argon ions at the pressure of 5×10^{-6} Torr and ion energy of 2500 eV for 30 min. Subsequently the alloy was subject to annealing at 500℃ in ultrahigh vacuum for 1 h, and then its XPS spectra were obtained. After admission of 0.1 monolayer oxygen, immediately specta were taken to study initial adsorption phenomena. XPS spectra were taken with an electron spectrometer (PHI Model 548) equipped with a data processing system. The spectral areas determined by computer integration were corrected for instrumental parameters, photoionization cross-section, and difference in electron mean-free-paths. The results were quantitatively interpreted with a novel calibration method.[12,13] The experimental data in Figure 1 indicate that the surface becomes enriched with maganeses by annealing in vacuum and that the adsorption of oxygen on the annealed surface causes enrichment. This is in qualitative agreement with those of the model predictions. Upon adsorbing oxygen, the observed manganese segregation seems to be induced not by the initial stage of oxidation (or the surface oxide formation), but mainly by the oxygen chemisoption. It is supported by the fact that any surface oxides were not observed at 530 eV right after the adsorption of oxygne on the annealed surface. For the clean surfaces, the heat of segregation of -15.2 ± 1.4 kJ/mole was obtained from the slope of Arrhenius plot of XPS data and is closed to the estimated value.

Cu-Mn alloys have attracted great scientific and technological interest due to their strong activity in CO oxidation, unusually high mechanical damping characteristic, and reversible shape memory effect. Nevertheless, surface segregation for Cu-Mn alloys has never bee studied with the exception of Hedge *et al.*[14] They obtained the heat of segregation of -25 kJ/mole for Cu-Mn (5%) alloy from Arrhenius plots of the Auger and XPS data. It appears to be exaggerated compared with the model estimation and XPS measurements here, probably due to the surface oxide formation. Since the initial monoxide formation begins even at 2 L exposure, special attention should be paid to designing experimentation.

The unified model presented here provides a meaningful semiquantitative framework for describing the surface segregation of alloys, as demonstrated by XPS measurements, and could be generalized and extended to other alloy systems. It is useful for estimating the surface compositionn versus bulk composition profiles, to get a first approximation to surface compositon for verification and interpretation of experimental results, and to predict general trends in materials performance.

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Stereoselective Reduction of 2-(1,3-dithian-2-yl)-pentan-3-one-with Baker's Yeast

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Asymmetric reduction of ketones with baker's yeast (*Saccharomyces cerevisiae*) is significantly being recognized as a useful method to obtain chiral building blocks for the synthesis of natural products[1]. β-Ketoesters are the extensibly studied as the substrates of baker's yeast reduction[2]. But the studies on the baker's yeast reduction of 2-methyl-3-oxopentanoate to the corresponding chiral hydroxyester have been limited until now[3].

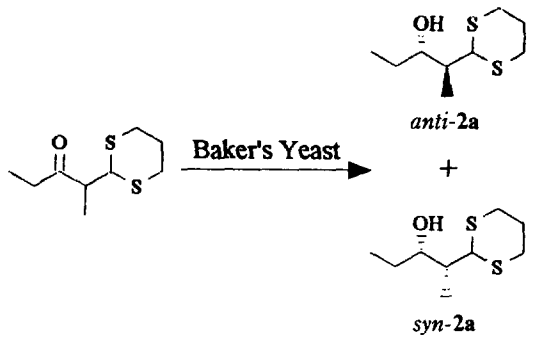
Recently, our laboratory reported the baker's yeast reduction of alkyl 2-methyl-3-oxopentanoate to the corresponding *anti*-2-methyl-3-hydroxy-pentanoate with relatively low enantioselectivity (34-66% e.e.) in spite of high diastereoselectivity (93-99%)[4].

Therefore, to improve the enantioselectivity of the baker's yeast reduction, we replaced ester group of 2-methyl-3-oxopentanoate with 1, 3-dithian-2-yl group[5].

