Synthesis of Iminoquinones from Anilines Using IBX in DMSO

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Abstract: An efficient and convenient procedure for the preparation of 2-amino-(1,4)-benzoquinone-4-phenylimides from anilines using a λ^5-iodane-1-hydroxy-1,2-benziodoxol-3(1*H*)-one-1-oxide (IBX) oxidation in dimethyl sulfoxide is described. This protocol offers a general approach to compounds consisting of an iminoquinone moiety with a wide range of functional groups. A single electron transfer (SET) process was postulated to explain the oxidation pathway.

Key words: IBX, iminoquinone, aniline, SET, oxidation

Since the discovery of Dess–Martin periodinane oxidation, there has been an increased interest in hypervalent iodine(V) compounds as versatile oxidation reagents.[1] In particular, the heterocyclic IBX (Figure 1) has been used extensively in the selective oxidation of alcohols,[2] halides,[3] dehydrogenation of ketones, aldehydes and N-heterocycles to the corresponding α,β-unsaturated analogues and heteroaromatics,[4] oxidative cleavage of dithioacetals and dithioketals,[4] selective deprotection of triethylsilyl ethers,[5] hydroxylation of α-alkynyl carbonyl compounds[6a] and oxidation of α-alkynyl alcohols to *Z*-enediones.[6b] However, to our knowledge IBX has not been used in the preparation of iminoquinones.

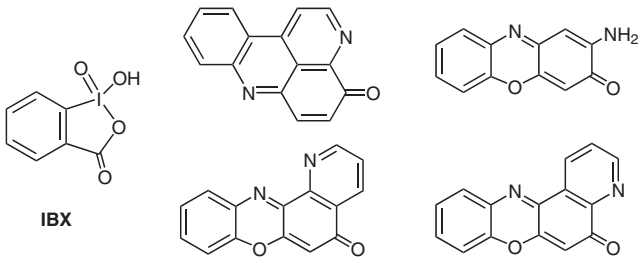


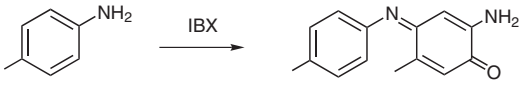
Figure 1 The structures of IBX, phenophenoxazione, benzophenoxazione and pyridophenoxazione

Iminoquinone moieties can be found in a number of natural and synthetic antiproliferative compounds, including phenophenoxazinone, benzophenoxazinone and pyridophenoxazinone consisting of either a linear or angular heterocyclic scaffold (Figure 1).[7] It has been shown that their antineoplastic activity correlates with the ability of the planar heterocyclic moiety to intercalate into double-stranded DNA. The phenoxazinone skeleton is also found in actinomycins,[8] an important family of antibiotics produced by actinomycetes, linking two pentapeptide chains. This pharmacophore is also found in meridine and neoamphimedine.[9]

Iminoquinones, as key building blocks of phenoxazinones have been synthesized using several methods, including metal catalysis,[10] natural enzymes,[11] UV lamps and photosensitisers.[12] Herein we report the expedient synthesis of iminoquinones by IBX oxidation of anilines in dimethyl sulfoxide.

In order to optimize the reaction, the IBX oxidation of 4-methylaniline was first examined under various conditions, the results are listed in Table 1. 2-Amino-5-methyl-1,4-benzoquinone-4-(4′-methyl)phenylimide (**1b**) was obtained almost quantitatively when a solution of 4-methylaniline and 1.25 equivalents of IBX in dimethyl sulfoxide was stirred at room temperature for 50 minutes (Table 1, entry 3). No over-oxidation was observed using

Table 1 Optimization of Reaction Conditions



1a **1b**

Entry[a]	IBX (equiv)	Solvent	Time (min)	Yield[b] (%)
1	0.25	DMSO	50	31
2	1.0	DMSO	50	82
3	1.25	DMSO	50	94
4	1.25	DMSO	30	84
5	2.5	DMSO	120	93
6	1.25	CH_2Cl_2–H_2O[c]	120	76
7	1.5	Acetone	50	26
8	1.5	$CHCl_3$	50	22
9	2.0	CH_2Cl_2	90	34
10	2.5	Acetone–H_2O[d]	90	31
11	2.5	CH_2Cl_2–H_2O[d]	120	36

[a] All reactions were run on a 3.0 mmol scale in 8 mL of solvent at room temperature.
[b] Isolated yield after column chromatography.
[c] CH_2Cl_2–H_2O (1:1 v/v); TEAB as a phase-transfer catalyst.
[d] Acetone/CH_2Cl_2–H_2O (10:1 mol/mol).

