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Simple preparation of chiral 1,3-dimethyl-2-iminoimidazolidines (monocyclic guanidines) and applications to asymmetric alkylative esterification

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Abstract

New chiral 1,3-dimethyl-2-iminoimidazolidines (monocyclic guanidines) were simply prepared by the action of primary amines on 2-chloro-1,3-dimethylimidazolinium chlorides, derived from the corresponding urea, in high yields. Modest asymmetric induction in alkylative esterification of benzoic acid with (1-bromoethyl)benzene was observed when the 1,3-dimethyl-4,5-diphenyl-2-[(1-phenyl- or 1-naphthyl)ethylimino]imidazolidines with all S (or R) configurations were used as bases.

1. Introduction

The use of chiral guanidine derivatives as synthetic tools has appeared limited because of difficulties in their preparation, in spite of the potential usefulness of guanidine derivatives as stronger bases than amines. Successful asymmetric inductions were observed in the aldol reaction[1] of benzaldehyde with nitromethane and in the Strecker amino acid synthesis[2] using guanidines with C_2-symmetry and a simple guanidine with a cyclic peptide, respectively, as catalysts. Recently Mioskowski et al.[3] reported the simple preparation of chiral guanidinium salts. We[4] have explored 2-chloro-1,3-dimethylimidazolinium chloride (DMC) **1** as a new dehydrating reagent to replace dicyclohexylcarbodiimide (DCC) **2** and demonstrated its synthetic utilities. 1,3-Dimethyl-2-iminoimidazolidines[5] as monocyclic guanidines could be easily prepared from DMC **1** and related compounds by the action of appropriate primary amines. Thus, we focused on the ability of chiral cyclic guanidines **3** based on 1,3-dimethylimidazolidines as functionalized catalysts for asymmetric induction.

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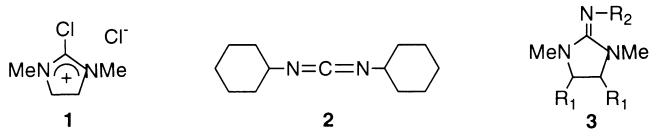
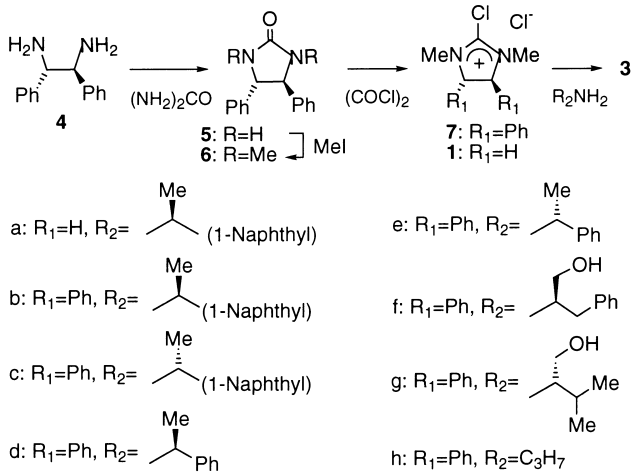


1 2 3

The formation of esters is a fundamental reaction in organic chemistry,[6] in which the most general method is acylation of an alcohol through O–acyl bond formation. Thus, there are known asymmetric esterifications using either achiral acylating agents in the presence of chiral auxiliaries such as optically active amines[7] and phosphines[8] or chiral acylating agents.[9] On the other hand, alkylation of carboxylic acids through O–alkyl bond formation is an alternative useful method because of the advantage of the neutral conditions, in which metal salts of acids were usually used as nucleophiles. Barton et al.[10] succeeded in the preparation of hindered esters from the corresponding guanidinium salts of carboxylic acids.[11] However, no reports on asymmetric esterification by this O-alkylation method have appeared to date. In this paper we present the simple preparation of chiral 1,3-dimethyl-2-iminoimidazolidines (monocyclic guanidines) **3** and their first application to the asymmetric alkylative esterification of benzoic acid **8** with (1-bromoethyl)benzene **9**.