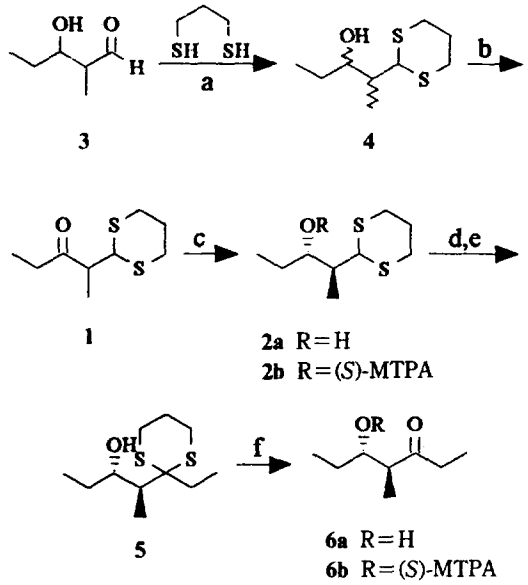
In this paper, we wish to report the highly diastereo-and enantioselective reduction of 2-(1,3-dithian-2-yl)-pentan-3-one **1** with baker's yeast to prepare 2-(1,3-dithian-2-yl)-pentan-3-ol **2a** as a novel chiral building block (Scheme 1).

The starting material **1** was prepared by thioacetalization of **3** with propanedithiol and $BF_3\cdot Et_2O$[6] followed by Swern oxidation of **4** with DMSO-TFAA[7] (Scheme 2)[8].

A typical procedure of the baker's yeast reduction is as



Scheme 1.



Scheme 2. Reagents and Reaction Conditions
(a) $BF_3 \cdot Et_2O$, CH_2Cl_2, −20℃, 4 hrs, 80.5%; (b) TFAA-DMSO, CH_2Cl_2, −65℃, 1 hrs, 99.3%; (c) BaKer's Yeast, 25℃, 250 rpm, 7 day, 9.9%; (d) 2 equivs. *n*-BuLi, THF, −30℃, 30 min→0℃, 8 hrs; (e) EtBr, THF, −78℃, 1 hr→0℃, 4 days, 52.8%; (f) $CuCl_2$, CuO, 90% acetone, Reflux, 2 hrs, 100%.

follows; A suspension of raw baker's yeast (Ottuki Co., Seoul, Korea, 60 g) and sucrose (20 g) in water (200 m*l*) was stirred at 25℃ for 1 hr, and **3** (0.5 g) in ethanol (0.5 m*l*) was added to the fermenting mixture. After 2 days, 30 g of baker's yeast was added and the mixture was stirred for another 2 days. Then, the suspension of baker's yeast (30 g) and sucrose (10 g) in water (100 m*l*) was added to the fermenting mixture, and the resulting mixture was stirred for additional 3 days. Celite and EtOAc were added and the mixture was stirred for 6 hrs, and then, filtered through a celite pad. The filtrate and the celite layer were extracted with EtOAc (×3), then filtered. The combined organic layers were washed with water, sat. $NaHCO_3$ sol'n and brine, dried (anh. $MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed on SiO_2 to give 0.05 g of **2a** (9.9%)[9].

The d.e. of **2a** by baker's yeast reduction was determinded by GLC[10] and the e.e. was determined by 500 MHz ^{1}H-NMR analysis of the corresponding (*S*)-(-)-MTPA ester[11] **2b**[12]. From these studies, the good result was obtained that **1** was reduced with high diastereoselectivity (*syn/anti*=3/97) and high enantioselectivity (98% e.e.).

To determine the abolute configuration of **2a**, 5-hydroxy-4-methyl-3-heptanone **6a**[13] was synthesized from **2a** (Scheme 2). The compound **2a** was lithiated with n-BuLi and alkylated with EtBr[14] to obtain **5**[15]. **6a** was obtained by hydrolysis of dithiane **5** with $CuCl_2/CuO$[16,17].

By analyzing corresponding (*S*)-(-)-MTPA ester[11] of **6a** on GLC(DB-1701)[18], the absolute configuration of *anti*-**6a** was found to be (4*S*, 5*S*) enantiomer (100% e.e.), and form these results, the absolute configuration of *anti*-**2a** from baker's yeast reduction was found to be 2*S*, 3*S*.