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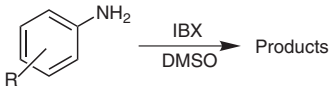
2.5 equivalents of IBX and a reaction time of two hours (Table 1, entry 5). The reaction was also carried out in some other common solvents including acetone, chloroform and dichloromethane with or without water. In all cases **1b** was obtained in lower yields, probably due to the low solubility of IBX in these solvent systems. In the presence of a phase-transfer catalyst, tetraethyl ammonium bromide (TEAB), **1b** was afforded in 76% yield when a mixture of the aniline and IBX in a two-phase system of water and dichloromethane (1:1) was stirred at room temperature for two hours (Table 1, entry 6).

Table 2 Scope of Substrates



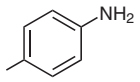
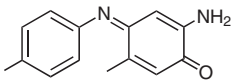
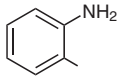
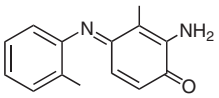
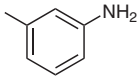
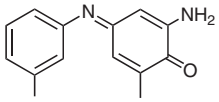
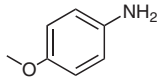
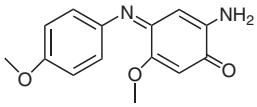
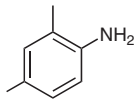
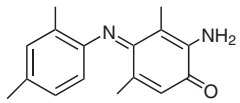
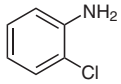
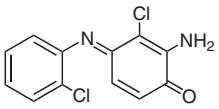
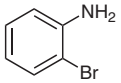
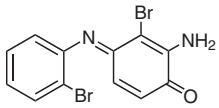
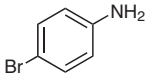
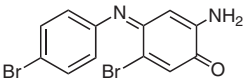
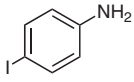
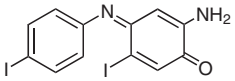
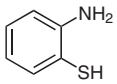
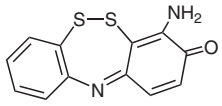
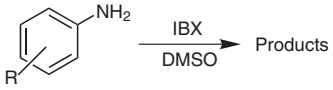
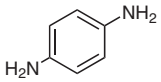
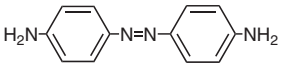
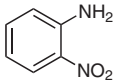
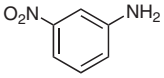
Entry[a]	Substrate[b]	Time (min)	Product	Yield (%)[c]
1	 **1a**	50	 **1b**	94
2	 **2a**	45	 **2b**	89
3	 **3a**	40	 **3b**	85
4	 **3a**	35	 **4b**	76
5	 **4a**	45	 **5b**	85
6	 **5a**	35	 **6b**	93
7	 **6a**	25	 **7b**	91
8	 **7a**	25	 **8b**	93
9	 **8a**	25	 **9b**	86
10	 **9a**	30	 **10b**	89

Table 2 Scope of Substrates (continued)



Entry[a]	Substrate[b]	Time (min)	Product	Yield (%)[c]
11	 **10a**	50	 **11b**	88
12[d]	 **12a**	–	–	–
13[d]	 **13a**	–	–	–

[a] All reactions were run on a 3.0 mmol scale using 1.25 equivalents of IBX in DMSO (8 mL) at room temperature.
[b] Substrates were commercially available and used without further purification.
[c] Isolated yield after column chromatography.
[d] No reaction with excess IBX at elevated temperature after 24 h.