2. Results and discussion

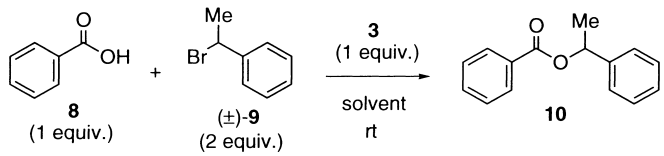
Preparation of guanidines **3** is shown in Scheme 1. A guanidine **3a** with one stereogenic center was easily obtained by action of a chiral primary amine to DMC **1**. Monocyclic guanidines **3b**–**h** with additional stereogenic centers were similarly prepared from the cyclic urea **5**,[12] derived from (1S,2S)-1,2-diphenyl-1,2-ethylenediamine **4**, through the corresponding imininum chloride **7** after methylation.



Scheme 1.

Before attempts at the asymmetric alkylative esterification, enantiomerically pure (R)-(−)-1-phenethyl benzoate **10**, $[\alpha]_D^{28}$ −28.3 (c=1.00, $CHCl_3$) {lit.[13] $[\alpha]_D$ −28.8 (c=0.89, $CHCl_3$)} was prepared in 92% yield by the condensation of benzoic acid **8** with (R)-(+)-1-phenethyl alcohol in the presence of DMC **1**. A solution of **8** (1 equiv.) and (1-bromoethyl)benzene **9** (2 equiv.) in either dichloromethane or benzene in the presence of a chiral guanidine **3** (1 equiv.) was stirred at room temperature. The reaction was monitored by TLC. After work-up, the crude product was purified by column chromatography. The optical purity of the benzoate **10** was determined from its specific rotation. The results are summarized in Table 1.

Table 1
Attempted asymmetric esterification of benzoic acid **8** with (1-bromoethyl)benzene **9** in the presence of a chiral cyclic guanidine **3**



8 (1 equiv.) + (±)-**9** (2 equiv.) → **10**

run	**3**	solvent	time	**10** (%)	$[\alpha]_D$ (temp)[a]	ee (%)[b]	Cofiguration
1	a	PhH[c]	14 h	NR[d]	—	—	—
2	a	CH_2Cl_2	14 h	84	0.8 (19)	2.7	S
3	b	CH_2Cl_2	2 d	95	-1.2 (23)	4.2	R
4	b	PhH[c]	2 d	74	-4.3 (23)	15.2	R
5	c	PhH[c]	7 d	66	1.6 (22)	5.7	S
6	d	PhH[c]	4 d	96	-4.2 (22)	15.0	R
7	e	PhH[c]	3 d	55	0.9 (23)	3.1	S
8	f	PhH[c]	8 d	87	0	0	—
9	g	PhH[c]/CH_2Cl_2 (10/7)	11 d	82	0.8 (23)	2.7	S
10	h	PhH[c]	4 d	96	-2.3 (23)	8.3	R
11	quinine	CH_2Cl_2	14 d	33	3.0 (23)	10.7	S

[a] $[\alpha]_D$ was measured in $CHCl_3$ in the concentration of 1.00. [b] The ee was estimated based on the $[\alpha]_D$ of (R)-(-)-**10**, $[\alpha]_D^{28}$ -28.3 (c=1.00, $CHCl_3$). [c] Benzene. [d] No reaction.

The simple guanidine **3a** without diphenyl substituents led to precipitation of the guanidium salt of **8** during the reaction when benzene was used as the solvent (run 1). Although the complete reaction was achieved by the replacement of benzene by dichloromethane, essentially no asymmetric induction was observed (run 2).

