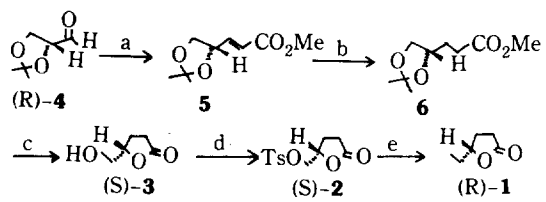
literature.



[a](a) $(MeO)_2POCH_2CO_2Me$. NaH. DME, rt → 60°C (b) H_2, Pd/C, EtOH (c) (i) 1.5 eqiv. LiOH, THF-H_2O (3:1), (ii) aq. AcOH (d) TsCl, pyr., CH_2Cl_2 (e) 2.0 eqiv. $(CH_3)_2$ CuLi, -70°C 2hr, -30°C 0.5 hr, 0°C 0.5 hr

Scheme 2. Synthesis of (R)-**1**[a]

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8. Satisfactory physical properties and spectroscopic data (^{1}H-NMR, IR, MS) were obtained for the compounds: (R)-2,3-O-isopropylideneglyceraldehyde (**4**); bp 39°C/15 mmHg; IR(NaCl, neat) 2850, 2750, 1725, 1180 cm^{-1}; ^{1}H-NMR (80MHz, $CDCl_3$) δ1.35(3H, s, CH_3), 1.46 (3H, s, CH_3), 4.01-4.18 (2H, d, OCH_2), 4.24-4.39 (1H, m, CH_2CHO), 9.85 (1H, s, CHCHO). Methyl (4S, 2E)-4,5-isopropylidenedioxypent-2-enoate (**5**); hexane: ethylacetate (9:1); $[\alpha]_D^{20}$ + 37.5° (c = 0.29, $CHCl_3$); IR (neat) 1700, 1650 cm^{-1}; ^{1}H-NMR δ1.42 (3H, s, CH_3), 1.45 (3H, s, CH_3), 3.63 (1H, m, CHHCHO), 3.75 (3H, s, OCH_3), 4.1 (1H, m, OCHHCHO), 4.65 (1H, m, CH_2CHO), 6.04 (1H, dd, J15 and 1.5Hz, CH = CH-CO), and 6.87 (1H, dd, J15 and 6Hz). Methyl(4S)-4,5-isopropylidenedioxypentanoate (**6**); bp 67-75°C/8 mmHg; IR(neat) 1700, 1650 cm^{-1}; ^{1}H-NMR δ1.42 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.9 (2H, m, CH_2), 2.5 (2H, m, $CH_2CO_2CH_3$), 3.63 (1H, m, CH-O), 3,75 (3H, s, OCH_3), 4.1 (2H, m, CH_2-O). (S)-(+)-5-hydroxymethyl-2-oxotetrahydrofuran (**3**); chloroform: methanol (98:2); $[\alpha]^{20}$ + 33.1° (c = 3.17, EtOH); IR (neat) 3400, 1765 cm^{-1}; ^{1}H-NMR δ 2.0-2.8 (4H, m, CH_2CH_2), 3.1 (1H, br.s, OH), 3.5-4.1 (2H, m, CH_2O), 4.6 (1H, m, -CH-O). (S)-(+)-p-toluenesulfonyloxymethyl-2-oxotetrahydrofuran (**2**); mp 85-7°C (ether; dichloromethane); $[\alpha]_D^{20}$ + 46.3° (c = 1.33, $CHCl_3$); IR (KBr, pellet) 1765 cm^{-1}; ^{1}H-NMR δ1.8-2.7 (4H, m, CH_2CH_2), 2.45 (3H, s, CH_3), 4.18 (2H, d, CH_2-O), 4.70 (1H, m, CH-O), 7.42 (2H, d, J = 10Hz), 7.85 (2H, d, J = 10Hz); MS 270 (M^+), 85 (base). (R)-(+)-hexan-4-olide (**1**); ether: hexane (3:2); $[\alpha]_D^{20}$ + 30.4° (c = 1.0, MeOH) [lit.,[2] $[\alpha]_D^{20}$ + 42.7° (c = 1, MeOH)]; IR (neat) 1770, 1170 cm^{-1}; ^{1}H-NMR δ 1.01 (3H, t, CH_3), 1.6-2.7 (6H, m, -$(CH_2)_2$-, -CH_2-), 4.6(1H, m, CH-O).
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Facile Cleavage of Tetrahydrofuran Derivatives with S-2-Pyridyl Thioates / $CuBr_2$ / CH_3CN†

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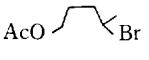
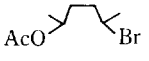
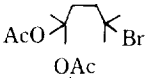
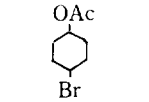
Previously we have reported a rapid and convenient preparation of sterically hindered carboxylic esters by the reaction of S-2-pyridyl thioates with alcohols in the presence of cupric bromide in acetonitrile.[1] We wish to report that S-2-pyridyl thioates/cupric bromide rapidly and cleanly cleaves tetrahydrofuran derivatives in acetonitrile at room temperature,[2-8] although S-2-pyridyl thioates/cupric bromide was inert to tetrahydrofuran derivatives at room temperature for a long period of time.[9] Thus, the success of the reaction depends crucially on the use of acetonitrile as a solvent, although the reason for this observation is rather unclear.

