SHORT PAPER

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Yellow HgO as an efficient cyclodesulfurising agent in the synthesis of 2-substituted aminobenzoxazoles from N-(2-hydroxyphenyl)-N′- phenylthioureas

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2-Substituted aminobenzoxazoles **2** were prepared in good yields by cyclodesulfurisation of N-(2-hydroxyphenyl)-N′-phenylthioureas **1** with yellow HgO.

Keywords: yellow HgO, cyclodesulfurising agent, 2-substituted aminobenzoxazoles

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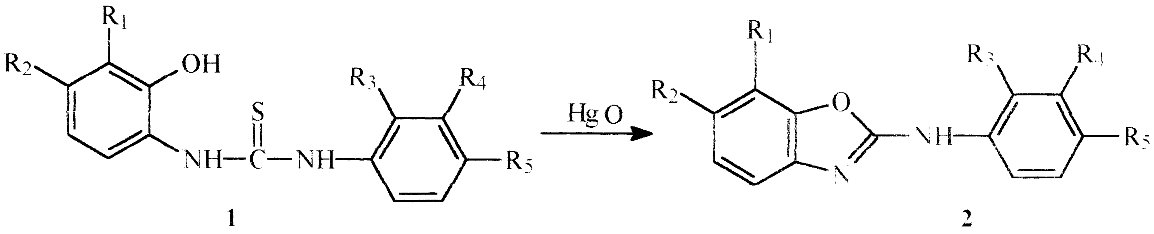
2-Substituted aminobenzoxazoles **2** showed good immunosuppressant, antifertility and herbicidal activity and were very effective against Marek's disease in chickens.[1,2] They were generally synthesized by cyclodesulfurization of N-(2-hydroxyphenyl)-N′-phenylthioureas **1** with nickel peroxide,[3] potassium superoxide[4] and dicyclohexylcarbodiimide,[5] or by treatment of 2-chlorobenzoxazole with anilines in THF.[6] We now report a one-pot facile synthesis of 2-substituted aminobenzoxazoles **2** by cyclodesulfurisation of N-(2-hydroxyphenyl)-N′-phenylthioureas **1** with yellow HgO (Scheme 1). The yields are slightly lower than those reported in the potassium superoxide method but higher than those in other methods. And this reaction has the advantages of short reaction time, mild reaction conditions and easy work-up.

The N-(2-hydroxyphenyl)-N′-phenylthioureas **1** can be easily prepared by treatment of the corresponding aryl isothiocyanate with *o*-aminophenol[3] and confirmed by elemental analysis and spectral data.

In conclusion, we have described a facile synthesis of 2-substituted aminobenzoxazoles **2** by cyclodesulfurisation of N-(2-hydroxyphenyl)-N′-phenylthioureas **1** with yellow HgO. Further study on the scope and limitation of this reaction is underway and will be reported in due course.

Experimental

Melting points were determined on a WRS-1 digital melting point apparatus made in Shanghai. IR spectra were recorded on a Nicolet FT-IR-20SX spectrophotometer. Mass spectra were recorded on a Hitachi M80 spectrophotometer. ^1H NMR spectra were recorded on a Brucker WP500SY(500 MHz) spectrometer with $(CD_3)_2CO$ as the solvent and TMS as internal standard. Elemental analyses were performed on an Italian MOD.1106 instrument.



1

2

2	R1	R2	R3	R4	R5
a	H	H	H	H	H
b	F	F	F	F	F
c	F	F	F	H	F
d	F	F	F	H	H
e	F	F	H	H	F
f	F	F	H	Cl	F
g	F	F	Cl	H	H
h	F	F	H	Cl	H
i	F	F	H	H	OH

Scheme 1

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

General procedure. To a solution of N-(2-hydroxyphenyl)-N′-phenylthioureas **1** (10 mmol) in 50 ml of CH_3OH-CH_3COCH_3 (1:1) was added HgO (21.6 g, 100 mmol), then the reaction mixture was stirred at room temperature for about 10 min and filtered. Removal of the solvent under reduced pressure gave a solid mass which was on recrystallisation from ethanol gave **2**.

2a: Yield 88%; m.p. 161–163^{o}C (lit.[5] 162–164^{o}C); IR (KBr) ν/cm^{-1} 3420 (NH), 1700 (C=N); *m/z* 210 (M^+) (Found C, 74.18; H, 4.80; N, 13.35. $C_{13}H_{10}N_2O$ requires C, 74.23; H, 4.79; N, 13.32%).