In the case of (4S,5S)-diphenyl substituted guanidines **3b**–**h**: (i) benzene was found to be a more suitable solvent than dichloromethane (runs 3 and 4); (ii) guanidines **3b** and **3d**, derived from (S)-1-naphthylethyl- or (S)-1-phenethylamines (runs 4 and 6), are more matched than **3c** and **3e** from the enantiomeric (R)-amines (runs 5 and 7); (iii) the absolute configuration of the product was dependent upon that of an amine outside of the imidazolidine ring in these cases; (iv) no improvement was observed when guanidines **3f**, **3g**, and **3h** derived from amino alcohols and an achiral amine, respectively, were used.

A comparable reaction using quinine as a base also resulted in an incomplete reaction with less effective asymmetric induction (run 11).

In conclusion, we could show the potential possibility of chiral monocyclic guanidines for basic auxiliaries in organic reactions. At present we are examining their further utility in asymmetric reactions such as the Michael reaction.

3. Experimental section

IR spectra were recorded with a JASCO IR-700 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution with JEOL JNM GSX-300 spectrometers with tetramethylsilane as an

internal reference. High resolution fast-atom bombardment MS (HRFABMS) was recorded on a JEOL JMS-HX 110A and JMS-700-T spectrometers with a direct inlet system. For column chromatography, silica gel 60 (70–230 mesh ASTM; Merck) was used, while for TLC and preparative TLC (PLC), silica gel GF254 (Merck) was used.

*3.1. (4S,5S)-1,3-Dimethyl-4,5-diphenylimidazolidin-2-one **6***

To a suspension of NaH (55% in mineral oil, 2.0 g, 46 mmol) in DMF (50 ml) under a nitrogen atmosphere, was added portionwise (4S,5S)-4,5-diphenylimidazolidin-2-one **5**[12] (5.0 g, 21 mmol) and the mixture was stirred at room temperature (rt) for 40 min. After addition of iodomethane (6.6 g, 46 mmol) the mixture was stirred at rt overnight, poured into 5% HCl, and then extracted with dichloromethane (2×100 ml). The organic solution was washed with water, dried ($MgSO_4$), and evaporated to dryness under reduced pressure. Purification of the residue by column chromatography ($CHCl_3$) followed by recrystallization from MeOH gave **6** as colorless prisms (5.5 g, 99%), mp 153–155°C. IR (KBr) ν cm^{-1}: 1700. ^{1}H-NMR δ: 2.70 (6H, s), 4.08 (2H, s), 7.12–7.15 (4H, m), 7.32–7.37 (6H, m). ^{13}C-NMR δ: 29.98, 70.31, 127.26, 128.42, 128.84, 138.04, 161.84. $[\alpha]_D^{24}$ +41.8 (c=1.00, $CHCl_3$). Anal. calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.64; H, 6.78; N, 10.47.

*3.2. (4S,5S)-2-Chloro-1,3-dimethyl-4,5-diphenylimidazolinium chloride **7***

A solution of **6** (4.3 g, 16 mmol) and oxalyl chloride (2.5 g, 19 mmol) in anhydrous benzene (100 ml) was refluxed for 12.5 h. After cooling, the precipitate was filtered, repeatedly washed with anhydrous benzene, and dried under reduced pressure to give **7** as hygroscopic colorless prisms (2.1 g, 41%), mp 220–221°C. ^{1}H-NMR δ: 3.21 (6H, s), 5.30 (2H, s), 7.43–7.45 (6H, m), 7.57–7.60 (4H, m). ^{13}C-NMR δ: 34.08, 75.10, 128.86, 129.68, 130.32, 132.59, 157.96. $[\alpha]_D^{27}$ −128.9 (c=1.00, $CHCl_3$). HRFABMS *m/z*: 285.1158 (calcd for $C_{17}H_{18}N_2Cl$: 285.1160).

