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·快递论文·

N-甲基苯胺类化合物与二醋酸碘苯在水相中的反应研究

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摘要: 首次报道了水相中二醋酸碘苯(PIDA)氧化取代 *N*-甲基苯胺合成多取代苯肼和 2-位取代苯醌的反应,合成了 8 个苯肼类化合物和 4 个苯醌类化合物,其中化合物 **2i** 为新化合物,其结构经 ^{1}H NMR, ^{13}C NMR 和HR-MS 表征。以 *N*-甲基苯胺为底物对反应条件进行了优化,最佳反应条件为:氢氧化钠 2 eq., PIDA 2 eq.,水为反应溶剂,于室温反应 3 h。并对反应机理进行了探讨。

关 键 词: 苯肼; 苯醌; 二醋酸碘苯; *N*-甲基苯胺; 氧化; 合成
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Study on the Reaction of *N*-methylaniline with Phenyl-λ^3-iodanediyl Diacetate in Water

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Abstract: The novel oxidation reaction of phenyl-λ^3-iodanediyl diacetate (PIDA) with substituted *N*-methylanilines in water was achieved to afford eight phenylhydrazines and four benzoquinones compounds. Among them, **2i** was a new compound. The structures were characterized by ^{1}H NMR, ^{13}C NMR and HR-MS. The reaction conditions were optimized with *N*-methylaniline as substrate. The optimum reaction conditions were as followed: sodium hydroxide 2 eq., PIDA 2 eq., H_2O as reaction solvent, reaction at room temperature for 3 h. The reaction mechanism was also discussed.

Keywords: hydrazine; benzoquinone; phenyl-λ^3-iodanediyl diacetate; *N*-methylaniline; oxidation; synthesis

多取代肼是一类重要的有机化合物,可以用于合成农药、药物和材料。例如有些肼类化合物可用于合成流感、肝炎、艾滋病和抗抑郁药的潜在药物[1-4]。醌是一类有颜色的物质,是合成染料的重要中间体。醌在生物体内可以参与氧化还原反应[5-6],具有抗氧化、抗癌、抗糖尿病和酶抑制活性[7-9]。因此,多取代肼和醌的合成一直是有机化学工作者关注的热点。

多取代肼主要有两种合成方法:(1)单取代肼的脱氢烷基化[10],该反应需使用强碱丁基锂和实验要求高。(2)二级胺的催化氧化偶联[11-15]。该反应需要在铜盐催化剂和有机溶剂中进行。

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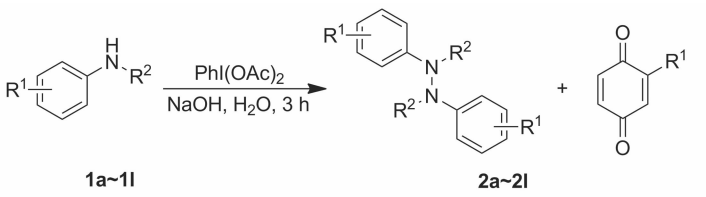


1a~1l 2a~2l

Comp	a	b	c	d	e	f	g	h	i	j	k	l
R^1	H	4-CH_3	4-Br	4-Cl	2-CH_3	2-Cl	2,6-2CH_3	3-CH_3	3-Cl	H	H	H
R^2	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	*N*-^{i}Pr	*N*-Pr	*N*-Ph
Yield%	72	78	58	50	92	70	81	35	61	61	30	45

Scheme 1

醌的合成方法主要有 4 种:(1)芳基酚直接氧化[16-18]。(2)对二苯甲醚类的去甲基化[19-25]。(3)芳环的直接氧化[26]。(4)对二苯酚的氧化[27-30]。这些反应也需要使用过度金属离子催化和有机溶剂。

本文首次报道了在水相中二醋酸碘苯(PIDA)与 *N*-取代苯胺(**1a~1l**)的氧化反应,根据底物的不同分别制备了取代肼和醌化合物(**2a~2l**, Scheme 1),其中化合物 **2i** 为新化合物,其结构经 ^{1}H NMR, ^{13}C NMR 和 HR-MS(ESI)表征。该反应绿色无污染,为肼类和醌类化合物的合成提供了一种简单有效的方法。

