Supporting Informations

Guanidines as a Nitrogen Source for Direct Conversion of Epoxides to Aziridines

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TOC

Experimental Section

General ^1H NMR spectra were measured in CDCl_3 , using tetramethylsilane as an internal standard. ^{13}C -NMR spectra were recorded using the middle resonance of CDCl_3 (77.0 ppm) as an internal standard. Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), and q (quartet), m (multiplet), dd (double doublets), dt (double triplets), ddt (double double triplets), dif. (diffused). EIMS were recorded with direct inlet or GC-MS. HRFABMS were recorded with *m*-nitrobenzyl alcohol as a matrix. Anhydrous dichloromethane (CH_2Cl_2) was purchased from Kanto Chemical. Chloroform was distilled without any additive. *N,N*-Dimethylformamide (DMF), triethylamine (Et_3N) and acetonitrile (CH_3CN) were distilled from calcium hydride (CaH_2). Epoxides ($\pm$)-**3b**¹, ($\pm$)-**3d**¹ and ($\pm$)-**3e**² were prepared according to the reported procedure.

2-Benzylimino-1,3-dimethylimidazolidine³ (**2a**): Typical Procedure for the Synthesis of Guanidines.

A solution of benzylamine (1.97 mL, 18.1 mM) in CH_2Cl_2 (18 mL) was slowly added to an ice-cooled solution of DMC (91% w/w, 5.59 g, 33.1 mM, 1.8 Meq) and Et_3N (9.73 mL, 69.8 mM, 3.8 Meq) in CH_2Cl_2 (50 mL) under argon and the whole was stirred at room temperature (rt) for 5 h and the solvent was evaporated. The residue was dissolved in H_2O (4 mL), basified with 20% aqueous NaOH to pH *ca* 12, and extracted with toluene (5 x 160 mL). The combined organic layers was washed with H_2O (10 x 10 mL) and brine (5 x 10 mL), dried over MgSO_4 , and evaporated *in vacuo* to give **2a** as a yellow oil (3.69 g). The purity was calculated as 92.1% from ^1H -NMR analysis. IR (neat, cm^{-1}) 1662. ^1H NMR (400 MHz) δ : 2.85 (6H, br s), 3.20 (4H, s), 4.67 (2H, s), 7.19 (1H, t, J = 7.6 Hz), 7.30 (2H, t, J = 7.3 Hz), 7.40 (2H, d, J = 7.9 Hz). ^{13}C NMR (100 MHz) δ : 36.1, 49.1, 50.4, 53.2, 125.5, 126.5, 127.7, 143.3, 157.6.

2-Allylimino-1,3-dimethylimidazolidine.

A yellow oil. IR (neat, cm^{-1}) 1654. ^1H NMR (400 MHz) δ : 2.81 (6H, br s), 3.16 (4H, s), 4.06 (2H,

dt, $J = 4.8, 2.0$ Hz), 5.06 (1H, dt, $J = 10.2, 2.0$ Hz), 5.26 (1H, dt, $J = 17.0, 2.0$ Hz), 6.13 (1H, ddt, $J = 17.0, 10.2, 4.8$ Hz). ^{13}C NMR (100 MHz) δ : 31.4, 45.0, 49.5, 113.3, 139.4, 157.9. HRFABMS m/z : 154.1351 (Calcd for $\text{C}_8\text{H}_{16}\text{N}_3$: 154.1344).

2-(*tert*-Butyloxycarbonylmethylimino)-1,3-dimethylimidazolidine.

A brown oil. IR (neat, cm^{-1}) 1736, 1655. ^1H NMR (400 MHz) δ : 1.47 (9H, s), 2.82 (6H, br s), 3.18 (4H, s), 4.13 (2H, s). ^{13}C NMR (100 MHz) δ : 28.1, 31.5, 45.0, 50.4, 80.2, 158.8, 172.5. HRFABMS m/z : 228.1722 (Calcd for $\text{C}_{11}\text{H}_{22}\text{N}_3\text{O}_2$: 228.1712).

2-(2-Propylimino)-1,3-dimethylimidazolidine.

A yellow oil. IR (neat, cm^{-1}) 1655. ^1H NMR (400 MHz) δ : 1.33 (6H, d, $J = 6.2$ Hz), 2.79 (6H, br s), 3.13 (4H, s), 3.89 (1H, septet, $J = 6.2$ Hz). ^{13}C NMR (100 MHz) δ : 26.2, 31.5, 45.0, 45.4, 155.7. HRFABMS m/z : 156.1508 (Calcd for $\text{C}_8\text{H}_{18}\text{N}_3$: 156.1501).