3.3. General procedure for preparation of (4S,5S)-2-imino-1,3-dimethyl-4,5-diphenylimidazolidines

To a solution of a primary amine (8.94 mmol) and triethylamine (1.81 g, 17.9 mmol) in dichloromethane (50 ml) was added dropwise a solution of either **1** or **7** (8.94 mmol) in dichloromethane (40 ml) at rt. The mixture was stirred at rt for 20 min, poured into dil. HCl, and extracted with dichloromethane (2×100 ml). The organic solution was evaporated to dryness. The residue was dissolved in water and washed with toluene (2×100 ml). The aqueous solution was made alkaline with dil. aq. NaOH and extracted with toluene. The toluene solution was dried (Na_2SO_4) and evaporated to dryness to yield pure guanidines. In some cases further purification was needed.

*3.4. 1,3-Dimethyl-2-[(1S)-1-(1-naphthyl)ethylimino]imidazolidine **3a***

Colorless fine prisms (recryst. from MeOH), mp 77–78°C, in 94% yield. IR (KBr) ν cm^{-1}: 1625. UV (MeOH) λ_{max} (ε): 224 (92900), 282 (7500). ^{1}H-NMR δ: 1.54 (3H, d, J=6.4 Hz), 2.77 (6H, br s), 3.09–3.19 (4H, m), 5.62 (1H, q, J=6.4 Hz), 7.26–7.52 (3H, m), 7.69 (1H, d, J=8.1 Hz), 7.85 (2H, d, J=7.7 Hz), 8.19 (1H, d, J=8.4 Hz). ^{13}C-NMR δ: 27.48, 50.98, 123.31, 123.35, 124.92, 125.41, 125.92, 126.33, 128.86, 130.24, 133.83, 145.24, 155.72. $[\alpha]_D^{23}$ +123.0 (c=1.00, $CHCl_3$). Anal. calcd for $C_{17}H_{21}N_3$: C, 76.38; H, 7.92; N, 15.72. Found: C, 76.42; H, 7.90; N, 15.83.

3.5. (4S,5S)-1,3-Dimethyl-4,5-diphenyl-2-[(1S)-1-(1-naphthyl)ethylimino]imidazolidine **3b**

Colorless prisms [purified by column chromatography (ethyl acetate:hexane=1:5)], mp 133–134°C, in 95% yield. IR (KBr) ν cm^{-1}: 1670. UV (MeOH) λ_{max} (ε): 224 (72200), 283 (6100). ^{1}H-NMR δ: 1.72 (3H, d, J=6.6 Hz), 2.74 (6H, s), 3.86 (2H, br s), 5.85 (1H, q, J=6.6 Hz), 6.88–7.27 (10H, m), 7.45–7.56 (3H, m), 7.77 (1H, d, J=7.7 Hz), 7.88–7.92 (2H, m), 8.31 (1H, d, J=8.3 Hz). ^{13}C-NMR δ: 27.36, 50.62, 123.32, 123.58, 124.99, 125.36, 125.77, 126.50, 127.46, 127.97, 128.46, 128.95, 130.56, 134.02, 138.65, 144.18, 155.80. $[\alpha]_D^{21}$ +105.4 (c=1.00, $CHCl_3$). Anal. calcd for $C_{29}H_{29}N_3$: C, 83.02; H, 6.97; N, 10.02. Found: C, 82.83; H, 6.98; N, 10.04.

3.6. (4S,5S)-1,3-Dimethyl-4,5-diphenyl-2-[(1R)-1-(1-naphthyl)ethylimino]imidazolidine **3c**

Amorphous mass, 80% yield. IR (KBr) ν cm^{-1}: 1650. UV (MeOH) λ_{max} (ε): 224 (97800), 282 (8600). ^{1}H-NMR δ: 1.62 (3H, d, J=6.4 Hz), 2.64 (6H, br s), 3.86 (2H, s), 5.75 (1H, q, J=6.4 Hz), 7.15–7.35 (10H, m), 7.42–7.54 (3H, m), 7.72 (1H, d, J=8.1 Hz), 7.86 (1H, d, J=7.7 Hz), 8.03 (1H, d, J=7.1 Hz), 8.24 (1H, d, J=8.3 Hz). ^{13}C-NMR δ: 27.14, 51.27, 123.36, 123.65, 124.95, 125.42, 126.00, 126.43, 127.60, 128.03, 128.49, 128.85, 130.29, 133.84, 138.71, 145.45, 155.74. $[\alpha]_D^{21}$ +3.3 (c=1.00, $CHCl_3$). Anal. calcd for $C_{29}H_{29}N_3$: C, 83.02; H, 6.97; N, 10.02. Found: C, 83.19; H, 7.01; N, 9.97.

