

Effects of Magnesium Salts and Amines on the Stereoselectivity in the Imine Aldol Reaction

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In the imine aldol reactions of **1 with aromatic aldehydes using magnesium salts in the presence of amines, the *threo/erythro* ratios of products increased in the order $\text{Mg}(\text{ClO}_4)_2 > \text{MgI}_2 > \text{MgBr}_2 > \text{MgCl}_2 > \text{Mg}(\text{OTf})_2$ and N,N,N',N' -tetramethylethylenediamine (TMEDA) $> \text{Et}_3\text{N}$. This increase in the *threo/erythro* ratios of products was estimated to be caused by a *retro-imine aldol* reaction under thermodynamic control.**

Key words magnesium; reverse stereoselectivity; imine aldol reaction; thermodynamic control; *retro-imine aldol* reaction

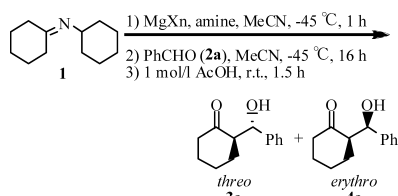
In previous studies, we have reported aldol-type reactions with magnesium salts in the presence of amines and shown the unique stereo- and chemoselectivity.^{1–6} In the course of study, we were interested in the effects of magnesium salts by differences in the counter anions and the effects of the amines. It is known that the counter anions of metal salts and amines affect the reactivity and/or selectivity in some aldol-type reactions.^{7–11} This paper describes the effects of magnesium salts and amines on the stereoselectivity of the imine aldol reaction³ of *N*-cyclohexylimine **1** with aromatic aldehydes.

Imine aldol reactions with PhCHO (**2a**) using various magnesium salts in the presence of Et_3N were examined, and the results are summarized in Table 1.

As shown in Table 1, variable stereoselectivity was observed. In the presence of Et_3N , the use of MgCl_2 , MgBr_2 , and $\text{Mg}(\text{OTf})_2$ gave *erythro*-excess products (*threo/erythro* = 7/93, 10/90 and 5/95), while the employment of MgI_2 and $\text{Mg}(\text{ClO}_4)_2$ resulted in the formation of *threo*-excess products (*threo/erythro* = 57/43 and 75/25). Interestingly, the *threo/erythro* ratios of products increased in the reaction with N,N,N',N' -tetramethylethylenediamine (TMEDA) instead of Et_3N , and the reversal of stereoselectivity was observed in the cases of MgCl_2 and MgBr_2 (*threo/erythro* = 7/93 $\rightarrow$ 91/9 and 10/90 $\rightarrow$ 81/19). Previously, we reported that the *threo* product was obtained under thermodynamic control, and the *erythro* product was formed under kinetic control in the imine aldol reaction of **1** with aromatic aldehydes using MgBr_2 in the presence of Et_3N .³ In contrast, H. X. Wei and co-workers have proposed the ‘boat-metal transition state’¹²) as the intermediate in the aldol reaction of ketones with aldehydes using MgI_2 in the presence of amine to explain the generation of *threo* products.¹¹) Thus, in order to identify the cause of the variable stereoselectivity depending on the kinds of magnesium salts and amines, the reactions employing $\text{Mg}(\text{OTf})_2$ and $\text{Mg}(\text{ClO}_4)_2$ in the presence of Et_3N , in which the reversal stereoselectivity was observed (Table 1, *threo/erythro* = 5/95 and 75/25), were carried out and the change in the *threo/erythro* ratios of products with time was confirmed. As shown in Table 2, the use of $\text{Mg}(\text{OTf})_2$ afforded the *erythro*-excess products regardless of the reaction time (*threo/erythro* = 5/95). However, in the case of $\text{Mg}(\text{ClO}_4)_2$, the *erythro*-excess products were converted to the *threo*-excess products as time advanced without a change

in yields (Table 2, *threo/erythro* = 43/57 $\rightarrow$ 75/25). The change in the *threo/erythro* ratios of products with time suggested that $\text{Mg}(\text{ClO}_4)_2$ gave the *threo* product **3a** under thermodynamic control, not *via* the ‘boat-metal transition state’. Because, if the reaction using $\text{Mg}(\text{ClO}_4)_2$ proceeded *via* the ‘boat-metal transition state’, the *threo/erythro* ratios of products wouldn’t change from the beginning of the reaction. In the case of $\text{Mg}(\text{OTf})_2$, the lack of change in the *threo/erythro* ratios of products with time suggested that the reaction proceeded under kinetic control and afforded the *erythro*-excess