2b: Yield 82%; m.p. 179–180^{o}C; IR (KBr) ν/cm^{-1} 3430 (NH), 1680 (C=N); ^{1}H NMR (CD_3COCD_3) δ 8.20 (1 H, m), 7.30 (1 H, qd, *J* 2.1, 9.1 Hz), 7.20–7.26 (2 H, m); *m/z* 300 (M^+) (Found C, 52.18; H, 1.67; N, 9.31. $C_{13}H_5F_5N_2O$ requires C, 52.01; H, 1.68; N, 9.33%).

2c: Yield 92%; m.p. 173–174^{o}C; IR (KBr) ν/cm^{-1} 3420 (NH), 1670 (C=N); ^{1}H NMR (CD_3COCD_3) δ 8.29 (1 H, td, *J* 5.9, 9.2 Hz), 7.15 (1 H, t, J=9.2 Hz), 7.17–7.22 (3 H, m,); *m/z* 282 (M^+) (Found C, 55.29; H, 2.12; N, 9.95. $C_{13}H_6F_4N_2O$ requires C, 55.33; H, 2.14; N, 9.93%).

2d: Yield 81%; m.p. 105–106^{o}C; IR (KBr) ν/cm^{-1} 3410 (NH), 1660 (C=N); ^{1}H NMR (CD_3COCD_3) δ 8.45 (1 H, t, *J* 8.3 Hz,), 7.14–7.30 (5 H, m); *m/z* 264 (M^+) (Found C, 59.23; H, 2.66; N, 10.53. $C_{13}H_7F_3N_2O$ requires C, 59.10; H, 2.67; N, 10.60%).

2e: Yield 84%; m.p. 227–228 ^{o}C; IR (KBr) ν/cm^{-1} 3420 (NH), 1700 (C=N); ^{1}H NMR (CD_3COCD_3) δ 7.87 (2 H, dd, *J* 5.9, 9.2 Hz), 7.19 (2 H, t, *J* 9.2 Hz), 7.20–7.24 (2 H, m); *m/z* 264 (M^+) (Found C, 59.25; H, 2.68; N, 10.49. $C_{13}H_7F_3N_2O$ requires C, 59.10; H, 2.67; N, 10.60%).

2f: Yield 94%; m.p. 240–241^{o}C; IR (KBr) ν/cm^{-1} 3420 (NH), 1700 (C=N); ^{1}H NMR (CD_3COCD_3) δ 8.15 (I H, dd, *J* 2.7, 6.5 Hz), 7.70 (1 H, ddd, *J* 2.8, 3.2, 9.0 Hz), 7.35 (1 H, t, *J* 9.0 Hz), 7.15–7.30 (2 H, m); *m/z* 300 (M^+) (Found C, 52.32; H, 2.00; N, 9.36. $C_{13}H_7F_3N_2O$ requires C, 52.28; H, 2.02; N, 9.38%).

2g: Yield 83%; m.p. 144–145 ^{o}C; IR (KBr) ν/cm^{-1} 3400 (NH), 1600 (C=N); ^{1}H NMR (CD_3COCD_3) δ 8.40 (1 H, dd, *J* 1.5, 8.0 Hz), 7.52 (1 H, dd, *J* 1.4, 8.0 Hz), 7.45 (1 H, td, *J* 1.4, 8.0 Hz), 7.18 (1 H, td, *J* 1.5, 8.0 Hz), 7.20–7.25 (2 H, m); *m/z* 282 (M^++2), 280 (M^+) (Found C, 55.52; H, 2.50; N, 9.96. $C_{13}H_7F_3N_2O$ requires C, 55.63; H, 2.51; N, 9.98%).

2h: Yield 88%; m.p. 184–185^{o}C; IR (KBr) ν/cm^{-1} 3420 (NH), 1700 (C=N); ^{1}H NMR (CD_3COCD_3) δ 8.07 (1 H, t, *J* 2.0 Hz), 7.60 (1 H, ddd, *J* 0.8, 2.0, 8.1 Hz), 7.54 (1 H, t, *J* 8.1 Hz), 7.71 (1 H, ddd, *J* 0.8, 2.0, 8.1 HZ), 7.20–7.30 (2 H, m); *m/z* 282 (M^++2), 280 (M^+) (Found C, 55.48; H, 2.53; N, 10.00. $C_{13}H_7F_3N_2O$ requires C, 55.63; H, 2.51; N, 9.98%).

2i: Yield 81%; m.p. 222–223^{o}C; IR (KBr) ν/cm^{-1} 3420 (NH), 3290 (OH), 1700 (C=N); ^{1}H NMR (CD_3COCD_3) δ 7.60 (2 H, d, *J* 6.8 Hz), 6.89 (2 H, d, *J* 9.1 Hz), 7.20–7.26 (2 H, m); *m/z* 262 (M^+) (Found C, 59.64; H, 3.06; N, 10.52. $C_{13}H_7F_3N_2O$ requires C, 59.55; H, 3.08; N, 10.68%).

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