

无溶剂条件下喹喔啉衍生物碳氮双键还原反应

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摘 要: 研究一种在室温、无溶剂条件下以硼氢化钠为还原剂还原喹喔啉衍生物碳氮双键的方法。考察还原剂、添加剂、溶剂、反应时间和温度对反应的影响。给出反应的优化条件,即以硼氢化钠(2当量)为还原剂,硅胶为添加剂,它们的质量比为1:3时,在室温研磨0.1 h,产物收率可达90%。目标产物经过了¹H NMR、¹³C NMR和HRMS确证。该合成方法具有条件温和、操作简单、反应时间短、产率高及对环境友好等优点,是一种高效的亚胺还原方法。

关键词: 还原; 无溶剂; 硼氢化钠; 喹喔啉

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Reduction of carbon-nitrogen double bonds of quinoxaline derivatives under solvent-free conditions

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Abstract: A method for reduction of carbon-nitrogen double bonds of quinoxaline derivatives was studied using sodium borohydride as reducing agent under solvent-free conditions at the room temperature. The effects of reducing agent, additive, solvent, reaction time and temperature on reaction were investigated. The results showed that the optimum reaction conditions were 1:3 mass ratio of borohydride (2.0 eq) as reducing agent and silica gel as additive; 90% yield was obtained under milling at the room temperature for 0.1 hour. The products were identified by ¹H NMR, ¹³C NMR and HRMS. This synthetic method boasts mild conditions, simple operation, short reaction time, high yield and eco-friendliness, and proves to be a highly efficient method for reduction of imines.

Keywords: reduction; solvent-free; sodium borohydride; quinoxaline

胺类化合物在天然产物、医药^[1]和农药^[2]中有着非常广泛的应用,而亚胺还原得到相应的胺是现代有机合成中形成C—N键的一种非常重要的方法,常用的方法有Pd, Ni, Pt等金属催化的氢化法^[3]和金

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属氢化物参与的还原法。前者受限于一些对还原剂敏感的官能团^[4],如碳碳双键、三键以及硝基、氰基、呋喃基等基团,而后者已发展出大量不同种类的还原剂。已见报道的还原剂有 NaBH_4 ^[5]、 $\text{NaBH}(\text{OAc})_3$ ^[6]、 NaBH_3CN ^[7]、 $(n\text{-Bu})_4\text{NBH}_3\text{CN}$ ^[8]、 $\text{NaBH}_4\text{-NiCl}_2$ ^[9]、 $\text{NaBH}_4\text{-ZnCl}_2$ ^[10]、 $\text{NaBH}_4\text{-ZrCl}_4$ ^[11]、 $\text{Ti}(\text{O}^i\text{Pr})_4\text{-NaBH}_4$ ^[12]、 $\text{Cu}(\text{PPh}_3)_2\text{BH}_4$ ^[13]、 $\text{Zr}(\text{BH}_4)_2\text{Cl}_2(\text{dabco})_2$ ^[14]、 $\text{ZnBH}_4\text{-SiO}_2$ ^[15]、 $\text{Et}_3\text{SiH-CF}_3\text{CO}_2\text{H}$ ^[16]、嘧啶-硼烷^[17]、甲基吡啶-硼烷^[18]、有机硅(PMHS)- $\text{Ti}(\text{O}^i\text{Pr})_4$ ^[19]等,但是上述还原剂都存在着一些不足之处,例如, NaBH_3CN 等还原试剂在后处理过程中产生极毒的氰化物,其他一些氢化物如硼氢化锌^[20]、硼化镍^[21]和(PMHS)- $\text{Ti}(\text{O}^i\text{Pr})_4$ ^[22]等对含有羰基、酯基、硝基的亚胺结构不能进行选择性的还原。

无溶剂合成法由于在反应过程中不使用有机溶剂,具有反应速度快、反应选择性好和后处理简单等优点,还可以得到一些常规液相反应得不到的产物而受到人们广泛的关注^[23]。2005年,Cho^[24]小组报道了无溶剂条件下以硼氢化钠为还原剂选择性还原亚胺化合物的方法,该方法适用于多种对还原剂敏感的官能团,反应时间短,条件温和,不失为一种还原亚胺的有效方法。