2-Phenylimino-1,3-dimethylimidazolidine.^{3,4}

A yellow oil. IR (neat, cm^{-1}) 1640. ^1H NMR (400 MHz) δ : 2.64 (6H, br s), 3.28 (4H, s), 6.83 (1H, t, $J = 7.5$ Hz), 6.87 (2H, d, $J = 7.5$ Hz), 7.17 (2H, t, $J = 7.5$ Hz).

($\pm$)-*o*-Methoxystyrene Oxide: Typical Procedure for the Synthesis of Styrene Oxides via Methylenation of Aldehydes.

Sodium hydride (60% in oil, 737 mg, 18.4 mM, 1.2 Meq) was placed in 100-mL egg-shaped flask and was washed with dry hexane in three times under argon. Trimethylsulfonium iodide (3.97 g, 8.1 mM, 1.2 Meq) and DMSO (25.0 mL) was successively added and the mixture was stirred at rt for 30 min. A solution of *o*-methoxybenzaldehyde (1.85 mL, 15.2 mM) in DMSO (5.0 mL) was added under ice-cooling and the whole was stirred at rt for 10 min. After addition of H_2O (40 mL), the mixture was extracted with Et_2O (3 x 200 mL). The combined organic layer was washed with H_2O (3 x 100 mL) and brine (1 x 100 mL), dried over Na_2SO_4 , and evaporated *in vacuo* to give a yellow oil (1.89 g). Distillation of the oil (bp₅ 130-140 °C with Kugelrohr apparatus) gave a colorless oil (1.55 g, 68%). ^1H NMR⁵ (400 MHz) δ : 2.71 (1H, dd, $J = 5.7, 2.7$ Hz), 3.14 (1H, dd, $J = 5.7, 4.2$

Hz), 3.87 (3H, s), 4.21 (1H, dd, $J = 4.2, 2.7$ Hz), 6.88 (1H, d, $J = 8.2$ Hz), 6.94 (1H, t, $J = 7.6$ Hz), 7.15 (1H, dd, $J = 7.6, 1.6$ Hz), 7.26 (1H, td, $J = 7.6, 1.6$ Hz). EIMS m/z : 151 (MH^+ , 3.8%), 150 (M^+ , 40%), 121 (68%), 91 (100%).

(±)-*p*-Methoxystyrene Oxide.

A colorless oil. Bp₃ 140-160 °C (Kugelrohr). ¹H NMR⁶ (400 MHz) δ: 2.81 (1H, dd, $J = 5.3, 2.6$ Hz), 3.13 (1H, dd, $J = 5.3, 4.2$ Hz), 3.81 (3H, s), 3.82 (1H, dd, $J = 4.2, 2.6$ Hz), 6.88 (2H, dif. d, $J = 8.8$ Hz), 7.21 (2H, dif. d, $J = 8.8$ Hz). EIMS m/z : 150 (M^+ , 20%), 121 (100%).

(±)-*p*-Methylstyrene Oxide: Typical Procedure for the Synthesis of Styrene Oxides *via* Epoxidation of Styrene.

To a solution of *p*-methylstyrene (496 mg, 4.20 mM) and methyltrioxorhenium (5.4 mg, 0.022 mM, 0.5 mol%) in CH₂Cl₂ (1.7 mL) was added a solution of pyridine (40 mg, 0.50 mM, 0.12 Meq) in CH₂Cl₂ (0.46 mL) and then 30% H₂O₂ (0.65 mL, 6.76 mM, 1.6 Meq) *via* syringe within 10 min. After stirring the mixture at rt for 4 h, further 30% H₂O₂ (0.65 mL, 6.76 mM, 1.6 Meq) was similarly added. The mixture was stirred for 24 h at rt, quenched with MnO₂ (1.0 mg), dried over Na₂SO₄, and evaporated *in vacuo* to give a colorless oil (520 mg). Distillation of the oil (bp₁₀ 160-165 °C with Kugelrohr apparatus) afforded a colorless oil (262 mg, 47%). ¹H NMR⁶ (400 MHz) δ: 2.33 (3H, s, CH₃), 2.76-2.79 (1H, m, 3-H), 3.09-3.12 (1H, m, 3-H), 3.81-3.82 (1H, m, 2-H), 7.08-7.31 (4H, m, Ar-H). EIMS m/z : 134 (M^+ , 33%), 119 (34%), 105 (100%), 91 (33%), 79 (72%).

(±)-*p*-Chlorostyrene Oxide.

