A novel stereospecific aminocyclopropanation *via* the dethiolation of thioamides promoted by the samarium/samarium diiodide mixed reagent

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The stereospecific aminocyclopropanation of styrene *via* the dethiolation of *N,N*-disubstituted aromatic thioamides promoted by the samarium/samarium diiodide mixed reagent has been successfully performed.

Keywords: samarium, stereospecificity, aminocyclopropanation, dethiolation, thioamides

As a powerful, versatile, and ether-soluble single-electron-transfer reducing reagent, samarium diiodide (SmI_2) has played an ever-increasing role in organic synthesis since its introduction by Kagan and his group.[1] Ogawa and his group found that a samarium/samarium diiodide mixed system successfully promotes the deoxygenative coupling of amides to provide *vic*-diaminoalkenes.[2] The coupling reaction is suggested to involve an α-aminocarbene species.[3] Later Ogawa performed the aminocyclopropanation *via* the deoxygenation of aromatic amides by the capture of the α-aminocarbene species with styrene.[4] Our group has found that the samarium/samarium diiodide mixed reagent can promote the cross-coupling of arylamides and diarylketones to provide enamines.[5]

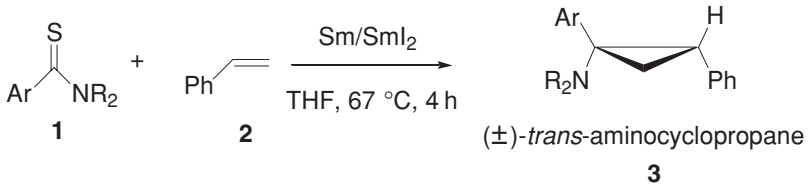
In contrast to amides, thioamides have remained almost unexplored. Considering the structural similarity of thioamides and amides, and the easier accessibility of thioamides than amides,[6] we have recently investigated the reactivity of thioamides with samarium reagents. Herein we report our results, *i.e.*, the synthesis of aminocyclopropanes *via* the dethiolation of *N,N*-disubstituted aromatic thioamides promoted by the samarium/samarium diiodide mixed reagent.

As shown in Scheme 1, the samarium/samarium diiodide mixed reagent can promote the reaction between aromatic thioamides **1** and styrene **2** to afford aminocyclopropanes **3** with stereospecificity when THF is used as a solvent.

A variety of *N,N*-disubstituted aromatic thioamides **1** were subjected to the reaction which proceeds smoothly and efficiently (Table 1). Besides styrene, we also tried to use other olefinic compounds such as 1-tetradecene, cyclohexene, ethyl acrylate, and butoxyethene. Surprisingly, in the case of an electron-deficient olefin like ethyl acrylate, the reduction of the olefin with Sm/SmI_2 takes place in preference to the reduction of the thioamide,[7] whereas electron-rich olefins like butoxyethene, and non-substituted olefins like 1-tetradecene and cyclohexene, do not react with the thioamides (the dethiolative coupling of the thioamides proceeded exclusively, which provided *vic*-diaminoalkenes).

All products listed in Table 1 were obtained as one pair of enantiomers, and identified with IR, ^{1}H NMR, ^{13}C NMR, mass spectra, and elemental analysis. To determine the stereochemistry of the aminocyclopropanes, we evaluated the HH NOESY diagram of 1-(*N,N*-diethylamino)-1-(benzo[1,3]dioxol-5-yl)-2-phenylcyclopropane **3j**. The cross signals at δ_H= 2.24-2.20 Hz and δ_H= 6.88 Hz show that the appropriate protons are close to one another. Consequently, the two aromatic groups adopt the *trans* configuration (two enantiomers).