3.7. (4S,5S)-1,3-Dimethyl-4,5-diphenyl-2-[(1S)-1-phenylethylimino]imidazolidine **3d**

Colorless fine prisms, mp 69–71°C, in 75% yield. IR (KBr) ν cm^{-1}: 1660. UV (MeOH) λ_{max} (ε): 207 (39300). ^{1}H-NMR δ: 1.57 (3H, d, J=6.4 Hz), 2.75 (6H, br s), 3.83 (2H, br s), 5.08 (1H, q, J=6.4 Hz), 7.04–7.37 (13H, m), 7.51 (2H, d, J=7.1 Hz). ^{13}C-NMR δ: 28.59, 54.25, 125.91, 126.21, 127.46, 127.98, 128.08, 128.32, 128.46, 138.68, 149.14, 156.33. $[\alpha]_D^{22}$ +40.2 (c=1.00, $CHCl_3$). Anal. calcd for $C_{25}H_{27}N_3$: C, 81.26; H, 7.36; N, 11.37. Found: C, 81.28; H, 7.35; N, 11.37.

3.8. (4S,5S)-1,3-Dimethyl-4,5-diphenyl-2-[(1R)-1-phenylethylimino]imidazolidine **3e**

Colorless fine prisms, mp 108–109°C, in 70% yield. IR (KBr) ν cm^{-1}: 1655. UV (MeOH) λ_{max} (ε): 208 (40600). ^{1}H-NMR δ: 1.48 (3H, d, J=6.4 Hz), 2.68 (6H, s), 3.86 (2H, s), 5.07 (1H, q, J=6.4 Hz), 7.03–7.05 (4H, m), 7.13–7.35 (9H, m), 7.53 (2H, d, J=7.1 Hz). ^{13}C-NMR δ: 27.59, 54.36, 125.87, 126.22, 127.53, 128.01, 128.06, 128.29, 128.47, 138.66, 149.26, 156.77. $[\alpha]_D^{22}$ +68.1 (c=1.00, $CHCl_3$). Anal. calcd for $C_{25}H_{27}N_3$: C, 81.26; H, 7.36; N, 11.37. Found: C, 81.31; H, 7.38; N, 11.41.

3.9. (4S,5S)-2-[(1R)-1-Benzyl-2-hydroxyethylimino]-1,3-dimethyl-4,5-diphenylimidazolidine **3f**

Colorless fine prisms, mp 112–114°C, in 85% yield. IR (KBr) ν cm^{-1}: 1625. UV (MeOH) λ_{max} (ε): 207 (38600). ^{1}H-NMR δ: 2.70 (6H, br s), 2.82 (2H, d, J=6.8 Hz), 3.60 (1H, dd, J=10.1, 6.0 Hz), 3.71 (1H, dd, J=10.1, 4.2 Hz), 3.57–3.73 (2H, m), 4.25–4.29 (1H, m), 7.04–7.36 (15H, m). ^{13}C-NMR δ: 40.20, 57.00, 66.22, 125.88, 127.48, 128.09, 128.12, 128.51, 129.73, 138.38, 140.09, 157.97. $[\alpha]_D^{23}$ +76.5 (c=1.00, $CHCl_3$). Anal. calcd for $C_{26}H_{29}N_3O$: C, 78.16; H, 7.32; N, 10.52. Found: C, 78.30; H, 7.43; N, 10.56.