Table 1. Stereoselectivity in the Imine Aldol Reaction of **1** with **2a**



MgXn ^a	Et_3N^b <i>threo/erythro</i> ^c (yield %) ^d	TMEDA ^b <i>threo/erythro</i> ^c (yield %) ^d
MgF_2	— (0)	—
MgCl_2	7/93 (90)	91/9 (93)
MgBr_2	10/90 (92)	81/19 (82)
MgI_2	57/43 (91)	78/22 (84)
$\text{Mg}(\text{OTf})_2$	5/95 (72)	16/84 (22)
$\text{Mg}(\text{ClO}_4)_2$	75/25 (84)	90/10 (90)
MgSO_4	— (0)	—

a) 1.2 mol eq of the magnesium salt was employed. b) 2.4 mol eq of the amine was employed. The ‘mol eq’ was based on the nitrogen atom of amine. c) Determined by 200 MHz ¹H-NMR analysis. d) Isolation yield of a mixture of **3a** and **4a**.

Table 2. Change in the Stereoselectivity with Time in the Reaction of **1** with **2a** Employing $\text{Mg}(\text{OTf})_2$ and $\text{Mg}(\text{ClO}_4)_2$

Reaction time	$\text{Mg}(\text{OTf})_2^a$ <i>threo/erythro</i> ^b (yield %) ^c	$\text{Mg}(\text{ClO}_4)_2^a$ <i>threo/erythro</i> ^b (yield %) ^c
10 min	5/95 (9)	43/57 (83)
30 min	—	58/42 (89)
16 h	5/95 (72)	75/25 (84)

a) Reaction condition: magnesium salts (1.2 mol eq)– Et_3N (2.4 mol eq) at -45°C . b) Determined by 200 MHz ¹H-NMR analysis. c) Isolation yield of a mixture of **3a** and **4a**.

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products. Further, the reactions using Et_3N and TMEDA in the presence of MgCl_2 were also examined, as shown in Table 3. The use of Et_3N gave rise to the *erythro*-excess products, regardless of the reaction time, and TMEDA changed the *threo/erythro* ratios of products with time like $\text{Mg}(\text{ClO}_4)_2$ did. These results were rationalized by the same reasons described above. Thus, the magnesium salts and amines were speculated to cause a *retro*-imine aldol reaction under thermodynamic control and to increase the *threo/erythro* ratios of products in the order $\text{Mg}(\text{ClO}_4)_2 > \text{MgI}_2 > \text{MgBr}_2 > \text{MgCl}_2 > \text{Mg}(\text{OTf})_2$ and $\text{TMEDA} > \text{Et}_3\text{N}$, as summarized in Fig. 1.

Table 4 shows representative results of the reaction of **1** with aromatic aldehydes **2a–f** under four kinds of conditions (A–D). The reactions under condition A using $\text{Mg}(\text{OTf})_2$ produced lower *threo/erythro* ratios of products than those under condition B employing $\text{Mg}(\text{ClO}_4)_2$, and the reversal of stereoselectivity was observed except in the reaction with **2d** (entry 4). The only reaction with **2a** and **2b** under condition C showed lower *threo/erythro* ratios of products than those under condition D using TMEDA (entries 1, 2). The effect of $\text{Mg}(\text{ClO}_4)_2$ was observed in the all reactions

Table 3. Change in the Stereoselectivity with Time in the Reaction of **1** with **2a** Employing Et_3N and TMEDA

