parameter used in the fitting is the standard deviation of the activation energy which decreases with temperature as indicated in Table 2. The fact that the standard deviation of activation energy in PMMA is about 2000 times larger than those used for NSO in ethanol indicates that thermal reaction is greatly influenced by the microscopic heterogeneity of molecular environments around PMC. The wide distribution of the activation energy may be understood in terms of the inherent disorder of the polymer. The photochromic compounds trapped in a sparse and widely separated set of local potential minima, which is inherent in polymer and coupled to the guest molecules, cannot thermally access to lowest minima at temperatures below T_g. As temperature increases, the parameter σ decreases. At last the width σ at T_g is expected to be the same with that in solution resulting in the first-order reaction as observed in azo compounds.[15]

In summary, the thermal fading reaction of NSO follows the first-order reaction in ethanol solution while it shows large departure from the single exponential decay in PMMA polymer. The deviation from the first order reaction of the monomolecular photochromic reaction in PMMA was explained using disorder of the matrix which causes the thermodynamic parameters to fluctuate around average value.

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A Facile Preparation of α-Amino-β-Methoxydiazines through the Lithianation Followed by Amination

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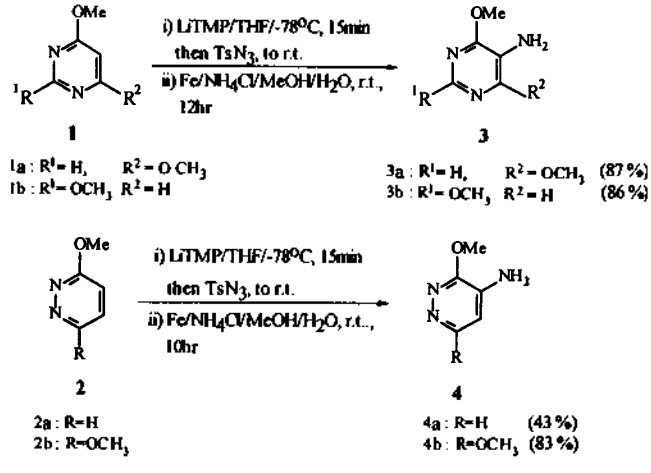
α-Amino-β-methoxydiazines are common synthons for the construction of a variety of diazine fused heterocycles by a^2, d^0/a^1, d^n combination.[1] Several routes for preparation have been known by reaction of α-amino-β-chlorodiazine with sodium methoxide followed by Hofmann rearrangement,[2] amination of methoxydiazine by potassium amide-liquid ammonia,[3] treatment of dichlorodiazine with ammonia solution followed by the reaction with sodium methoxide.[4] However, these methods require harsh reaction conditions and result in low yields and selectivities. In connection with our project for the synthesis of diazine heterocycles, we devised an alternative method for the preparation of the α-amino-β-methoxydiazines, which included the regiospecific introduction of nitrogen functionality to methoxydiazine by directed orthometalation.[5] While some examples for introducing carbon electrophiles to the methoxydiazines by orthometalation have been known,[6] to the best of our knowledge, amination of diazines by the orthometalation has not been reported. We report herein a facile one-pot preparation of α-amino-β-methoxydiazines *via* the orthoazidation followed by a reduction.

Result and Discussion

Compound **1a** was treated with LiTMP in THF and the resulting lithiated compound was reacted with tosyl azide. This amination condition seems to be essential for regiospecific and efficient generation of **3a**. When TMEDA (tetramethylethylenediamine) was used as a chelating agent only a trace amount of **3a** could be obtained. The reaction mixture was treated subsequently with an excess amount of Fe/NH_4



Scheme 1.

Cl in methanol-water (1 : 1) mixed solvent at room temperature to afford the desired **3a**. This condition was previously employed for the chemoselective reduction of nitro group on aromatic rings with various labile functionalities.[7] In this study, we found that Fe/NH_4Cl in methanol-water (1 : 1) condition was also very effective for the mild reduction of azido group on diazine heterocycles. In an essentially identical fashion, methoxydiazines **1**[8] and **2**[9] were transformed smoothly into the corresponding aminomethoxydiazines **3**[10] and **4**[3] in excellent yields, respectively. The results are summarized in Scheme 1. Due to easy access of starting materials, good yield and simple one-pot procedure, these synthetic approaches can be compared favorably with other methods.