The reaction was carried out with equimolar amounts of S-2-pyridyl methanethioate and cupric bromide using a slight

† This paper is dedicated to Professor Sae-Hee Chang on the occasion of his 60th birthday.

Table 1. The Cleavage of Tetrahydrofurans with CH_3CO-S-2-Py / $CuBr_2$ / CH_3CN[a]

Substrate	Product	Yield, %[b]
		80
		93[c]
		75
		80
		71

[a]The reaction was carried out with at room temperature for 1 h. [b]Isolated yields. [c]4% of 5-bromo-2-pentyl acetate was also formed.

excess (1.2 equiv) of tetrahydrofuran derivatives in acetonitrile at room temperature. The reactions were generally complete within 1 h. Under the present conditions, tetrahydrofuran was converted into 4-bromobutyl acetate in 80% isolated yield. As shown in Table I, 2,5-dimethyltetrahydrofuran, 2,2,5,5-tetramethyltetrahydrofuran, and 7-oxabicyclo[2.2.1]heptane worked equally well. The present system showed a high regioselectivity in the cleavage of 2-methyltetrahydrofuran. Thus, 2-methyltetrahydrofuran was converted into a mixture of 4-bromopentyl acetate and 5-bromo-2-pentyl acetate in a ratio of 96:4, determined by GLC analysis, suggesting that the ring opening reaction may proceed via S_N1 process. The regioselectivity achieved with the present system is better that recently reported acetyl bromide/zinc chloride.[8] It is noteworthy that S-2-pyridyl thioates/$CuBr_2$/CH_3CN system did not cleave tetrahydropyran derivatives under forcing conditions, although it cleaved readily epoxide derivatives.[10]

In summary, we believe that the present procedure for acylative cleavage of tetrahydrofuran derivatives reported herein provides a useful alternative to currently available methods in terms of mild conditions and high regioselective cleavage of unsymmetrical tetrahydrofuran derivatives.

The typical procedure for the cleavage of tetrahydrofuran derivatives is as follows. To a suspended solution of S-2-pyridyl methanethioate (460 mg, 3.0 mmol) and cupric bromide (670 mg, 3.0 mmol) in acetonitrile (9 m*l*) at room temperature was added 2-methyltetrahydrofuran (360μl, 3.6 mmol). The reaction mixture was stirred at room temperature for 1 h, poured into a mixture of saturated NH_4Cl solution (30 m*l*) and saturated $NaHCO_3$ (10 m*l*), and extracted three times with methylene chloride (20 m*l* × 3). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure. The residue was purified by distillation with a Kugelrohr apparatus to give a 96:4 mixture of 4-bromopentyl acetate and 5-bromo-2-pentyl acetate (582 mg, 93% based on S-2-pyridyl methanethioate). The product ratio was determined by GLC analysis: bp 93-95 °C (20 mm) [lit.[8] 65-68 °C (2.5 mm)] ; ^1H NMR ($CDCl_3$) δ1.75 (d, 3H, J = 6 Hz, CH_3CHBr), 1.7-2.0 (m, 4H, CH_2), 2.05 (s, 3H, $OCOCH_3$), 3.9-4.3 (m, 3H, CHBr, CH_2OAc). A weak doublet at δ1.25 indicated the presence of ~5% 5-bromo-2-pentyl acetate; IR(film) 1735 cm^{-1}.

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9. Reaction of S-2-pyridyl methanethioate with equimolar amounts of cupric bromide in tetrahydrofuran at 50 °C for 12 h did not give 4-bromobutyl acetate to an observable extent. Furthermore, the use of diethyl ether and toluene as solvent was totally ineffective for the cleavage of tetrahydrofuran derivatives, although the use of dichloromethane was effective to some extent.
10. The acylative cleavage of tetrahydrofuran did not occur in refluxing acetonitrile for 12 h, whereas epibromohydrin was converted into a mixture of 2-acetoxy-1,3-dibromopropane and 1-acetoxy-2,3-dibromopropane in a ratio of 7:3 at room temperature within 20 min.