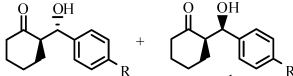
Reaction time	Et_3N^a <i>threo/erythro</i> ^b (yield %) ^c	TMEDA ^a <i>threo/erythro</i> ^b (yield %) ^c
10 min	7/93 (50)	7/93 (60)
2 h	—	32/68 (79)
16 h	7/93 (90)	91/ 9 (93)

a) Reaction condition: MgCl_2 (1.2 mol eq)–amines (2.4 mol eq) at -45°C . The “mol eq” of the amine was based on the nitrogen atom. b) Determined by 200 MHz ^1H -NMR analysis. c) Isolation yield of a mixture of **3a** and **4a**.

Product	System	MgXn	Amine
<i>erythro</i> 4a	Kinetic control	$\text{Mg}(\text{OTf})_2$	Et_3N
↓	↓	MgCl_2	
<i>threo</i> 3a	Thermodynamic control	MgBr_2	
		MgI_2	
		$\text{Mg}(\text{ClO}_4)_2$	TMEDA

Fig. 1. Summary of the Stereoselectivity in the Imine Aldol Reaction of **1** with **2a**

Table 4. Stereoselectivity in the Imine Aldol Reaction with Various Aldehydes

1) Conditions A - D 2) R--CHO, MeCN, -45 °C, 16 h 3) 1 mol/l AcOH, r.t., 1.5 h						
Entry	R	Products	Condition A ^{a)} <i>threo/erythro</i> ^{b)} (yield %) ^{c)}	Condition B ^{a)} <i>threo/erythro</i> ^{b)} (yield %) ^{c)}	Condition C ^{a)} <i>threo/erythro</i> ^{b)} (yield %) ^{c)}	Condition D ^{a)} <i>threo/erythro</i> ^{b)} (yield %) ^{c)}
1	H	3a/4a	5/95 (72)	75/25 (84)	7/93 (90)	91/ 9 (87)
2	MeO	3b/4b	8/92 (30)	75/25 (73)	12/88 (70)	68/32 (55)
3	Me	3c/4c	5/95 (64)	76/24 (81)	9/91 (82)	9/91 (85)
4	Ph	3d/4d	9/91 (71)	33/67 (88)	7/93 (91)	8/92 (87)
5	Cl	3e/4e	8/92 (86)	67/33 (84)	17/83 (86)	7/93 (91)
6	MeO ₂ C	3f/4f	20/80 (84)	65/35 (89)	24/76 (90)	15/85 (93)

a) Condition A: $\text{Mg}(\text{OTf})_2$ (1.2 mol eq)– Et_3N (2.4 mol eq) at -45°C for 1 h, condition B: $\text{Mg}(\text{ClO}_4)_2$ (1.2 mol eq)– Et_3N (2.4 mol eq) at -45°C for 1 h, condition C: MgCl_2 (1.2 mol eq)– Et_3N (2.4 mol eq) at -45°C for 1 h, condition D: MgCl_2 (1.2 mol eq)–TMEDA (2.4 mol eq) at -45°C for 1 h. The “mol eq” of amine was based on the nitrogen atom. b) Determined by 200 MHz ^1H -NMR analysis. c) Isolation yield of a mixture of **3a–f** and **4a–f**.

of **1** with **2a–f**, though TMEDA had only a limited effect on the imine aldol reaction.

Experimental

All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. IR spectra were obtained on a JASCO FT/IR-420 IR Fourier transform spectrometer. ^1H -NMR (200, 400 MHz) spectra were recorded on a JEOL JNM-FX200 or JEOL JNM-GSX400 spectrometer. Chemical shifts are given in δ values (ppm) using tetramethylsilane (TMS) as an internal standard. Electron impact (EI)-MS were recorded on a JEOL JMS SX-102A spectrometer. Elementary combustion analyses were performed on a Yanaco CHN CORDER MT-5. All reactions were monitored by TLC employing 0.25-mm silica gel plates (Merck 5715; 60 F_{254}). Column chromatography was carried out on silica gel [Kanto Chemical 60N; 63–210 μm]. All reagents were used as purchased.