A colorless oil. Bp₁₀ 160-165 °C. ¹H NMR⁷ (400 MHz) δ: 2.73-2.75 (1H, m), 3.12-3.14 (1H, m), 3.82-3.83 (1H, m), 7.20 (2H, dif. d, $J = 8.6$ Hz), 7.31 (2H, dif. d, $J = 8.8$ Hz). EIMS m/z : 156 [($M+2$)⁺, 9%], 154 (M^+ , 29%), 125 (65%), 119 (54%), 91 (46%), 89 (100%).

(±)-1-Benzyl-2-phenylaziridine (5a): Typical Procedure for the Synthesis of Aziridines from Guanidines and Styrene Oxides.

A mixture of **2a** (102 mg, 0.50 mM) and ($\pm$)-**3a** (60 mg, 0.50 mM) in solvent (1 mL) was refluxed for 7 days under argon (in the presence of an additives if necessary). The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (hexane-AcOEt = 20:1) to give **5a** as a colorless oil. ^1H NMR⁸ (400 MHz) δ : 1.85 (1H, d, J = 6.6 Hz), 1.99 (1H, d, J = 3.3 Hz), 2.51 (1H, dd, J = 6.6, 3.3 Hz), 3.60, 3.69 (each 1H, d, J = 13.7 Hz), 7.20-7.38 (10H, m). EIMS m/z : 209 (M^+ , 2.4%), 208 (11%), 118 (28%), 91 (100%).

($\pm$)-1-Allyl-2-phenylaziridine (Entry 1 in Table 3).

A colorless oil. ^1H NMR (400 MHz) δ : 1.73 (1H, d, J = 6.5 Hz), 1.95 (1H, d, J = 3.4 Hz), 2.36 (1H, dd, J = 6.5, 3.4 Hz), 2.99 (1H, dddd, J = 14.1, 5.5, 1.5, 1.3 Hz), 3.13 (1H, ddd, J = 14.1, 5.5, 1.5 Hz), 5.12 (1H, ddt, J = 10.4, 1.8, 1.3 Hz), 5.24 (1H, ddt, J = 17.2, 1.8, 1.5 Hz), 5.97 (1H, ddt, J = 17.2, 10.4, 5.5 Hz), 7.20-7.33 (5H, m). HRFABMS m/z : 160.1114 (Calcd for $\text{C}_{11}\text{H}_{13}\text{N}$: 160.1126).

($\pm$)-tert-Butoxycarbonylmethyl-2-phenylaziridine (Entry 2 in Table 3).

A colorless oil. IR (neat, cm^{-1}) 1743 (C=O). ^1H NMR (400 MHz) δ : 1.44 (9H, s), 1.77 (1H, d, J = 6.6 Hz), 2.05 (1H, d, J = 3.7 Hz), 2.45 (1H, dd, J = 6.6, 3.7 Hz), 3.12, 3.21 (each 1H, d, J = 16.0 Hz), 7.21-7.30 (5H, m). ^{13}C NMR (100 MHz) δ : 28.0, 37.5, 41.4, 62.6, 81.2, 126.3, 127.0, 128.2, 139.4, 169.4. HRFABMS m/z : 234.1477 (Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: 234.1494).

($\pm$)-1-(2-Propyl)-2-phenylaziridine (Entry 3 in Table 3).

A colorless oil. ^1H NMR (400 MHz) δ : 1.18 (6H, dd, J = 6.3, 1.1 Hz), 1.62 (1H, septet, J = 6.3 Hz), 1.66 (1H, d, J = 6.6 Hz), 1.90 (1H, d, J = 3.4 Hz), 2.35 (1H, dd, J = 6.6, 3.4 Hz), 7.19-7.31 (5H, m). ^{13}C NMR (100 MHz) δ : 21.8, 22.3, 36.5, 40.9, 61.8, 126.4, 126.7, 128.2, 140.5. HRFABMS m/z : 162.1271 (Calcd for $\text{C}_{11}\text{H}_{16}\text{N}$: 162.1283).

($\pm$)-1-Benzyl-2-(2-methoxyphenyl)aziridine (Entry 5 in Table 3).

A colorless oil. ^1H NMR (400 MHz) δ : 1.84 (1H, d, J = 6.6 Hz), 1.91 (1H, d, J = 3.5 Hz), 2.87 (1H, dd, J = 6.6, 3.5 Hz), 3.65 (2H, s), 3.82 (3H, s), 6.83 (1H, d, J = 8.2 Hz), 6.90 (1H, dd, J = 7.5, 7.1 Hz), 7.16-7.26 (3H, m), 7.31 (2H, dd, J = 7.3, 7.3 Hz), 7.40 (2H, d, J = 7.1 Hz). ^{13}C NMR (100 MHz) δ : 36.5, 37.3, 55.3, 64.8, 109.9, 120.6, 126.5, 126.8, 127.6, 128.0, 128.2, 128.3, 139.3, 157.0.