The mechanism of this reaction is not clear. However, on the deoxygenative coupling of amides promoted by the Sm/SmI_2 mixed reagent, Ogawa thought that an α-aminocarbene species might be involved.[2] According to



Scheme 1

Table 1 Aminocyclopropanation of styrene *via* the dethiolation of *N,N*-disubstituted aromatic thioamides promoted by Sm/SmI_2[a, b]

Entry	Ar,	NR_2 in thioamides **1**	Yields of **3**/% [c]
1	4-$MeOC_6H_4$,	Morpholino (**1a**)	45 (**3a**)
2	C_6H_5,	Morpholino (**1b**)	43 (**3b**)
3	4-$MeOC_6H_4$,	Piperidino (**1c**)	51 (**3c**)
4	Benzo[1,3]dioxol-5-yl,	Morpholino (**1d**)	54 (**3d**)
5	4-Cl C_6H_4,	Morpholino (**1e**)	43 (**3e**)
6	4-MeC_6H_4,	Morpholino (**1f**)	47 (**3f**)
7	Benzo[1,3]dioxol-5-yl,	Piperidino (**1g**)	53 (**3g**)
8	4-$MeOC_6H_4$,	Pyrrolidinyl (**1h**)	56 (**3h**)
9	Benzo[1,3]dioxol-5-yl,	Pyrrolidinyl (**1i**)	57 (**3i**)
10	Benzo[1,3]dioxol-5-yl,	NEt_2 (**1j**)	33 (**3j**)

[a]Thioamide (1 mmol), styrene (5 ml), Sm (1.1 mmol), SmI_2 (2.2 mmol), THF (5 ml), 67 °C, 4 h. [b]All products were identified with IR, ^{1}H NMR, ^{13}C NMR, MS, and EA. [c]Isolated yields.

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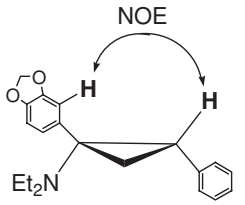
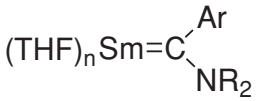


3j



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other sources,[8-11] we presume that a Sm α-aminocarbenoid **4** may be the intermediate in this reaction, which is later captured by excess styrene.[4]

Interestingly, as shown in Table 1, the electronic effects of the substituents did not influence the yields significantly. It appears, however, that the substrates bearing bulkier substituents gave higher yields. This fact, to some extent, supports our hypothesis for the mechanism involving the Sm α-aminocarbenoid, although precise details remain unknown. We supposed that the relatively long life of the generated intermediates bearing bulky substituents might contribute to suppression of the dimerisation of them, so diminishing the by-products, *vic*-diaminoalkenes.

In summary, this work describes another route to aminocyclopropanes by the capture of the Sm α-aminocarbenoid with styrene *via* the dethiolation of aromatic thioamides promoted by the samarium/samarium diiodide mixed reagent. Further studies on the samarium/samarium diiodide mixed reagent are underway.

Experimental

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Metallic samarium (99.9%) and all the other solvents were purchased from commercial sources and were not further purified before use. The thioamides were synthesised by the literature method.[6] ^{1}H NMR spectra were recorded on a Bruker AC-400 (400MHz) spectrometer as $CDCl_3$ solutions using TMS as the internal standard. Chemical shifts (δ) are reported in ppm and coupling constants *J* given in Hz. IR spectra were determined on a Bruker Vector-22 infrared instrument. Melting points were determined on an X-4 micro melting point apparatus and are uncorrected. Mass spectra were obtained on an HP-5989B Mass spectrometer. Elemental analyses were performed on a Carlo Erba EA-1110 instrument.

Typical procedure for the synthesis of aminocyclopropanes: Under a nitrogen atmosphere, a solution of thioamide (1 mmol) and styrene (5 ml) was added to a solution of SmI_2 (2.2 mmol) and Sm (1 mmol) in THF (5 ml) at room temperature. The mixture was stirred at 67 °C for 4 h (The reaction was monitored by TLC analysis). After the reaction was complete, saturated $NaHCO_3$ (30 ml) was added to the reaction mixture, and the product was extracted with diethyl ether (30 ml × 3). The combined extracts were dried over Na_2SO_4, and the solvent was removed in vacuo. Using cyclohexane/ether (10:1) as an eluent, the residue was purified by column chromatography to afford the desired product. The solid crude products were recrystallised from ethanol to give the pure products.