喹啉类化合物是一类有应用价值的杂环化合物,具有多种生物活性,如氯喹啉衍生物是一类重要的除草剂^[25]。我们在生物活性分子的研究中,设计了含氯喹啉结构单元的希夫碱。由于此类化合物的还原反应还未见文献报道,我们尝试在室温、无溶剂条件下采用研磨法还原希夫碱,并顺利得到了还原产物,本文报道相应的研究结果。

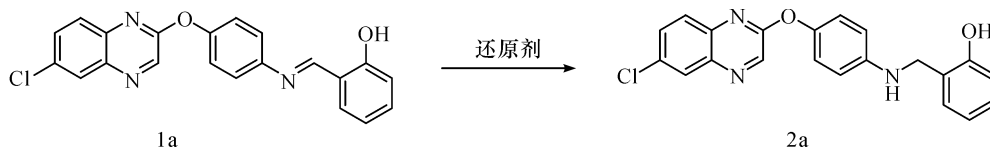
1 试验部分

1.1 仪器与试剂

^1H NMR 和 ^{13}C NMR 在 Bruker Advance DMX400(400M)上测定, CDCl_3 为溶剂, TMS 为内标;高分辨质谱在 HP5973GCMS 气相色谱质谱联用仪上进行测定。反应进程用 TLC 跟踪检测,用紫外灯或者碘显色。实验所用试剂均为市售 AR 或 CP 试剂。

1.2 试验方法

1.2.1 还原剂的选择



将还原剂 20 mmol 和四氢呋喃 20 mL 加入反应瓶中,搅拌均匀后再加入化合物 1a 10 mmol 和 5 滴甲醇继续搅拌 30 min。反应完成后真空旋蒸除去溶剂,加入 10 mL 水和 10 mL 乙酸乙酯,抽滤,再用 20 mL 水和 30 mL 乙酸乙酯洗涤滤饼,有机相用饱和食盐水洗涤,无水硫酸镁干燥,旋蒸除去溶剂,经乙醇重结晶得到目标产物 2a,具体如表 1 所示。

1.2.2 无溶剂反应优化

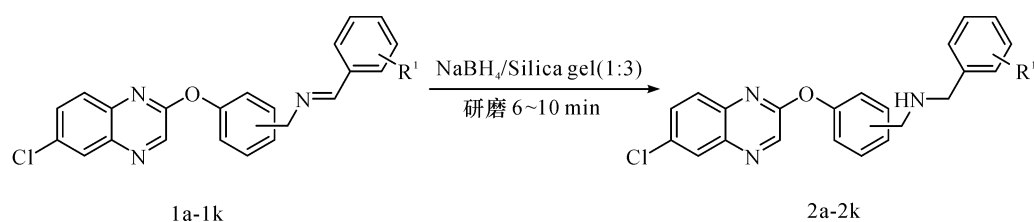
将硼氢化钠 757 mg(20 mmol)和添加剂 2.27 g 在研钵中研磨,研磨均匀后再加入化合物 1a 10 mmol 和 5 滴甲醇继续研磨 6~10 min。反应毕,加入 10 mL 水和 10 mL 乙酸乙酯,抽滤,再用 20 mL 水和 30 mL 乙酸乙酯洗涤滤饼,有机相用饱和食盐水洗涤,无水硫酸镁干燥,旋蒸除去溶剂,经乙醇重结晶得到目标产物 2a,具体如表 1 所示。

表 1 反应条件优化

Table 1 Optimization of reaction conditions

试验序号	还原剂	溶剂	温度/℃	时间/h	2a 的收率/%
1	LiAlH_4	THF	25	0.5	0
2	KBH_4	THF	25	0.5	30
3	NaBH_4	THF	25	0.5	45
4	$\text{NaBH}_4/\text{ZnCl}_2$ (1:3)	—	25	0.1	78
5	$\text{NaBH}_4/\text{Al}_2\text{O}_3$ (1:3)	—	25	0.1	83
6	$\text{NaBH}_4/\text{Silica gel}$ (1:3)	—	25	0.1	90