1 实验部分

1.1 仪器与试剂

Bruker advance 400 型核磁共振仪($CDCl_3$ 为溶剂,TMS 为内标);TOF 型质谱仪(ESI-TOF)。

所用试剂均为分析纯。

1.2 合成

(1) **2a~2l** 的合成(以 **2a** 为例)

在反应管中依次加入 *N*-甲基苯胺(**1a**)0.107 g(1 mmol), PIDA 0.644 g(2 mmol), NaOH 0.080 g(2 mmol)和水 3 mL,搅拌下于室温反应 3 h。反应液加入 H_2O 20 mL,用乙酸乙酯 60 mL 萃取 3 次,减压浓缩,残余物经硅胶柱层析[洗脱剂:*V*(乙酸乙酯)/*V*(石油醚) = 1/20]纯化得 **2a** 0.076 g。

用类似方法合成 **2b~2l**。

N,*N*-二甲基-*N*,*N*-二苯基肼(**2a**):收率 72%, m. p. 30 ~ 31 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (t, *J* = 7.5 Hz, 4H, ArH), 6.78 ~ 6.84 (m, 6H, ArH), 2.97 (s, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 129.7, 118.9, 112.9, 34.3; HR-MS(ESI) *m/z*: Calcd for $C_{14}H_{16}N_2$ [M^+] 212.131 3, found 212.131 3。

N,*N*-二甲基-*N*,*N*-二(4-甲基苯基)肼(**2b**):收率 78%, m. p. 63 ~ 65 ℃; ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.05(d, *J* = 6.8 Hz, 4H, ArH), 6.76 (d, *J* = 6.8 Hz, 4H, ArH), 2.92 (s, 6H, 2CH_3), 2.26 (s, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 130.2, 128.1, 113.1, 34.0, 20.8; HR-MS(ESI) *m/z*: Calcd for $C_{16}H_{20}N_2$[M^+]240.162 6, found 240.162 6。

N,*N*-二甲基-*N*,*N*-二(4-溴苯基)肼(**2c**):收率 58%, m. p. 81 ~ 83 ℃; ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.33(d, *J* = 9.0 Hz, 4H, ArH), 6.69 (d, *J* = 9.0 Hz, 4H, ArH), 2.95 (s, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.1, 138.4, 132.5, 114.7, 34.3; HR-MS(ESI) *m/z*: Calcd for $C_{14}H_{14}N_2Br_2$ [M^+] 371.948 3, found 371.949 5。

N,*N*-二甲基-*N*,*N*-二(4-氯苯基)肼(**2d**):收率 50%, m. p. 71 ~ 73 ℃; ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.19(d, *J* = 8.9 Hz, 2H, ArH), 6.74 (d, *J* = 8.9 Hz, 2H, ArH), 2.95 (s, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.8, 129.6, 124.2, 114.3, 34.3; HR-MS(ESI) *m/z*: Calcd for $C_{14}H_{14}N_2Cl_2$ [M]$^+$ 282.050 5, found 282.051 0。

2-甲基[1,4]苯醌(**2e**):收率 92%, m. p. 66 ~ 67 ℃; ^{1}H NMR(400 MHz, $CDCl_3$) δ: 6.77(d, *J* = 10.1 Hz, 1H, ArH), 6.72(dd, *J* = 2.4 Hz, 10.1 Hz, 1H, ArH), 6.62 ~ 6.63(m, 1H, ArH), 2.07(d, *J* = 1.4 Hz, 3H, CH_3); ^{13}C NMR(100

MHz, $CDCl_3$) δ: 188.2, 188.0, 146.3, 137.0, 136.9, 133.8, 16.3. HR-MS(ESI) *m/z*: Calcd for $C_7H_6O_2[M^+]$122.036 8, found 122.036 7。