In conclusion, the baker's yeast reduction of 2-(1,3-dithian-2-yl)-pentan-3-one **1** provides novel chiral building block, (2*S*, 3*S*)-2-(1,3-dithian-2-yl)-pentan-3-ol **2a** with excellent diastereo- and enantioselectivity. It should be expected that this chiral alcohol could be useful for natural product synthesis because of the easy convertibility to other functional groups and non-functional structures. And, on the grounds of the above results, we found that 1,3-dithian-2-yl group highly controls the stereoselectivity of the yeast reduction.

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8. **1**: ^{1}H-NMR (500 MHz, $CDCl_3$) 1.07-1.10 (t, 3H), 1.24-1.25 (d, 3H), 1.86-2.12 (m, 2H), 2.54-2.58 (qd, 2H), 2.82-2.92 (m, 4H), 2.93-2.98 (qd, 1H), 4.25-4.27 (d, 1H).
9. *anti*-**2a**: ^{1}H-NMR (500 MHz, $CDCl_3$) 0.95-1.01 (m, 3H), 1.06-1.08 (d, 3H, J=7.00), 1.34-1.47 (m, 2H), 1.53-1.68 (m, 2H), 1.82-1.95 (m, 1H), 2.10-2.15 (m, 1H), 2.84-3.03 (m, 4H), 3.54-3.59 (m, 1H), 4.56-4.57 (d, 1H, J=3.28). GC-MSD (HP-FFAP) *m/z syn*-**2a**: 58(41) 73(54) 89(31) 149(100) 167 (35) *anti*-**2a**: 57(24) 73(36) 89(23) 133(12) 149(100) 167 (31).
10. Supelcowax™ 10 (60 m×0.25 mm I.D., 0.25 μm d_f), N_2, 220℃ isothermal. The composition of **2a**: *Syn*-**2a** (Rt 28. 46 min, area 3%), *anti*-**2a** (Rt 28.85 min, area 97%).
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12. The 3*S*-isomers always show upper field signals (triplet) for the terminal CH_3CH_2-resonances than 3*R*-isomers (e.g. CC_3CH_2-signal of 2*S*, 3*S* isomer of **2a** was at 0.828-0.798, and for other isomers signal were contered at low-

er field postition (2*R*, 3*S*: 0.887-0.857, 2*R*, 3*R*: 0.938-0.908, 2*S*, 3*R*: 0.959-0.929).)[11].
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15. **5** : ^{1}H-NMR (500 MHz, $CDCl_3$) 0.96-1.09 (m, 9H), 1.38-1.47 (m, 1H), 1.69-1.75 (m, 2H), 186-1.97 (m, 2H), 2.08-2.24 (m, 2H), 2.75-2.97 (m, 4H), 3.67 (b, 1H), 3.85-3.89 (m, 1H).
16. P. Stütz and P. A. Stadler, *Org. Synth.*, **56**, 8 (1977).
17. *anti*-**6a**: ^{1}H-NMR (270 MHz, $CDCl_3$) 0.95-1.1 (m, 9H), 1.35-1.5 (m, 2H), 2.5-2.7 (m, 3H), 3.25 (br, 1H), 3.65, 3.80 (m, m, 1H), GC-MSD (HP-1) *anti*-**6a**: 29(45), 41(13), 55 (24), 57(100), 70(25), 86(19), 97(7), 115(10), 126(8), *syn*-**6a** : 29(42), 41(14), 55(16), 57(100), 70(14), 86(25), 97(10), 115 (5), 126(9). These ^{1}H-NMR and MS data consist with the data from literature[13b].
18. To determine the absolute configuration and the ratio of enantiomers of **6a**, their (*S*)-(-)-MTPA ester **6b** were analyzed by GLC [DB-1701, 30 m×0.25 mm I.D., 0.25 μm d_f, N_2, 180℃ (20 min) to 280℃ (5℃/min)] and were compared to the data from the literature[4] (The absolute configuration of **6a** was confirmed by the coinjection of **6b** with the (*S*)-(-)-MTPA ester of synthetic racemic **6a**). The composition of **6a**: 4*S*, 5*S* (Rt 25.84 min, area 100%), 4*R*, 5*R* (Rt 25.96 min, area 0%).

