahydropyran-2-yloxy)-2-cyclohexene was subjected to the same reaction to give 1-methyl-3-(methylthio)-1-cyclohexene in 99% yield: $^1$H NMR ($CDCl_3$) $\delta$ 1.55–1.75 (m, 2 H), 1.65 (s, 3 H), 1.80–1.95 (m, 4 H), 2.08 (s, 3 H), 3.28 (m, 1 H), 5.44 (m, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.9, 20.1, 23.8, 28.2, 29.8, 42.5, 121.8, 137.4; HRMS calcd for $C_8H_{14}S$ 142.0816, found 142.0840.

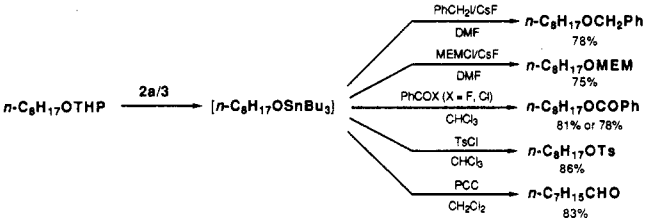
Subjection of *trans*-1-phenyl-3-(tetrahydropyran-2-yloxy)-1-butene to the same reaction afforded, after 3 h, 98% yield of *trans*-3-(methylthio)-1-phenyl-1-butene: $^1$H NMR ($CDCl_3$) $\delta$ 1.41 (d, 3 H, $J$ = 6.6 Hz), 2.01 (s, 3 H), 3.37 (m, 1 H), 6.04 (dd, 1 H, $J$ = 8.8 and 15.7 Hz), 6.34 (d, 1 H, $J$ = 15.7 Hz), 7.20–7.40 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.8, 20.1, 43.9, 126.1, 127.3, 128.4, 129.4, 131.7, 136.6; HRMS calcd for $C_{11}H_{14}S$ 178.0816, found 178.0796.

**Conversion to Benzyl Ether.** To a toluene solution (4 mL) of octyl THP ether (215 mg, 1 mmol) were added **2a** (371 mg, 1.1 mmol) and **3** (1.0 M toluene solution, 1 mL, 1 mmol) at 0 °C, and

**Scheme I**




**Scheme II**




the solution was stirred for 7 h. The solvent was evaporated in vacuo, and then DMF (5 mL) was added. To this solution were added benzyl iodide (297 mg, 1.3 mmol), CsF (198 mg, 1.3 mmol), and MS 3A (200 mg). The reaction mixture was stirred for 20 h at room temperature and poured into water. The mixture was extracted with ethyl acetate. After drying ($Na_2SO_4$) and evaporation, GLC analysis of the residue indicated formation of benzyl octyl ether in 78% yield.

**Conversion to MEM Ether.** To a DMF solution obtained according to the completely same procedure as above were added MEM chloride (436 mg, 3.5 mmol), CsF (228 mg, 1.5 mmol), and MS 3A (200 mg). The reaction mixture was stirred at room temperature for 12 h. The workup as described above afforded 75% yield of MEM octyl ether based on GLC analysis.

**Conversion to Benzoate.** The reaction of **1**, **2**, and **3** was carried out in the same way as above. Then, the toluene solvent was replaced by chloroform (5 mL). To this solution were added benzoyl fluoride (310 mg, 2.5 mmol) and MS 3A (200 mg). The mixture was stirred for 70 h. The workup analogous to the above operation afforded octyl benzoate (81% based on GLC). When benzoyl chloride was employed, the yield was 78%.

**Conversion to Tosylate.** The manipulation was analogous to the benzoylation except that tosyl chloride (381 mg, 2 mmol) was employed in place of benzoyl fluoride and that the reaction temperature was maintained at 40 °C for 70 h. The yield of the tosylate was 86% based on GLC. Column chromatography (hexane–benzene, 95:5) afforded the isolated product (218 mg, 77%).

**Conversion to Aldehyde.** The initial toluene solvent was replaced by dichloromethane (5 mL). To this solution was added PCC (432 mg, 2 mmol) and MS 3A (200 mg). The reaction mixture was stirred at room temperature for 10 h. The usual workup afforded octanal (106 mg, 83%).

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## Solution Geometry of β-Cyclodextrin–1-Bromoadamantane Host–Guest Complex As Determined by $^1$H{$^1$H} Intermolecular NOE and MM2 Calculations

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Host–guest chemistry[1-4] is gaining widespread interest because of its obvious implications in molecular recogni-

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