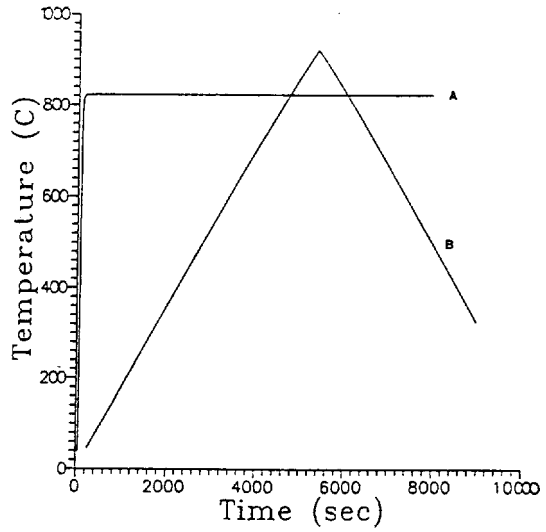

Figure 3. Temperature profiles of a DTA furnace programmed by an external 12-bit digital-to-analog converter using a personal computer. The curve A is a constant temperature regulation at 820℃ and the curve B is a linear ramp (105℃/10 min) up to 920℃ and back to 300℃.

comparator starts to generate pulses for fine regulation of the system temperature (time region T2). The pulse width will vary within the proportional band depending on the magnitude of the temperature differences between the modulated temperature signal and the set-point temperature signal. This enables the furnace power supply to operate in pulse switching mode instead of operating in either fully on or fully off mode. If the system temperature is too cold then the furnace power supply will be fully off to decrease the system temperature (time region T3). The switching of the furnace power supply was done by a transistor switch circuit using three NPN power transistors (one 2N3055 and two MJ802) to withstand repeated high loads of the furnace heater.

The temperature difference between the programmed temperature and the system temperature under control can be minimized by adjusting the offset of the multiplier. The reference temperature signal can be programmed in two ways. If only a fixed temperature is desired, one can supply a fixed voltage using a simple voltage divider. Also, the temperature controller can be programmed by an external source such as digital-to-alanlog converter (DAC). In this way, the system temperature can be programmed through a personal computer to function in various modes. The comparator generates pulses whose pulse width varies depending on the temperature differences between the reference and the system under control. These pulses are used to switch the furnace power supply ON or OFF.

The temperature profiles of a furnace controlled by the controller is shown in Figure 3. We used a home made differential thermal analysis furnace for system evaluation. A DAC output of a data acquisition board[3] is connected to the reference temperature signal input of the controller. The proportional bandwidth is adjusted to 20% of the reference temperature signal. However, the optimum bandwidth must be obtained by trial and error because different heat capacity of the furnace requires different bandwidth. The furnace temperature is programmed by software using a personal computer. The temperature regulation at a fixed temperature showed ± 0.15℃ accuracy and the temperature ramp whose rate is programmable by software also showed reasonable linearity up to 600℃. At high temperatures above 600℃, the temperature ramp profile showed nonlinearity. It is belived that the nonlinearity is mainly due to the nonlinear response of the temperature sensor used. The temperature sensor used is the combination of a K-type thermocouple and a AD597 (Analog Device) thermocouple amplifier[4]. The nonlinearity can be corrected easily if the temperature controller is controlled by a computer by adding offsets to the reference temperature, otherwise it must be corrected by obtaining a calibration curve at high temperatures. The temperature controller can be made using readily available components at low cost. The complete system can be built with less than ₩50,000. Also, compact design with reasonable accuracy makes it ideal for the system temperature control in various chemical instrumentations.

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Stereochemical Control in Baker's Yeast Reduction. 2: Stereoselective Reduction of Alkyl 2-Methyl-3-oxopentanoates under Different Conditions

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Baker's yeast (*Saccharomyces cerevisiae*) has often been applied to stereoselectively convert 2-methyl-3-oxobutanoate derivatives to the corresponding chiral hydroxy ester derivatives.[1] However, the studies on the baker's yeast reduction of alkyl 2-methyl-3-oxopentanoate derivatives (**1**) to the corresponding hydroxy ester derivatives **2** as the useful chiral building blocks[2] is limited until now.[3] Recently, our laboratory has reported by the baker's yeast reduction of **1** to the corresponding *anti*-alkyl 3-hydroxy-2-methylpentanoate (**2**) with high diastereoselectivity.[4] Especially, butyl 2-methyl-3-oxopentanoate was reduced to *anti*-butyl 3-hydroxy-2-methylpentanoate in remarkably high diastereomeric excess (*de*,

Table 1. Effect of the Amount of Allyl Alcohol on the Baker's Yeast Reduction[a] of Ethyl 2-Methyl-3-oxopentanoate (**1a**) and Octyl 2-Methyl-3-oxopentanoate (**1b**)