2-氯[1,4]苯醌(**2f**): 收率 70%, m. p. 55 ~ 56 ℃; ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.03(d, J = 2.1 Hz, 1H, ArH), 6.94(d, J = 10.1 Hz, 1H, ArH), 6.83(dd, J = 2.1 Hz, 10.1 Hz, 1H, ArH); ^{13}C NMR(100 MHz, $CDCl_3$) δ: 185.5, 179.7, 144.6, 137.3, 136.5, 134.2; HR-MS(ESI) *m/z*: Calcd for $C_6H_3O_2Cl[M^+]$141.982 2, found 141.982 3。

2,6-二甲基[1,4]苯醌(**2g**): 收率 81%, m. p. 65 ~ 66 ℃; ^{1}H NMR(400 MHz, $CDCl_3$) δ: 6.56(s, 2H, ArH), 2.06(s, 6H, $2CH_3$); ^{13}C NMR(100 MHz, $CDCl_3$) δ: 188.6, 188.1, 146.2, 133.7, 16.4; HR-MS(ESI) *m/z*: Calcd for $C_8H_8O_2[M^+]$136.052 4, found 136.052 6。

N,*N*-二甲基-*N*,*N*-二(3-甲基苯基)肼(**2h**): 收率 35%, m. p. 42 ~ 44 ℃(反应分离出 **2e**,收率 45%); ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.15(d, J = 7.8 Hz, 2H, ArH), 6.64 ~ 6.70(m, 6H, ArH), 2.97(s, 6H, $2CH_3$), 2.31(s, 6H, $2CH_3$); ^{13}C NMR(100 MHz, $CDCl_3$) δ: 139.6, 129.6, 119.8, 113.6, 110.2, 110.0, 34.2, 22.3; HR-MS(ESI) *m/z*: Calcd for $C_{16}H_{20}N_2$ $[M^+]$240.162 6, found 240.162 6。

N,*N*-二甲基-*N*,*N*-二(3-氯苯基)肼(**2i**): 收率 61%, m. p. 52 ~ 53 ℃(反应分离出 **2f**,收率 20%); ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.17(t, J = 7.9 Hz, 2H, ArH), 6.79 ~ 6.81(m, 4H, ArH), 6.66 ~ 6.69(m, 2H, ArH), 2.98(s, 6H, $2CH_3$); ^{13}C NMR(100 MHz, $CDCl_3$) δ: 150.2, 135.8, 130.8, 119.3, 113.0, 111.2, 34.5; HR-MS(ESI) *m/z*: Calcd for $C_{14}H_{14}N_2Cl_2[M^+]$ 282.050 5, found 282.050 3。

[1,4]苯醌(**2j**): 收率 61%, m. p. 113 ~ 115 ℃; ^{1}H NMR(400 MHz, $CDCl_3$) δ: 6.80(s, 4H, ArH); ^{13}C NMR(100 MHz, $CDCl_3$) δ: 187.7, 137.0; HR-MS(ESI) *m/z*: Calcd for $C_6H_4O_2$ $[M^+]$108.021 1, found 108.021 3。

N,*N*-二苯基-*N*,*N*-二丙基)肼(**2k**): 收率 30%, m. p. 70 ~ 71 ℃(反应分离出 **2j**,收率 35%); ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.21(t, J = 7.7 Hz, 4H, ArH), 6.75(t, J = 7.3 Hz, 2H, ArH), 6.71(d, J = 8.5 Hz, 4H, ArH), 3.39(t, J = 8.1 Hz, 4H, $2CH_2$), 1.73 ~ 1.75(m, 4H, $2CH_2$), 0.93(t, J = 7.4 Hz, 6H, $2CH_3$); ^{13}C NMR(100 MHz, $CDCl_3$) δ: 148.7, 129.7, 118.3, 112.7, 53.4, 21.8, 12.1; HR-MS(ESI) *m/z*: Calcd for $C_{18}H_{24}N_2$ $[M^+]$268.193 9, found 268.194 0。