Experimental section

The typical procedure is as follows; To a solution 2,2,6,6-tetramethylpiperidine (1.5 mL, 8.9 mmol) in THF (20 mL) was added *n*-butyllithium (5.4 mL, 1.6 M in hexane, 8.6 mmol) at −78 ℃ under a nitrogen atmosphere. The resulting mixture was stirred for 30 min at −78 ℃, and then canulated to THF solution (10 mL) of 4,6-dimethoxypyrimidine **1a** (1 g, 7.1 mmol) at −78 ℃. After being stirred for 15 min at −78 ℃, tosyl azide (1.8 g, 9.1 mmol) was added to the resulting solution. The mixture was warmed to room temperature and the solvent was removed under reduced pressure. The resulting residue was dissolved in methanol-water (1 : 1) mixed solvent, and then treated successively with Fe (2 g, 35.8 mmol) and NH_4Cl (1.9 g, 35.5 mmol). After the mixture was stirred for 12h at room temperature, usual workup followed chromatography on silica gel (chloroform/methanol) gave **3a** as white crystals in 87% yield.

5-amino-4,6-dimethoxypyrimidine (3a). white powder; mp 93-95 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (br s, NH_2), 4.01 (s, OCH_3), 7.98 (s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.6, 114.6, 145.6, 157.8; EI-MS (m/z, relative intensity) 155 (M^+, 100%), 154 (39), 140 (27), 126 (26), 112 (35), 108 (21), 97 (12), 85 (34), 72 (14); IR ν_{max} (KBr) cm^{-1} 3440, 3309.

5-amino-2,4-dimethoxypyrimidine (3b). white powder; mp 84-86 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (br s, NH_2), 3.92 (s, OCH_3), 4.03 (s, OCH_3), 7.71 (s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.7, 55.1, 124.2, 141.2, 159.1, 161.5; EI-MS (m/z, relative intensity) 155 (M^+, 100%), 154 (39), 140 (28), 126 (42), 125 (48), 85 (23), 83 (30), 70 (24), 57 (25); IR ν_{max} (KBr) cm^{-1} 3407, 3325.

4-amino-3-methoxypyridazine (4a). white powder; mp 126-128 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, OCH_3), 4.51 (br s, NH_2), 6.54 (d, J=5.24 Hz, C_5-H), 8.41 (d, J=5.24 Hz, C_6-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 108.1, 136.5, 148.2, 156.3; EI-MS (m/z, relative intensity): 125 (M^+, 100%), 124 (42), 96 (47), 69 (28), 68 (39); IR ν_{max} (KBr) cm^{-1} 3466, 3309.

4-amino-3,6-dimethoxypyridazine (4b). white powder; mp 177-179 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, OCH_3), 4.07 (s, OCH_3), 4.42 (br s, NH_2), 6.07 (s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.8, 55.1, 97.5, 138.8, 153.9, 163.7; EI-MS (m/z, relative intensity) 155 (M^+, 100%), 154 (82), 126 (17), 95 (21), 68 (40), 67 (20); IR ν_{max} (KBr) cm^{-1} 3423, 3326.

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Calix[4]arene : An Efficient Synthesis of 5-*tert*-Butyl-11-methyl-17,23-diphenyl-25,26,27,28-tetrahydroxycalix[4]arene

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Calixarenes are synthetic macrocycles available in a variety of ring sizes and interesting both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structure and have received a great deal of attention in recent years.[1~3]

One of the main features of naturally occurring host molecules is their capacity for enantioselective recognition. Various attempts have therefore been made to obtain chiral host molecules based on calixarenes. The most simple method to convert calixarene into chiral derivatives is the introduction of chiral substituent at the lower[4,5] or upper[6,7] rim of calixarene skeleton. More interest has been focused on the possibility of synthesizing "inherently" chiral calix[4]arenes, which are built up of nonchiral subunits and consequently owe their chirality to the fact that the calixarene molecule