1.2.3 反应底物对还原反应的影响



将硼氢化钠 757 mg (20 mmol) 和硅胶 2.27 g 在研钵中研磨, 研磨均匀后再加入化合物 1a—1k 10 mmol 和 5 滴甲醇继续研磨 6~10 min。反应毕, 加入 10 mL 水和 10 mL 乙酸乙酯, 抽滤, 再用 20 mL 水和 30 mL 乙酸乙酯洗涤滤饼, 有机相用饱和食盐水洗涤, 无水硫酸镁干燥, 旋蒸除去溶剂, 经乙醇重结晶得到目标产物 2a—2k, 具体如表 2 所示。

表 2 喹喔啉衍生物 2a—2k 的合成

Table 2 Synthesis of quinoxaline derivatives 2a-2k

化合物	产物	收率/%	化合物	产物	收率/%
2a		90	2g		86
2b		82	2h		69
2c		83	2i		88
2d		81	2j		93
2e		89	2k		92
2f		77			

2a: 黄色固体, 产率 90%; 熔点 197~198 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.68(s, 1H), 8.05(s, 1H), 7.70(d, $J=8.4$ Hz, 1H), 7.60(d, $J=6.8$ Hz, 1H), 7.38~7.32(m, 2H), 7.16(d, $J=8.4$ Hz, 3H), 6.92(d, $J=6.4$ Hz, 3H), 4.46(s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 157.8, 155.0, 153.5, 148.7, 140.0, 139.6, 138.4, 132.9, 131.5, 130.2, 129.2, 128.8, 127.8, 122.8, 120.1, 116.4, 112.7, 108.1, 44.3; HRMS(EI-TOF) 理论值 $\text{C}_{21}\text{H}_{16}\text{ClN}_3\text{O}_2$ (M^+) 377.093 1, 实测值 377.093 3。

2b: 橘红色固体, 产率 82%; 熔点 136~137 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.65(s, 1H), 8.04(s, 1H), 7.69(d, $J=9.2$ Hz, 1H), 7.60(d, $J=7.6$ Hz, 1H), 7.29(d, $J=8.0$ Hz, 1H), 7.21~7.13(m, 2H),

6.88~6.83(m,2H),6.77~6.71(m,3H),4.38(s,2H); ^{13}C NMR(100 MHz, CDCl_3) δ : 156.8,156.0,153.5,148.8,140.0,139.6,138.4,132.9,131.1,130.2,129.2,128.9,128.8,127.8,122.8,120.1,116.4,112.7,112.6,108.1,47.6;HRMS(EI-TOF)理论值 $\text{C}_{21}\text{H}_{16}\text{ClN}_3\text{O}_2(\text{M}^+)$ 377.093 1,实测值 377.093 0。

2c:白色固体,产率 83%;熔点 205~206 $^{\circ}\text{C}$; ^1H NMR(400 MHz, CDCl_3) δ : 9.89(s,1H),8.79(s,1H),8.08(s,1H),7.71(s,2H),7.21(d, J =6.4 Hz,1H),7.08~7.06(m,1H),7.01(d, J =8.8 Hz,2H),6.83(d, J =8.8 Hz,1H),6.61(d, J =8.8 Hz,2H),4.19(s,2H); ^{13}C NMR(100 MHz, CDCl_3) δ : 158.4,147.1,147.0,145.0,144.2,140.1,139.6,138.5,132.5,131.3,129.3,128.7,127.8,127.6,123.9,123.8,123.2,112.4,48.3;HRMS(EI-TOF)理论值 $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_2\text{Cl}_2(\text{M}^+)$ 411.054 1,实测值 411.054 5。

2d:褐色固体,产率 83%;熔点 167~168 $^{\circ}\text{C}$; ^1H NMR(400 MHz, DMSO-d_6) δ : 9.82(s,1H),8.79(s,1H),8.09(s,1H),7.72(s,2H),7.18~7.11(m,2H),7.07(dd, J =8.4, J =2.4 Hz,1H),6.78(d, J =8.8 Hz,1H),6.51~6.43(m,3H),6.37(t, J =8.0 Hz,1H),4.17(s,2H); ^{13}C NMR(100 MHz, DMSO-d_6) δ : 159.2,157.0,147.1,144.9,140.5,139.8,138.4,132.7,132.0,131.3,129.6,128.8,127.8,126.7,122.9,121.2,119.0,116.5,115.8,112.6,45.9;HRMS(EI-TOF)理论值 $\text{C}_{21}\text{H}_{15}\text{Cl}_2\text{N}_3\text{O}_2(\text{M}^+)$ 411.054 1,实测值 411.053 6。