Typical Procedure for the Reaction of **1 with **2a** Using $\text{Mg}(\text{OTf})_2$ in the Presence of Et_3N (Table 1)** To a suspension of 1.2 mol eq of $\text{Mg}(\text{OTf})_2$ (726 mg, 2.3 mmol) in MeCN (9 ml) was added a solution of **1** (346 mg, 1.9 mmol) and 2.4 mol eq of Et_3N (0.645 ml, 4.6 mmol) in MeCN (4 ml) at -45°C under argon. After being stirred at -45°C for 1 h, a solution of 1 mol eq of **2a** (205 mg, 1.9 mmol) in MeCN (3 ml) was added and stirred at -45°C for 16 h. The reaction mixture was quenched with 1 mol/l AcOH at room temperature for 1.5 h and extracted with CH_2Cl_2 . The CH_2Cl_2 extract was washed with saturated NaHCO_3 and brine, dried over MgSO_4 , and evaporated *in vacuo*. The residue of *threo* **3a** and *erythro* **4a** in the ratio of 5 : 95 was purified by column chromatography (eluent AcOEt –*n*-hexane, 3/7) to give the mixture of *threo* **3a** and *erythro* **4a** (282 mg, 72%). Ratio determination was carried out by ^1H -NMR analysis (200 MHz, CDCl_3).

Compound **3a**¹³: Pale yellow needles (CH_2Cl_2 –*n*-hexane), mp 73 – 74°C . ^1H -NMR (400 MHz, CDCl_3) δ : 1.2–1.3 (1H, m), 1.5–1.7 (3H, m), 1.7–1.8 (1H, m), 2.0–2.1 (1H, m), 2.3–2.4 (1H, m), 2.4–2.5 (1H, m), 2.6–2.7 (1H, m), 3.98 (1H, d, $J=2.9$ Hz), 4.78 (1H, dd, $J=2.9$, 8.8 Hz), 7.3–7.4 (5H, m). IR (KBr) cm^{-1} : 3555, 1703, 1448, 1133, 1061, 986, 702, 677. EI-MS m/z : 204.1142 (Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$: 204.1150).

Compound **4a**¹³: Colorless needles (CH_2Cl_2 –*n*-hexane), mp 105 – 107°C . ^1H -NMR (400 MHz, CDCl_3) δ : 1.5–1.6 (1H, m), 1.6–1.8 (3H, m), 1.8–1.9 (1H, m), 2.0–2.1 (1H, m), 2.3–2.5 (2H, m), 2.5–2.6 (1H, m), 3.08 (1H, d, $J=2.4$ Hz), 5.39 (1H, br s), 7.2–7.4 (5H, m). IR (KBr) cm^{-1} : 3503, 1687, 1131, 777, 746, 704, 553. EI-MS m/z : 204.1131 (Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$: 204.1150).

Compound **3b**¹⁴: Colorless prisms (Et_2O –*n*-hexane), mp 79 – 80°C . ^1H -NMR (400 MHz, CDCl_3) δ : 1.2–1.3 (1H, m), 1.5–1.8 (4H, m), 2.0–2.1 (1H, m), 2.3–2.4 (1H, m), 2.4–2.5 (1H, m), 2.5–2.6 (1H, m), 3.80 (3H, s), 3.94 (1H, d, $J=2.9$ Hz), 4.74 (1H, dd, $J=2.9$, 8.8 Hz), 6.88 (2H, d, $J=8.8$ Hz), 7.24 (2H, d, $J=8.8$ Hz). IR (KBr) cm^{-1} : 3462, 1708, 1515, 1252, 1174, 1029, 829, 559. EI-MS m/z : 234.1260 (Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$: 234.1256).