1-Morpholino-1-(4-methoxyphenyl)-2-phenylcyclopropane **(3a)**: Pale yellow solid. M.p. 81–82 °C. IR ν_{max}(KBr)/cm^{-1}: 3073, 2997, 2956, 2954, 2853, 2812, 1607, 1510, 1457, 1378, 1296, 1250, 1174, 1114, 1027, 994, 837, 766, 751, 696. ^{1}H NMR δ_H ($CDCl_3$): 7.43 (d, 2H, *J* = 7.2Hz, Ar–H), 7.29–7.18 (m, 5H, Ar–H), 6.87 (dd, 2H, *J* = 2.4, 8.8Hz, Ar–H), 3.80 (s, 3H, CH_3–O–), 3.45–3.41 (m, 2H, –CH_2–O–), 3.35 (brs, 2H, –CH_2–O–), 2.38–2.34 (m, 3H, –CH_2–N– and cyclopropane–H), 2.14 (brs, 2H, –CH_2–N–), 1.43–1.40 (m, 1H, cyclopropane–H), 1.36 (dd, 1H, *J* = 4.4, 9.2Hz, cyclopropane–H). ^{13}C NMR δ ($CDCl_3$): 159.2, 138.7, 132.1, 130.9, 128.7, 127.7, 126.1, 113.6, 67.5, 56.7, 54.8, 50.2, 32.5, 21.3. MS, *m/z* (%): 309 (M$^+$, 26.97), 133 (100.00). Anal. calcd. for $C_{20}H_{23}NO_2$: C 77.6, H 7.5, N 4.5. Found: C 77.3, H 7.5, N 4.8 %.

1-Morpholino-1,2-diphenylcyclopropane **(3b)**: Yellow oil. IR ν_{max}(film)/cm^{-1}: 3057, 3024, 2954, 2930, 2851, 2819, 1734, 1681, 1601, 1498, 1450, 1298, 1273, 1116, 1030, 994, 853, 769, 750, 700. ^{1}H NMR δ_H ($CDCl_3$): 7.43 (d, 2H, *J* = 7.6Hz, Ar–H), 7.35–7.25 (m, 7H, Ar–H), 7.19–7.16 (m, 1H, Ar–H), 3.44–3.40 (m, 2H, –CH_2–O–), 3.34 (brs, 2H, –CH_2–O–), 2.41–2.37 (m, 3H, –CH_2–N– and cyclopropane–H), 2.15 (brs, 2H, –CH_2–N–), 1.45–1.43 (m, 1H, cyclopropane–H), 1.38 (dd, 1H, *J* = 4.8, 8.8Hz, cyclopropane–H). ^{13}C NMR δ ($CDCl_3$): 138.2, 138.0, 130.7, 128.4, 127.9, 127.4, 125.7, 67.2, 55.1, 49.8, 31.9, 20.7. MS, *m/z* (%): 279 (M$^+$, 30.06), 188 (100.00). Anal. calcd. for $C_{19}H_{21}NO$: C 81.7, H 7.6, N 5.0. Found: C 81.8, H 7.3, N 5.3 %.

1-Piperidino-1-(4-methoxyphenyl)-2-phenylcyclopropane **(3c)**: Pale yellow solid. M.p. 64–66 °C. IR ν_{max}(KBr)/cm^{-1}: 3028, 3001, 2932, 2850, 2791, 2737, 1607, 1578, 1511, 1456, 1370, 1318, 1294, 1245, 1173, 1118, 1037, 948, 909, 830, 749, 696. ^{1}H NMR δ_H ($CDCl_3$): 7.44 (d, 2H, *J* = 8.0Hz, Ar–H), 7.28–7.23 (m, 4H, Ar–H), 7.19–7.15 (m, 1H, Ar–H), 6.86 (d, 2H, *J* = 8.0Hz, Ar–H), 3.79 (s, 3H, CH_3–O–), 2.31–2.28 (m, 3H, –CH_2–N– and cyclopropane–H), 2.11–2.06 (m, 2H, –CH_2–N–), 1.36–1.33 (m, 2H, cyclopropane–H), 1.28–1.15 (m, 6H, –$CH_2CH_2CH_2$–). ^{13}C NMR δ ($CDCl_3$): 158.5, 139.0, 131.6, 131.3, 128.3, 127.2, 125.4, 112.9, 55.3, 55.2, 50.9, 32.3, 26.2, 24.5, 21.9. MS, *m/z* (%): 307 (M$^+$, 36.06), 216 (100.00). Anal. calcd. for $C_{21}H_{25}NO$: C 82.0, H 8.2, N 4.6. Found: C 82.2, H 8.05, N 4.7 %.