2e:黄色固体,产率 89%;熔点 199~200 $^{\circ}\text{C}$; ^1H NMR(400 MHz, CDCl_3) δ : 8.68(s,1H),8.15(d, J =6.4 Hz,2H),8.05(s,1H),7.68(d, J =8.8 Hz,1H),7.61~7.58(m,1H),7.19(d, J =8.8 Hz,2H),6.97~6.93(m,3H),4.57(s,2H); ^{13}C NMR(100 MHz, CDCl_3) δ : 162.0,157.5,154.0,150.4,141.4,140.1,139.7,138.6,132.1,131.9,130.5,129.3,127.9,127.0,124.7,124.3,115.5,110.1,109.0,105.1,41.2;HRMS(EI-TOF)理论值 $\text{C}_{21}\text{H}_{15}\text{ClN}_4\text{O}_4(\text{M}^+)$ 422.078 2,实测值 422.078 6。

2f:淡黄色固体,产率 77%;熔点 145~146 $^{\circ}\text{C}$; ^1H NMR(400 MHz, DMSO-d_6) δ : 11.26(s,1H),8.77(s,1H),8.11~8.08(m,2H),8.02~7.99(m,1H),7.73~7.65(m,1H),7.14(t, J =8.0 Hz,1H),6.95(d, J =8.8 Hz,1H),6.53~6.44(m,4H),4.25(s,2H); ^{13}C NMR(100 MHz, DMSO-d_6) δ : 158.2,157.0,147.1,144.9,142.5,139.8,138.4,132.7,132.5,131.3,129.6,128.8,127.8,126.7,122.9,121.2,119.0,116.5,115.8,112.6,46.3;HRMS(EI-TOF)理论值 $\text{C}_{21}\text{H}_{15}\text{ClN}_4\text{O}_4(\text{M}^+)$ 422.078 2,实测值 422.078 9。

2g:黄色固体,产率 86%;熔点 181~182 $^{\circ}\text{C}$; ^1H NMR(400 MHz, CDCl_3) δ : 8.65(s,1H),8.05(s,1H),7.71(d, J =8.8 Hz,1H),7.59(d, J =8.8 Hz,1H),7.09(d, J =8.0 Hz,2H),6.93(s,1H),6.84(s,2H),6.77(d, J =8.0 Hz,2H),4.41(s,2H),3.91(s,3H); ^{13}C NMR(100 MHz, CDCl_3) δ : 157.5,146.6,145.8,144.1,143.9,140.1,139.5,138.6,132.4,130.9,128.7,127.7,124.3,122.0,121.1,119.5,114.1,109.9,55.9,44.3;HRMS(EI-TOF)理论值 $\text{C}_{22}\text{H}_{18}\text{ClN}_3\text{O}_3(\text{M}^+)$ 407.103 7,实测值 407.103 3。

2h:灰色固体,产率 69%;熔点 134~135 $^{\circ}\text{C}$; ^1H NMR(400 MHz, CDCl_3) δ : 8.62(s,1H),8.03(s,1H),7.71(d, J =9.2 Hz,1H),7.59(d, J =9.2 Hz,1H),7.21(t, J =8.0 Hz,1H),6.90~6.87(m,1H),6.80(d, J =4.8 Hz,2H),6.59(t, J =6.4 Hz,3H),6.05(s,1H),4.36(s,2H),3.87(s,3H); ^{13}C NMR(100 MHz, CDCl_3) δ : 158.3,155.5,146.7,145.8,144.1,142.9,140.1,139.5,137.6,132.4,130.5,128.7,127.8,124.3,122.0,121.1,119.5,114.1,109.9,57.9,45.3;HRMS(EI-TOF)理论值 $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_3\text{Cl}(\text{M}^+)$ 407.103 7,实测值 407.104 1。

2i:桔红色固体,产率 88%;熔点 171~172 $^{\circ}\text{C}$; ^1H NMR(400 MHz, CDCl_3) δ : 8.64(s,1H),8.21(d, J =8.0 Hz,2H),8.02(s,1H),7.67(d, J =8.8 Hz,1H),7.56(d, J =8.0 Hz,3H),7.08(d, J =8.4 Hz,2H),6.64(d, J =8.4 Hz,2H),4.49(s,2H),4.32(s,1H); ^{13}C NMR(100 MHz, CDCl_3) δ : 157.4,147.1,147.0,145.0,144.2,140.1,139.6,138.5,132.5,130.9,129.3,128.7,127.8,127.6,123.9,122.2,