Compound **4b**¹⁴: Colorless needles (Et_2O –*n*-hexane), mp 126 – 127°C . ^1H -NMR (400 MHz, CDCl_3) δ : 1.5–1.6 (1H, m), 1.6–1.9 (4H, m), 2.0–2.1 (1H, m), 2.3–2.5 (2H, m), 2.5–2.6 (1H, m), 3.04 (1H, d, $J=2.9$ Hz), 3.80 (3H, s), 5.32 (1H, t, $J=2.9$ Hz), 6.87 (2H, d, $J=8.3$ Hz), 7.22 (2H, d,

$J=8.3$ Hz). IR (KBr) cm^{-1} : 3441, 1696, 1511, 1250, 1170, 834. EI-MS m/z : 234.1256 (Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$: 234.1256).

Compound **3e**¹⁴: Colorless prisms (Et_2O - n -hexane), mp 91–92 °C. ^1H -NMR (400 MHz, CDCl_3) δ : 1.2–1.3 (1H, m), 1.5–1.7 (3H, m), 1.7–1.8 (1H, m), 2.0–2.1 (1H, m), 2.3–2.4 (1H, m), 2.34 (3H, s), 2.4–2.5 (1H, m), 2.6–2.7 (1H, m), 3.92 (1H, d, $J=2.9$ Hz), 4.75 (1H, dd, $J=2.9$, 8.9 Hz), 7.15 (2H, d, $J=8.3$ Hz), 7.20 (2H, d, $J=8.3$ Hz). IR (KBr) cm^{-1} : 3517, 1689, 1297, 1130, 1044, 823, 554. EI-MS m/z : 218.1292 (Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: 218.1307).

Compound **4e**¹⁴: Colorless prisms (Et_2O - n -hexane), mp 111–113 °C. ^1H -NMR (400 MHz, CDCl_3) δ : 1.5–1.6 (1H, m), 1.6–1.8 (3H, m), 1.8–1.9 (1H, m), 2.0–2.1 (1H, m), 2.3–2.4 (1H, m), 2.34 (3H, s), 2.4–2.5 (1H, m), 2.5–2.6 (1H, m), 2.99 (1H, d, $J=2.9$ Hz), 5.35 (1H, t, $J=2.9$ Hz), 7.14 (2H, d, $J=8.3$ Hz), 7.19 (2H, d, $J=8.3$ Hz). IR (KBr) cm^{-1} : 3471, 1697, 1133, 1120, 1091, 985, 825, 533. EI-MS m/z : 218.1304 (Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: 218.1307).

Compound **3d**: Colorless needles (CH_2Cl_2 - n -hexane), mp 142–143 °C. ^1H -NMR (400 MHz, CDCl_3) δ : 1.3–1.4 (1H, m), 1.5–1.7 (3H, m), 1.8–1.9 (1H, m), 2.0–2.1 (1H, m), 2.3–2.4 (1H, m), 2.4–2.5 (1H, m), 2.6–2.7 (1H, m), 4.01 (1H, d, $J=2.4$ Hz), 4.84 (1H, dd, $J=2.4$, 8.8 Hz), 7.35 (1H, t, $J=7.8$ Hz), 7.40 (2H, d, $J=7.8$ Hz), 7.44 (2H, t, $J=7.8$ Hz), 7.58 (2H, d, $J=7.8$ Hz), 7.59 (2H, d, $J=7.8$ Hz). IR (KBr) cm^{-1} : 3493, 1693, 1488, 1128, 846, 776, 762, 699. EI-MS m/z : 280.1455 (Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$: 280.1463). Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$: C, 81.39; H, 7.19. Found: C, 81.21; H, 7.24.

Compound **4d**: Colorless needles (Et_2O - n -hexane), mp 138–139 °C. ^1H -NMR (400 MHz, CDCl_3) δ : 1.5–1.6 (1H, m), 1.6–1.9 (4H, m), 2.0–2.1 (1H, m), 2.3–2.4 (1H, m), 2.4–2.5 (1H, m), 2.6–2.7 (1H, m), 3.08 (1H, d, $J=2.4$ Hz), 5.44 (1H, t, $J=2.4$ Hz), 7.34 (1H, t, $J=7.8$ Hz), 7.38 (2H, d, $J=7.8$ Hz), 7.44 (2H, t, $J=7.8$ Hz), 7.58 (2H, d, $J=8.3$ Hz), 7.60 (2H, d, $J=8.3$ Hz). IR (KBr) cm^{-1} : 3449, 1699, 1488, 1110, 1093, 750, 692. EI-MS m/z : 280.1483 (Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$: 280.1463). Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$: C, 81.39; H, 7.19. Found: C, 81.28; H, 7.23.