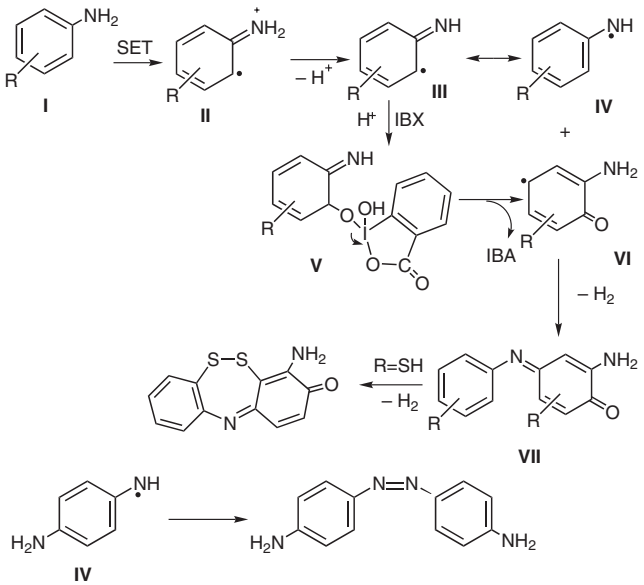
The IBX oxidation reaction was extended to anilines with various substituents using the optimized conditions, the results are listed in Table 2. The desired products were obtained in high yields (>76%) using dimethyl sulfoxide as the solvent and with substrates bearing substituents including *o*-Me, *m*-Me, *p*-Me, *o*,*p*-diMe, *o*-Cl, *p*-OMe, *o*-Br, *p*-Br, *p*-I, *o*-SH, *p*-NH_2 (Table 2, entries1–11). However, substrates bearing the strong electron-withdrawing nitro group showed no reaction even when an excess of IBX was used at an elevated temperature (Table 2, entries 12 and 13). In the case of 2-aminothiophenol (Table 2, entry 10) the oxidation reaction gave a tricyclic compound **10b** in 89% yield with the formation of an S–S bond. In another particular case, oxidation of 1,4-phenylenediamine afforded 4,4′-diazenediylbisaniline (**11b**) in 88% yield (Table 2, entry 11). Interestingly, no over-oxidation or polymerization was observed, providing a convenient procedure to synthesize 4,4′-diazenediylbisanilines. These compounds have a variety of potential applications, such as in organic non-linear optics, optical storage media, as chemosensors and as photochemical switches.[14]

According to the literature[15] and our observations, a SET process was postulated for the oxidation pathway (Scheme 1). Initially, the aniline **I** loses one electron to IBX via a SET process to form the activated intermediate **II**, which loses a proton to form a species with two resonance states **III** and **IV**.

Intermolecular transfer of an oxygen atom from IBX to the radical **III** via the intermediate **V** gives the radical **VI**, which combines with **IV** affording the final product.

The mercapto-substituted product is further dehydrogenated to give the tricyclic iminoquinone **10b** as product, possibly due to the fact that there is an easy transformation of the mercapto group into an S–S bond in the presence of the oxidant and also a favorable steric effect.

The imine-centered radicals bearing basic amino groups give their homo-coupled products. We suggest that the slight acidity of IBX[16] plays an essential role in the process from **III** to **V**. In other words, the acidic conditions favor formation of radical **III**, whereas the second amino group is responsible for neutralization or reducing the acidity of IBX and this results in the conversion of **III** into **IV**, followed by homo-coupling to produce 4,4′-diazenediylbisaniline.



Scheme 1 Proposed Mechanism for the IBX Oxidation Reaction

In summary, we have developed an efficient synthetic route to access 2-amino-1,4-benzoquinone-4-phenylimides using an IBX oxidation of anilines with a variety of substituents. This method might find application in the synthesis of polycyclic targets and natural products consisting of iminoquinone moieties. A SET process was postulated for the oxidation pathway.

All NMR spectra were recorded on a Bruker Avance Digital spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR); chemical shifts were expressed in δ units using TMS as the internal reference in $CDCl_3$. IR spectra were recorded on a Shimadzu IR-408 spectrometer. Mass spectra were recorded on a HP5989B mass spectrometer. Melting points were uncorrected. IBX was prepared using a literature procedure.[17]

General Procedure

To a solution of IBX (1.05 g, 3.75 mmol) in DMSO (8 mL) was added aniline (3.0 mmol) in one portion. The mixture was stirred at r.t. until complete consumption of the aniline (monitored by TLC). H_2O (8 mL) was then added, and the mixture was extracted with CH_2Cl_2 (5 × 8 mL). The combined extracts were dried over anhyd Na_2SO_4. After filtration the solvent was removed and the residue was purified by silica gel column chromatography to afford the final compound.

2-Amino-5-methyl-(1,4)-benzoquinone-4-(4-methyl)phenylimide (1b)

Bright red-orange solid; mp 148–149 °C.

IR (KBr): 3466, 3354, 2920, 1652, 1600, 1497, 1243, 861, 845, 812 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 5.0 Hz, 2 H), 6.72 (d, *J* = 5.0 Hz, 2 H), 6.47 (s, 1 H), 5.86 (s, 1 H), 4.43 (s, 2 H), 2.35 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.79, 159.00, 151.63, 148.65, 142.92, 133.91, 129.26, 128.23, 120.16, 96.38, 21.07, 17.68.

MS (FAB): *m*/*z* = 226.8 [M + H$^+$].

MS (EI): *m*/*z* (%) = 226 (48), 225 (35), 211 (100), 91 (29), 65 (19).

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.34; H, 6.19; N, 12.39. Found: C, 74.32; H, 6.43; N, 12.39.

2-Amino-3-methyl-(1,4)-benzoquinone-4-(2-methyl)phenylimide (2b)

Bright red-orange solid; mp 87–89 °C.