1-Morpholino-1-(benzo[1,3]dioxol-5-yl)-2-phenylcyclopropane **(3d)**: Yellow oil. IR ν_{max}(film)/cm^{-1}: 3066, 2954, 2851, 2819, 1605, 1487, 1456, 1435, 1341, 1245, 1224, 1204, 1116, 1039, 994, 937, 849, 770, 696. ^{1}H NMR δ_H ($CDCl_3$): 7.40 (d, 2H, *J* = 8.0Hz, Ar–H), 7.27–7.23 (m, 2H, Ar–H), 7.18–7.15 (m, 1H, Ar–H), 6.78 (s, 1H, Ar–H), 6.76 (brs, 2H, Ar–H), 5.90 (s, 2H, –O–CH_2–O–), 3.43–3.40 (m, 2H, –CH_2–O–), 3.34 (brs, 2H, –CH_2–O–), 2.36–2.33 (m, 3H, –CH_2–N– and cyclopropane–H), 2.13 (brs, 2H, –CH_2–N–), 1.39–1.37 (m, 1H, cyclopropane–H), 1.33 (dd, 1H, *J* = 4.8, 8.8Hz, cyclopropane–H). ^{13}C NMR δ ($CDCl_3$): 147.2, 146.7, 138.1, 132.2, 128.4, 127.4, 125.8, 123.9, 111.0, 108.0, 101.1, 67.1, 54.8, 49.8, 32.4, 21.1. MS, *m/z* (%): 323 (M$^+$, 45.86), 322 (100.00). Anal. calcd. for $C_{20}H_{21}NO_3$: C 74.3, H 6.55, N 4.3. Found: C 74.45, H 6.4, N 4.5 %.

1-Morpholino-1-(4-chlorophenyl)-2-phenylcyclopropane **(3e)**: Yellow oil. IR ν_{max}(film)/cm^{-1}: 3061, 3024, 2927, 2851, 2818, 1603, 1492, 1452, 1372, 1297, 1271, 1204, 1116, 1091, 1018, 994, 958, 854, 829, 769, 697. ^{1}H NMR δ_H ($CDCl_3$): 7.41 (d, 2H, *J* = 7.6Hz, Ar–H), 7.31–7.25 (m, 4H, Ar–H), 7.23–7.16 (m, 3H, Ar–H), 3.44–3.40 (m, 2H, –CH_2–O–), 3.34 (brs, 2H, –CH_2–O–), 2.36–2.32 (m, 3H, –CH_2–N– and cyclopropane–H), 2.11 (brs, 2H, –CH_2–N–), 1.45–1.43 (m, 1H, cyclopropane–H), 1.34 (dd, 1H, *J* = 5.2, 9.2Hz, cyclopropane–H). ^{13}C NMR δ ($CDCl_3$): 137.7, 136.5, 133.2, 131.9, 128.4, 128.1, 127.4, 125.9, 67.1, 54.3, 49.7, 32.0, 20.7. MS, *m/z* (%): 313 (M$^+$, 19.38), 315 (M$^+$ + 2, 6.95), 222 (100.00). Anal. calcd. for $C_{19}H_{20}ClNO$: C 72.7, H 6.4, N 4.5. Found: C 73.0, H 6.3, N 4.6 %.