N,*N*,*N*′,*N*′-四苯基肼(**2l**): 收率 45%, m. p. 146 ~ 147 ℃; ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.31(d, J = 8.4 Hz, 8H, ArH), 7.19(t, J = 7.9 Hz, 8H, ArH), 6.89(t, J = 7.3 Hz, 4H, ArH); ^{13}C NMR(100 MHz, $CDCl_3$) δ: 143.9, 129.6, 122.5, 118.5; HR-MS(ESI) *m/z*: Calcd for $C_{24}H_{20}N_2[M^+]$336.162 6, found 336.162 4。

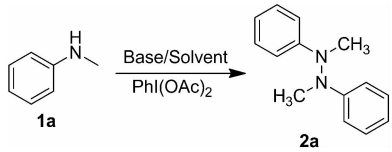
2　结果与讨论

2.1　条件优化

在初始的条件筛选中我们选取 *N*-甲基苯胺(**1a**)作为模板反应底物(表 1)。

表 1　反应条件优化[a]

Table 1　Optimization of the reaction conditions



No.	PIDA	Base(Dosage/eq.)	Solvent	Yield[b]/%
1	2.0	-	H_2O	15
2	2.0	K_2CO_3(2.0)	H_2O	40
3	2.0	NaOH(2.0)	H_2O	75
4	1.0	NaOH(2.0)	H_2O	40
5	1.5	NaOH(2.0)	H_2O	56
6	2.5	NaOH(2.0)	H_2O	63
7	2.0	NaOH(2.0)	CH_2Cl_2	68
8	2.0	NaOH(2.0)	MeOH	Trace
9	2.0	NaOH(2.0)	MeCN	36
10	2.0	NaOH(2.0)	THF	55
11	2.0	NaOH(2.0)	H_2O	72[c]
12	2.0	NaOH(2.0)	H_2O	70[d]
13	2.0	NaOH(2.0)	H_2O	52[e]

[a] All reactions were conducted on a 1.0 mmol scale at room temperaturefor 3 h; [b] Isolated yield; [c] 3.5 h; [d] 35 ℃; [e] 10 ℃。

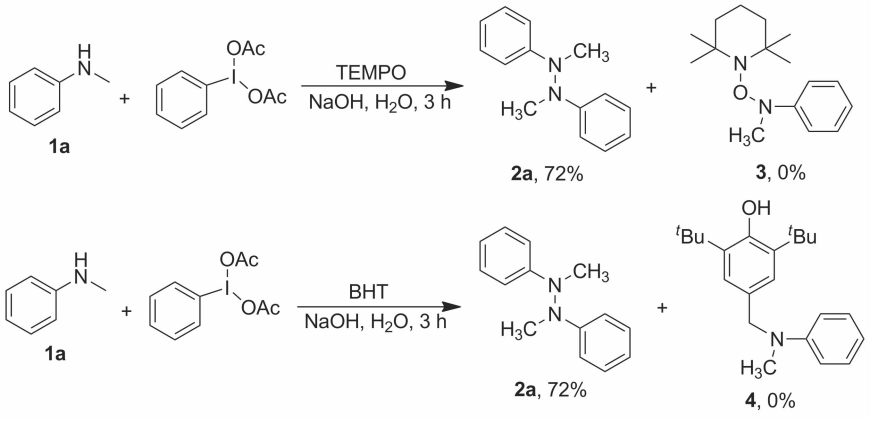
当使用 2 eq. PIDA 作为氧化剂,水作为反应溶剂时,*N*,*N*-二甲基-*N*,*N*-二苯基肼(**2a**)收率为 15%(表 1, No. 1)。当体系加入 2 eq. 碳酸钾时,**2a** 的收率提高到 40%(表 1, No. 2),我们认为可能是碱促进了产物的去质子化。使用更强的碱氢氧化钠时,**2a** 的收率较高(表 1, No. 3)。随后我们对氧化剂的用量进行优化,但 **2a** 收率并未增加(表 1, No. 4 ~ 6)。溶剂筛选实验表明,水是最佳反应溶剂(表 1, No. 7 ~ 10)。综上所述,最佳反应条件为:2 eq. PIDA, 2 eq. NaOH,水为反应溶剂,于室温反应 3 h。