Facile Conversion of Carboxamides to Nitriles

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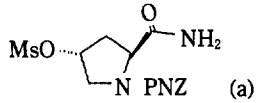
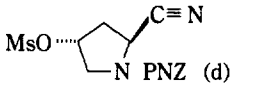
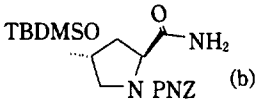
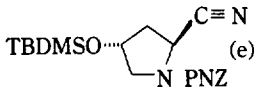
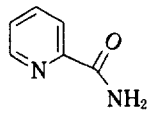
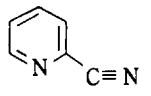
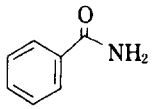
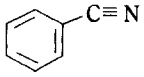
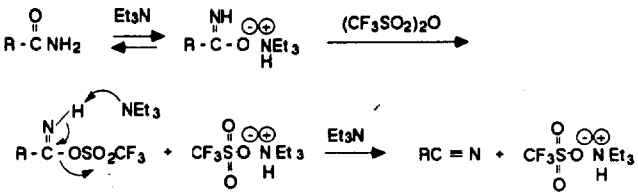
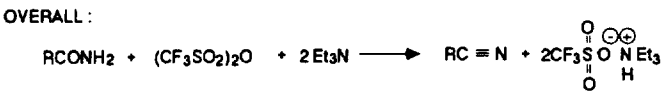
The transformation of carboxamides into nitriles is well documented. The amides which can be converted to nitriles under relatively drastic conditions involving the basic reagents, include mesitamide with sodium hydroxide in refluxing ethylene glycol[1], phenylacetamide with *n*-butyllithium[2], benzamide with silazanes at 220℃[3]. On the other hand acidic reagents appear to offer milder conditions (at room temperature or below) and better yields: Trichloroacetyl chloride[4], ethylpolyphosphate[5], trimethylsilyl polyphosphate[6], cyanuric chloride/dimethylformamide[7], Vilsmeier reagent[8], trifluoroacetic anhydride[9], titanium tetrachloride[10], triphenylphosphine[11], boron trifluoride[12], phosphoryl chloride/pyridine[13], aluminum chloride[14], chlorosulfonyl isocyanate[15], thionyl chloride[16]. However, there still exists a need for the development of new, mild methods for the transformation. The trifluoromethanesulfonyl ("trifyl") group has been shown to be an effective activator for sulfoxonium oxidation (dimethyl sulfide ditriflate by virtue of the exceptionally strong electron with drawing capability of the trifyl group)[16,17]. The use of triphenylphosphine ditriflate as dehydrating reagent was demonstrated[17]. To our best knowledge, there has not been reported the direct application of trifluoromethanesulfonic anhydride for conversion of amides to nitriles. The conditions of present method used are mild (0℃ or below), yields are high (see Table 1), and the reaction is complete within a short time (1 hour).

Table 1. Preparation of Nitriles from Amides with trifluoromethanesulfonic Anhydride

Amides	Nitriles	Yield#
 (a)	 (d)	84%
 (b)	 (e)	78%
		90%
		65%

1) Ms: Methanesulfonyl, TBDMS: *tert*-butyldimethylsilyl, PNZ: *p*-Nitrobenzyloxycarbonyl. 2) #: % yield purified by column chromatography. 3) Synthesis of Amides (a), (b): See ref. 19. 4) Identification Data of (d), (e): See ref. 18. 5) Synthesized cyanopyridine and benzonitrile were identified by comparison with known standards.





Scheme 1.

By analogy to the general mechanism proposed for this type of dehydration by a derivated acidic reagent, the reaction probably undergoes according to the pathway and the stoichiometry shown in the following scheme (Scheme 1).

Experimental Section

A typical procedure is as follows: To a magnetically stirred