3.10. (4S,5S)-1,3-Dimethyl-4,5-diphenyl-2-[(1S)-1-hydroxymethyl-2-methylpropylimino]imidazolidine ***3g***

Colorless oil, 74% yield. IR (KBr) ν cm^{-1}: 1665. UV (MeOH) λ_{max} (ε): 207 (35000). ^{1}H-NMR δ: 1.03 (3H, d, J=6.8 Hz), 1.04 (3H, d, J=7.0 Hz), 1.81–1.95 (1H, m), 2.70 (6H, br s), 3.56–3.67 (2H, m), 3.75–3.80 (1H, m), 3.89 (2H, br s), 7.12–7.15 (4H, m), 7.23–7.39 (6H, m). ^{13}C-NMR δ: 18.66, 20.29, 32.25, 60.63, 64.07, 127.51, 128.16, 128.32, 128.58, 138.46, 156.68. $[\alpha]_D^{20}$ +36.3 (c=1.00, $CHCl_3$). HRFABMS *m/z*: 352.2372 (calcd for $C_{22}H_{30}N_3O$: 352.2389).

3.11. (4S,5S)-1,3-Dimethyl-4,5-diphenyl-2-propyliminoimidazolidine ***3h***

Colorless fine prisms (recryst. from hexane), mp 83–85°C, in 90% yield. IR (KBr) ν cm^{-1}: 1645. ^{1}H-NMR δ: 1.01 (3H, t, J=7.3 Hz), 1.24–1.27 (2H, m), 2.62 (3H, br s), 2.79 (3H, br s), 3.33–3.42 (1H, m), 3.50–3.59 (1H, m), 3.84 (2H, s), 7.12–7.18 (4H, m), 7.26–7.33 (6H, m). ^{13}C-NMR δ: 13.36, 27.99, 50.92, 129.01, 129.46, 129.93, 140.07, 158.42. $[\alpha]_D^{22}$ +69.7 (c=1.00, $CHCl_3$). Anal. calcd for $C_{20}H_{25}N_3$: C, 78.14; H, 8.20; N, 13.67. Found: C, 77.96; H, 8.31; N, 13.59.

3.12. Preparation of optically pure (R)-(−)-***10***

To a solution of **8** (1.00 g, 8.19 mmol), (R)-(+)-1-phenylethanol (1.00 g, 8.19 mmol) and **1** (1.66 g, 9.83 mmol) in acetonitrile (20 ml) was added dropwise pyridine (1.55 g, 19.7 mmol) at rt. The mixture was stirred at rt for 23 h, poured into water and extracted with dichloromethane (2×30 ml). The organic solution was successively washed with 5% HCl, sat. aq. $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated to dryness. The residue was purified by column chromatography (ethyl acetate:hexane=1:50) to give (R)-(−)-**10** (1.70 g, 92%) as a colorless oil, $[\alpha]_D^{28}$ −28.3 (c=1.00, $CHCl_3$) {lit.[13] $[\alpha]_D$ −28.8 (c=0.89, $CHCl_3$)}.

3.13. Asymmetric alkylation in the presence of ***3b***: typical procedure (run 4 in Table 1)

To a solution of **8** (0.140 g, 1.15 mmol) and **9** (0.426 g, 2.30 mmol) in benzene (10 ml) was added (4S,5S)-4,5-diphenyl-1,3-dimethyl-2-[(1S)-1-(1-naphthyl)ethylimino]imidazolidine **3b** (0.483 g, 1.15 mmol). The mixture was stirred at rt for 2 days, diluted with benzene (30 ml), successively washed with 5% HCl, water and sat. aq. $NaHCO_3$, dried ($MgSO_4$), and evaporated to dryness. The residue was purified by column chromatography (ethyl acetate:hexane=1:100) to give **10** (0.193 g, 74%) as a colorless oil, $[\alpha]_D^{23}$ −4.3 (c=1.00, $CHCl_3$).

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