HRFABMS m/z : 240.1388 (Calcd for $C_{16}H_{18}NO$: 240.1388).

Assignment of ($\pm$)-1-Benzyl-2-(4-methoxyphenyl)aziridine in the Crude Product (Entry 6 in Table 3).

1H NMR (400 MHz) δ : 1.81 (1H, d, $J = 6.6$ Hz), 1.96 (1H, d, $J = 3.5$ Hz), 2.46 (1H, dd, $J = 6.6, 3.5$ Hz), 3.57, 3.69 (each 1H, d, $J = 13.7$ Hz), 3.78 (3H, s), 6.83 (2H, d, $J = 8.4$ Hz), 7.16-7.37 (7H, m). EIMS (GC type) m/z : 240 (MH^+ , 5%), 239 (M^+ , 32%), 122 (91%), 91 (100%).

Assignment of ($\pm$)-1-Benzyl-2-(4-methylphenyl)aziridine in the Crude Product (Entry 7 in Table 3).

1H NMR (400 MHz) δ : 1.81 (1H, d, $J = 6.6$ Hz), 1.96 (1H, d, $J = 3.3$ Hz), 2.31 (3H, s), 2.46 (1H, dd, $J = 6.6, 3.3$ Hz), 3.57, 3.69 (each 1H, d, $J = 13.7$ Hz), 7.08-7.37 (9H, m). EIMS (GC type) m/z : 223 (M^+ , 7%), 222 (19%), 105 (100%), 91 (29%).

Assignment of ($\pm$)-1-Benzyl-2-(4-chlorophenyl)aziridine in the Crude Product (Entry 8 in Table 3).

1H NMR (400 MHz) δ : 1.85 (1H, d, $J = 6.6$ Hz), 1.93 (1H, d, $J = 3.3$ Hz), 2.46 (1H, dd, $J = 6.4, 3.3$ Hz), 3.57, 3.70 (each 1H, d, $J = 13.7$ Hz), 7.17-7.36 (9H, m). EIMS (GC type) m/z : 243 (M^+ , 3%), 154 (18%), 152 (58%), 127 (32%), 125 (100%), 91 (33%), 89 (26%).

References

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2-Benzylimino-1,3-dimethylimidazolidine (2a) ¹H NMR (CDCl₃).

2-Benzylimino-1,3-dimethylimidazolidine (2a) ^{13}C NMR (CDCl_3).

2-Allylimino-1,3-dimethylimidazolidine ^1H NMR (CDCl_3).

2-Allylimino-1,3-dimethylimidazolidine ^{13}C NMR (CDCl_3).

2-(*tert*-Butyloxycarbonylmethylimino)-1,3-dimethylimidazolidine. ^1H NMR (CDCl_3).

2-(2-Propylimino)-1,3-dimethylimidazolidine. ^1H NMR (CDCl_3).

2-Phenylimino-1,3-dimethylimidazolidine. ^1H NMR (CDCl_3).

(±)-*o*-Methoxystyrene Oxide. ^1H NMR (CDCl_3).

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(±)-*p*-Methoxystyrene Oxide. ^1H NMR (CDCl_3).

(±)-*p*-Methylstyrene Oxide. ^1H NMR (CDCl_3).

(±)-*p*-Chlorostyrene Oxide ¹H NMR (CDCl₃).

(±)-1-Benzyl-2-phenylaziridine (5a) ^1H NMR (CDCl_3).

(±)-1-Allyl-2-phenylaziridine ¹H NMR (CDCl₃).

(±)-*tert*-Butoxycarbonylmethyl-2-phenylaziridine. ^1H NMR (CDCl_3).

(±)-tert-Butoxycarbonylmethyl-2-phenylaziridine. ¹³C NMR (CDCl₃).

(±)-1-(2-Propyl)-2-phenylaziridine. ^1H NMR (CDCl_3).

(±)-1-(2-Propyl)-2-phenylaziridine. ^{13}C NMR (CDCl_3).

6 ($\pm$)-1-Benzyl-2-(2-methoxyphenyl)azidirine. ^1H NMR (CDCl_3).

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(±)-1-Benzyl-2-(2-methoxyphenyl)aziridine. ^{13}C NMR (CDCl_3).

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Chromatogram

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hexane

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Autozero [min] : 0.00

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現在日時: 28-Jan-2003 18:17:30

ユーザー : FURUTA

グループ : FURUTA

システムプログラム:

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4		20.413	334417	15315750.204	88.22

ピーク総面積= 17360890.883 [uAU. Sec]