Substrate	Allyl alcohol(g/l)	*anti/syn* Ratio[b]	Reduction ratio(%)[c]
1a	1	95/5	>95
	2	97/3	52.2
	3	98/2	48.4
	5	>99	43.8
	10	>99	17.3
1b	1	46/54	25
	2	88/12	3.2
	3	–	1.8
	5	–	–
	10	–	–

[a]RBY 30 g, distilled water 50 m*l*, sucrose 4 g, substrate 1 mmol. [b]*anti/syn* Ratios were measured by GLC analysis[HP-1, 25 m ×0.2 mm I.D.×0.11 μm, N_2 0.55 m*l*/min, injector 280℃, FID 300℃, split 30 : 1, 60℃ (2 min), to 280℃ (5℃/min)]. The structure of *anti* and *syn* isomers were identified with ^{13}C-NMR[11] and ^{1}H-NMR (270 MHz).[12] [c]Reduction ratios were determined by GLC and equation : (product **2**/substrate unreduced)×100.

>96%). But other esters **1** except butyl ester demonstrated slightly lower *de*(94-76%),[4] so we elaborated reduction conditions to increase *de* using allyl alcohol,[5] and glucose or sucrose[6c] as stereochemical control additives[6] in yeast reduction. In Table 1 were summarized the results of raw baker's yeast (RBY, Ottuki Co.) reduction of ethyl ester **1a** and octyl ester **1b** at various allyl alcohol concentrations. Ethyl ester **1a** was reduced with high diastereoselectivity as the concentration of allyl alcohol increased. Octyl ester **1b** was reduced with low *anti/syn* ratio (46/54) at 1 g/*l* of allyl alcohol, while the *anti/syn* ratio was enhanced to 88/12 at higher allyl alcohol concentration (*i.e.*, 2 g/*l*).

When ethyl ester **1a** was reduced with baker's yeast in the presence of allyl alcohol and gulcose, *anti*-**2a** was obtained in more than 93%. Whereas sucrose was added instead of glucose, *anti*-**2a** was obtained in more than 97% with slightly higher reduction ratio. Meanwhile, octyl ester **1b** was treated with sucrose of various concentration in the absence of allyl alcohol. At 2.5 g/50 m*l* of sucrose concentration, the reduction ratio was 36.3% and *anti/syn* ratio was 95/5 after 60 hr cultivation, and at 5 g/50 m*l* of sucrose, reduction ratio was 15.3% and *anti/syn* ratio was 98/2. Treatment of the same system at 10 g/10 m*l* of sucrose gave low reduction ratio (<5%).

Consequently, by controlling sucrose concentration, diastereoselectivity enhancement in the reduction of **1b** was achieved. And the diastereoselectivity in the reduction of **1a** was increased by the aid of allyl alcohol and sucrose.

To determine the absolute configuration and enantiomeric excess(*ee*) of **2a** and **2b**, 5-hydroxy-4-methyl-3-heptanone (**3**) was synthesized from **2a** and **2b**.[7] By measuring optical rotation and analyzing corresponding MTPA esters[8] on GLC,[9] absolute configuration of *anti*-**3a** was found to be (4*R*, 5*R*) enantiomer (34% *ee*), *anti*-**3b**, (4*S*, 5*S*) enantiomer (66% *ee*). On the grounds of the above results, ethyl ester **1a** was affected by allyl alcohol in the diastereoselective reduction with low enantioselectivity. This result was different from that of baker's yeast reduction of ethyl 3-oxopentanoate in the presence of allyl alcohol.[5] In the case of **1b**, modest enantioelctivity in baker's yeast reduction was due to the steric bulkiness of carboalkoxy group.[10]

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9. The absolute configurations of the stereoisomers of **3** were determined by comparison of the $[\alpha]_D$ data from the literature.[7] Compound **3a**, $[\alpha]_D^{23}-4.3°$ (*c* 0.03, ether) (lit[7]: 4*R*, 5*R*-**3**, $[\alpha]_D^{23}-37.8°$), **3b**, $[\alpha]_D^{23}+10°$ (*c* 0.05, ether), (lit[7]: 4*S*, 5*S*-**3**, $[\alpha]_D^{23}+36.8°$). To determine the ratio of enantiomers of compound **3**, their MTPA esters were analyzed by GLC[DB1701, 25 m×0.25 mm I.D.×0.241 μm, 180℃ (20 min) to 280℃ (5℃/min)]. The composition of **3b** was as follows: 4*S*, 5*S* (Rt, 24.07 min; area 31%), 4*R*, 5*R* (24.20 min, 67%), *syn* isomer (24.66 min, 2%), *syn* isomer (24.81 min, –%). The composition of **3b**: 4*S*, 5*S* (83%), 4*R*, 5*R* (14%), *syn* isomer (2%), *syn* isomer (–%).
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