113.4, 47.9; HRMS(EI-TOF) 理论值 $C_{21}H_{15}ClN_4O_3 (M^+)$ 406.083 3, 实测值 406.083 4。

2j: 淡黄色固体, 产率 93%; 熔点 137~138 °C; 1H NMR(400 MHz, $CDCl_3$) δ : 8.63(s, 1H), 8.19(d, $J=8.0$ Hz, 2H), 8.04(s, 1H), 7.66(d, $J=9.2$ Hz, 1H), 7.59(d, $J=9.2$ Hz, 1H), 7.53(d, $J=8.4$ Hz, 2H), 7.22(d, $J=8.0$ Hz, 1H), 6.64(d, $J=8.0$ Hz, 1H), 6.52(d, $J=8.4$ Hz, 1H), 6.46(s, 1H), 4.48(s, 1H), 4.39(s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$) δ : 158.4, 147.4, 147.0, 145.0, 144.2, 140.1, 138.6, 138.5, 132.7, 130.9, 129.3, 128.2, 127.8, 125.6, 123.9, 123.8, 122.2, 113.4, 49.4; HRMS(EI-TOF) 理论值 $C_{21}H_{15}ClN_4O_3 (M^+)$ 406.083 3, 实测值 406.083 7。

2k: 淡黄色固体, 产率 92%; 熔点 106~107 °C; 1H NMR(400 MHz, $CDCl_3$) δ : 8.05(s, 1H), 7.88(s, 1H), 7.71(d, $J=8.8$ Hz, 1H), 7.58(d, $J=8.8$ Hz, 1H), 7.24~7.20(m, 3H), 6.95(d, $J=8.0$ Hz, 2H), 6.84(d, $J=8.8$ Hz, 3H), 5.20(s, 2H); ^{13}C NMR(100 MHz, $CDCl_3$) δ : 156.2, 152.1, 140.3, 137.5, 136.0, 134.2, 133.1, 131.1, 130.1, 129.3, 129.1, 128.4, 128.3, 127.7, 126.8, 117.2, 53.1; HRMS(EI-TOF) 理论值 $C_{21}H_{15}ClN_3O_2 (M^+)$ 395.059 2, 实测值 395.060 5。

2 结果与讨论

2.1 还原剂的选择

首先以化合物 1a 为反应底物进行还原反应的探索研究。如表 1 所示, 在四氢呋喃(THF)溶剂体系中考察了还原剂 $LiAlH_4$ 、 KBH_4 和 $NaBH_4$ 对反应收率的影响, 发现 $LiAlH_4$ 对反应极为不利, 没有得到相应的目标产物 2a; 相反, 用还原能力相对较弱的 $NaBH_4$ 以 45% 的收率得到了目标产物 2a。

2.2 无溶剂反应优化

进一步的试验表明, 在无溶剂反应条件下, 以 $NaBH_4$ 为还原剂, 不仅能使反应时间缩短, 而且收率也显著提高(表 1)。因此, 还原反应的优化条件是: $NaBH_4$ 为还原剂, 无溶剂条件下研磨 6 min。

2.3 反应底物对还原反应的影响

在上述最佳反应条件下, 考察了各种反应底物对还原反应的影响(表 2)。试验结果表明, 苯环上取代基的电子效应对反应影响不大, 反应均可以顺利进行, 并获得相应的目标还原产物。当苯环上带有酚羟基时, 除产物 2h 收率相对偏低外, 其他的产物都有较高的收率(2a—2g)。对于苯环上不带酚羟基的底物, 该反应也能获得很高的收率(2i—2k)。

3 结 论

本研究以具有生物活性的氯喹啉衍生物为目标分子, 发展了一种以硼氢化钠为还原剂, 室温无溶剂还原氯喹啉碳氮双键的方法。该方法收率高、条件温和、操作简单、反应时间短、环境友好, 是一种高效的亚胺还原方法, 为建立分子多样性的化合物库提供了一条有效的途径。

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