1-Morpholino-1-(4-methylphenyl)-2-phenylcyclopropane **(3f)**: Yellow oil. IR ν_{max}(film)/cm^{-1}: 3024, 2953, 2928, 2851, 2818, 1603, 1513, 1496, 1453, 1297, 1261, 1204, 1116, 1070, 1029, 994, 955, 916, 854, 813, 768, 750, 697. ^{1}H NMR δ_H ($CDCl_3$): 7.43 (d, 2H, *J* = 8.0Hz, Ar-H), 7.29-7.25 (m, 2H, Ar-H), 7.21-7.19 (m, 3H, Ar-H), 7.15 (d, 2H, *J* = 8.0Hz, Ar-H), 3.45-3.41 (m, 2H, -CH_2-O-), 3.35 (brs, 2H, -CH_2-O-), 2.39-2.37 (m, 3H, -CH_2-N- and cyclopropane-H), 2.35 (s, 3H, Ar-CH_3), 2.15 (brs, 2H, -CH_2-N-), 1.41-1.36 (m, 2H, cyclopropane-H). ^{13}C NMR δ ($CDCl_3$): 138.3, 137.0, 135.1, 130.6, 128.6, 128.4, 127.4, 125.7, 67.2, 54.8, 49.8, 32.0, 21.2, 20.8. MS, *m/z* (%): 293 (M$^+$, 30.84), 202 (100.00). Anal. calcd. for $C_{20}H_{23}NO$: C 81.9, H 7.9, N 4.8. Found: C 82.0, H 7.9, N 4.95 %.

1-Piperidino-1-(benzo[1,3]dioxol-5-yl)-2-phenylcyclopropane **(3g)**: Pale yellow solid. M.p. 71–72 °C. IR ν_{max}(KBr)/cm^{-1}: 3073, 3007, 2934, 2851, 2798, 1606, 1503, 1486, 1456, 1434, 1336, 1318, 1245, 1222, 1145, 1119, 1070, 1040, 990, 927, 895, 881, 860, 815, 765, 750. ^{1}H NMR δ_H ($CDCl_3$): 7.40 (d, 2H, *J* = 7.6Hz, Ar–H), 7.25–7.22 (m, 2H, Ar–H), 7.17–7.13 (m, 1H, Ar–H), 6.80 (s, 1H, Ar–H), 6.77 (d, 1H, *J* = 8.0Hz, Ar–H), 6.74 (d, 1H, *J* = 8.0Hz, Ar–H), 5.86 (s, 2H, –O–CH_2–O–), 2.30–2.26 (m, 3H, –CH_2–N– and cyclopropane–H), 2.10–2.06 (m, 2H, –CH_2–N–), 1.34–1.30 (m, 2H, cyclopropane–H), 1.29–1.15 (m, 6H, –$CH_2CH_2CH_2$–). ^{13}C NMR δ ($CDCl_3$): 146.9, 146.4, 138.8, 133.0, 128.3, 127.2, 125.4, 123.8, 110.9, 107.4, 100.9, 55.7, 50.9, 32.6, 26.2, 24.5, 22.0. MS, *m/z* (%): 321 (M$^+$, 24.77), 230 (100.00). Anal. calcd. for $C_{21}H_{23}NO_2$: C 78.5, H 7.2, N 4.4. Found: C 78.6, H 7.0, N 4.5 %.

1-Pyrrolidinyl-1-(4-methoxyphenyl)-2-phenylcyclopropane **(3h)**: Pale yellow solid. M.p. 48–50 °C. IR ν_{max}(KBr)/cm^{-1}: 3003, 2967, 2933, 2797, 1682, 1606, 1576, 1511, 1456, 1382, 1293, 1246, 1180, 1174, 1148, 1106, 1070, 1030, 970, 924, 890, 830, 775, 754. ^{1}H NMR δ_H ($CDCl_3$): 7.40 (d, 2H, *J* = 7.2Hz, Ar–H), 7.27–7.23 (m, 4H, Ar–H), 7.18–7.15 (m, 1H, Ar–H), 6.87 (d, 2H, *J* = 8.0Hz, Ar–H), 3.78 (s, 3H, CH_3–O–), 2.38 (dd, 2H, *J* = 7.2, 12.8Hz, –CH_2–N–), 2.33–2.29 (m, 1H, cyclopropane–H), 2.15 (dd, 2H, *J* = 7.2, 12.8Hz, –CH_2–N–), 1.46–1.33 (m, 6H, cyclopropane–H and –CH_2–CH_2–). ^{13}C NMR δ ($CDCl_3$): 158.4, 139.4, 132.0, 130.6, 128.1, 127.3, 125.3, 113.0, 55.3, 49.9, 47.7, 32.2, 23.1, 21.2. MS, *m/z* (%): 293 (M^+, 14.29), 271 (100.00). Anal. calcd. for $C_{20}H_{23}NO$: C 81.9, H 7.9, N 4.8. Found: C 82.0, H 7.8, N 4.85 %.