Compound **3e**¹³: Colorless prisms (CH_2Cl_2 - n -hexane), mp 97–98 °C. ^1H -NMR (400 MHz, CDCl_3) δ : 1.2–1.3 (1H, m), 1.5–1.7 (3H, m), 1.7–1.8 (1H, m), 2.0–2.1 (1H, m), 2.3–2.4 (1H, m), 2.4–2.5 (1H, m), 2.5–2.6 (1H, m), 4.00 (1H, d, $J=2.9$ Hz), 4.76 (1H, dd, $J=2.9$, 8.8 Hz), 7.26 (2H, d, $J=8.3$ Hz), 7.32 (2H, d, $J=8.3$ Hz). IR (KBr) cm^{-1} : 3420, 1698, 1486, 1128, 1090, 1013, 831, 556. EI-MS m/z : 238.0756 (Calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{Cl}$: 238.0761).

Compound **4e**¹³: Colorless prisms (CH_2Cl_2 - n -hexane), mp 119–120 °C. ^1H -NMR (400 MHz, CDCl_3) δ : 1.5–1.6 (1H, m), 1.6–1.7 (3H, m), 1.8–1.9 (1H, m), 2.0–2.1 (1H, m), 2.3–2.4 (1H, m), 2.4–2.5 (1H, m), 2.5–2.6 (1H, m), 3.09 (1H, d, $J=2.9$ Hz), 5.35 (1H, t, $J=2.9$ Hz), 7.24 (2H, d, $J=8.3$ Hz), 7.30 (2H, d, $J=8.3$ Hz). IR (KBr) cm^{-1} : 3530, 1703, 1491, 1314, 1129, 1087, 833, 542. EI-MS m/z : 238.0753 (Calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{Cl}$: 238.0761).

Compound **3f**¹⁵: Colorless needles (Et_2O - n -hexane), mp 109–110 °C.

^1H -NMR (400 MHz, CDCl_3) δ : 1.3–1.4 (1H, m), 1.5–1.7 (3H, m), 1.7–1.8 (1H, m), 2.0–2.1 (1H, m), 2.3–2.4 (1H, m), 2.4–2.5 (1H, m), 2.5–2.6 (1H, m), 3.91 (3H, s), 4.04 (1H, d, $J=2.9$ Hz), 4.85 (1H, dd, $J=2.9$, 8.8 Hz), 7.40 (2H, d, $J=8.3$ Hz), 8.02 (2H, d, $J=8.3$ Hz). IR (KBr) cm^{-1} : 3526, 1717, 1694, 1446, 1313, 1283, 1117, 750. EI-MS m/z : 262.1202 (Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4$: 262.1205).

Compound **4f**¹⁵: Colorless needles (Et_2O - n -hexane), mp 132–134 °C. ^1H -NMR (400 MHz, CDCl_3) δ : 1.4–1.5 (1H, m), 1.6–1.8 (3H, m), 1.8–1.9 (1H, m), 2.0–2.1 (1H, m), 2.3–2.5 (2H, m), 2.6–2.7 (1H, m), 3.14 (1H, d, $J=2.9$ Hz), 3.91 (3H, s), 5.45 (1H, t, $J=2.9$ Hz), 7.38 (2H, d, $J=8.3$ Hz), 8.01 (2H, d, $J=8.3$ Hz). IR (KBr) cm^{-1} : 3535, 1699, 1313, 1282, 1120, 1106, 1091, 712. EI-MS m/z : 262.1216 (Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4$: 262.1205).

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