2.2　底物拓展

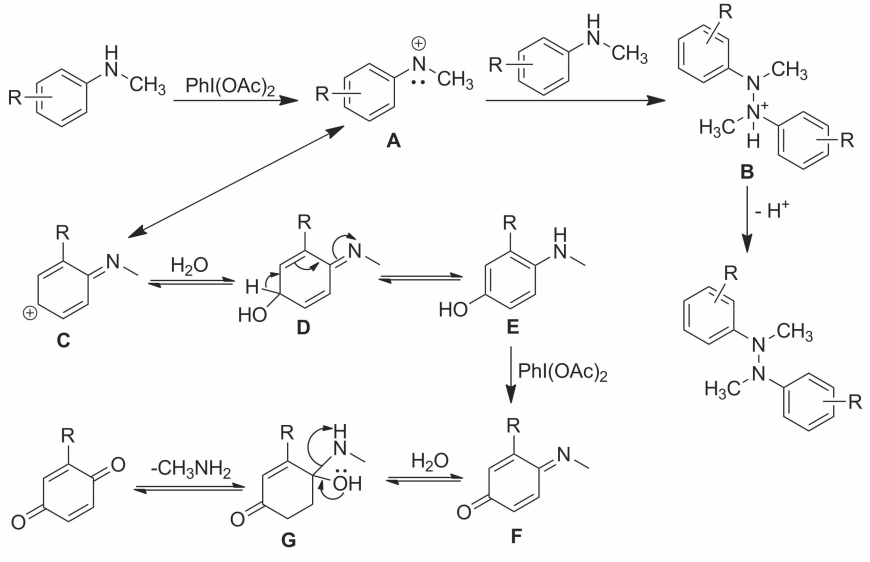
在优化的反应条件下对底物进行了拓展,实验结果见 Scheme 1。*N*-甲基苯胺对位有供电子基时,取代肼的收率较高(**2b**, 78%)。另一方面,*N*-甲基苯胺对位有拉电子基时,取代肼的收率较低(**2c**, **2d**)。令人惊奇的是,当 *N*-甲基苯胺的邻位有取代基时,反应得到的产物不是肼而是醌(**2e ~ 2g**)。当 *N*-甲基苯胺的间位有取代基时,反应得到的产物是肼和醌的混合物(**2h ~ 2i**)。我们改变苯胺氮原子上的取代基,做进一步的实验(**2j**, **2k**, **2l**)。发现当氮原子上的取代基为异丙基时,主要得到对二苯醌。当取代基为正丙基时,得到肼和醌的混合物。当取代基为苯基时,得到单一的取代肼(**2l**)。

2.3　控制实验

本研究对反应进行了控制实验(Scheme 2)。当反应体系加入 2 eq. 自由基捕捉剂(TEMPO 和 BHT)时,反应可以顺利获得目标产物。由此证明:反应过程可能未经历自由基这一过程。



Scheme 2



Scheme 3

2.4　反应机理

根据控制实验结果,提出了可能的反应机理(Scheme 3)。首先,取代的 *N*-甲基苯胺在 PIDA 作用下,被氧化为氮正离子(**A**),随后 **A** 与原料取代的 *N*-甲基苯胺反应得到 **B**, **B** 脱去质子得到多取代肼。而当苯环邻位有取代基时,中间体 **A** 迅速互变为中间体 **C**,体系内的水亲核进攻 **C** 得中间体 **D**, **D** 脱去质子得到 **E**, **E** 被 PIDA 氧化脱氢得到中间体 **F**,最后 **F** 水解得到 2-取代醌。

3　结论

研究了取代的 *N*-甲基苯胺与二醋酸碘苯(PIDA)的反应,根据取代基的位置不同分别得到了多取代肼和邻位取代的醌。该合成方法具有反应条件温和,操作简单,溶剂绿色等优点。为合成多取代肼和 2 - 位取代的醌提供了一种简单有效的合成方法。通过控制实验,提出了可能的反应机理。

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