1-Pyrrolidinyl-1-(benzo[1,3]dioxol-5-yl)-2-phenylcyclopropane **(3i)**: Pale yellow solid. M.p. 101–102 °C. IR ν_{max}(KBr)/cm^{-1}: 3076, 3001, 2969, 2903, 2818, 2800, 1599, 1503, 1487, 1456, 1432, 1378, 1253, 1220, 1153, 1112, 1036, 931, 879, 817, 770, 694. ^{1}H NMR δ_H ($CDCl_3$): 7.38 (d, 2H, *J* = 7.6Hz, Ar–H), 7.27–7.23 (m, 2H, Ar–H), 7.19–7.15 (m, 1H, Ar–H), 6.83 (s, 1H, Ar–H), 6.80–6.77 (m, 2H, Ar–H), 5.93 (s, 2H, –O–CH_2–O–), 2.39 (dd, 2H, *J* = 6.8, 12.8Hz, –CH_2–N–), 2.33–2.29 (m, 1H, cyclopropane–H), 2.14 (dd, 2H, *J* = 6.8, 12.8Hz, –CH_2–N–), 1.45–1.34 (m, 6H, cyclopropane–H and –CH_2–CH_2–). ^{13}C NMR δ ($CDCl_3$): 146.9, 146.3, 139.0, 132.3, 128.1, 127.3, 125.4, 124.1, 111.3, 107.5, 100.9, 50.3, 47.7, 32.4, 23.1, 21.3. MS, *m/z* (%): 307 (M^+, 18.54), 216 (100.00). Anal. calcd. for $C_{20}H_{21}NO_2$: C 78.15, H 6.9, N 4.6. Found: C 78.4, H 6.7, N 4.7 %.

1-(N,N-diethylamino)-1-(benzo[1,3]dioxol-5-yl)-2-phenylcyclopropane **(3j)**: Yellow oil. IR ν_{max}(film)/cm^{-1}: 2969, 2931, 2894, 2817, 1605, 1502, 1486, 1456, 1433, 1379, 1338, 1247, 1226, 1147, 1114, 1040, 941, 881, 812, 751, 696. ^{1}H NMR δ_H ($CDCl_3$): 7.37 (d, 2H, *J* = 7.6Hz, Ar–H), 7.26–7.22 (m, 2H, Ar–H), 7.17–7.13 (m, 1H, Ar–H), 6.88 (s, 1H, Ar–H), 6.84 (d, 1H, *J* = 8.0Hz, Ar–H), 6.73 (d, 1H, *J* = 8.0Hz, Ar–H), 5.86 (s, 2H, –O–CH_2–O–), 2.39–2.30 (m, 4H, –CH_2–N–), 2.24–2.20 (m, 1H, cyclopropane–H), 1.54–1.51 (m, 1H, cyclopropane–H), 1.41 (dd, 1H, *J* = 4.8, 9.2Hz, cyclopropane–H), 0.76 (brs, 6H, –CH_3). ^{13}C NMR δ ($CDCl_3$): 147.1, 146.3, 138.9, 134.9, 128.7, 127.3, 125.5, 123.4, 110.6, 107.6, 101.0, 54.9, 46.4, 31.3, 23.0, 14.3. MS, *m/z* (%): 309 (M^+, 63.98), 308 (100.00). Anal. calcd. for $C_{20}H_{23}NO_2$: C 77.6, H 7.5, N 4.5. Found: C 77.9, H 7.25, N 4.7 %.

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