IR (KBr): 3407, 3330, 2921, 1655, 1632, 1616, 1447, 1405, 1237, 1084, 833, 775, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 4.8 Hz, 1 H), 7.16 (t, *J* = 4.8 Hz, 1 H), 7.06 (t, *J* = 4.5 Hz, 1 H), 6.82 (d, *J* = 6.8 Hz, 1 H), 6.51 (d, *J* = 4.8 Hz, 1 H), 6.38 (d, *J* = 6.3 Hz, 1 H), 4.41 (s, 2 H), 2.15 (s, 3 H), 2.12 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.13, 156.81, 149.53, 140.38, 130.54, 130.29, 129.77, 129.08, 126.05, 124.92, 119.70, 114.77, 18.01, 10.23.

MS (FAB): *m*/*z* = 226.9 [M + H$^+$].

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.34; H, 6.19; N, 12.39. Found: C, 74.30; H 6.41; N, 12.38.

2-Amino-6-methyl-(1,4)-benzoquinone-4-(3-methyl)phenylimide (3b)

Bright red-orange solid; mp 93–95 °C.

IR (KBr): 3415, 3328, 2926, 1664, 1607, 1447, 1405, 1256, 1084, 833, 800 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (s, 1 H), 6.96 (s, 2 H), 6.66 (s, 2 H), 5.86 (s, 1 H), 4.63 (s, 2 H), 2.34 (s, 3 H), 2.08 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.66, 158.33, 150.83, 143.48, 139.73, 138.50, 138.15, 128.47, 125.06, 120.97, 111.87, 95.71, 21.34, 15.41.

MS (FAB): *m*/*z* = 226.9 [M + H$^+$].

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.34; H, 6.19; N, 12.39. Found: C, 74.32; H, 6.38; N, 12.36.

2-Amino-5-methoxy-(1,4)-benzoquinone-4-(4-methoxy)phenylimide (4b)

Black-red solid; mp 183–185 °C.

IR (KBr): 3403, 3319, 3162, 2926, 1662, 1598, 1497, 1442, 1245, 1218, 1033, 852 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86–6.92 (m, 4 H), 5.88 (s, 1 H), 5.84 (s, 1 H), 4.71 (s, 2 H), 3.91 (s, 3 H), 3.82 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.34, 164.63, 157.06, 154.59, 143.51, 142.83, 122.05, 114.07, 103.50, 93.97, 56.49, 55.45.

MS (FAB): *m*/*z* = 258.9 [M + H$^+$].

Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 65.23; H, 5.44; N, 10.83.

2-Amino-3,5-dimethyl-(1,4)-benzoquinone-4-(2,4-dimethyl)phenylimide (5b)

Bright red-orange solid; mp 137–139 °C.

IR (KBr): 3483, 3361, 2919, 1660, 1595, 1570, 1543, 1486, 1407, 1364, 1239, 860, 824 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00 (s, 1 H), 6.91 (t, *J* = 4.8 Hz, 1 H), 6.42 (s, 1 H), 6.35 (d, *J* = 4.8 Hz, 1 H), 4.33 (s, 2 H), 2.30 (s, 6 H), 2.11 (s, 3 H), 1.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.53, 156.98, 153.34, 148.46, 142.14, 133.40. 130.98, 126.66, 116.84, 108.39, 20.65, 19.15, 17.93, 13.82.

MS (FAB): *m*/*z* = 254.8 [M + H$^+$].

Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.45; H, 7.09; N, 11.11.

2-Amino-3-chloro-(1,4)-benzoquinone-4-(2-chloro)phenylimide (6b)

Bright red-orange solid; mp 128–130 °C.

IR (KBr): 3475, 3370, 1653, 1623, 1598, 1562, 1392, 1338, 838, 766, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 5.0 Hz, 1 H), 7.25 (t, *J* = 4.8 Hz, 1 H), 7.10 (t, *J* = 4.8 Hz, 1 H), 6.76–6.82 (m, 2 H), 6.44 (d, *J* = 6.3 Hz, 1 H), 5.10 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.95, 153.72, 146.74, 140.81, 129.89, 129.49, 129.04, 126.93, 126.02, 124.77, 121.48, 111.99.

MS (FAB): *m*/*z* = 258.8 [M + H$^+$].

Anal. Calcd for $C_{12}H_8Cl_2N_2O$: C, 53.96; H, 3.02; N, 10.49. Found: C, 53.92; H, 2.98; N, 10.52.

2-Amino-3-bromo-(1,4)-benzoquinone-4-(2-bromo)phenylimide (7b)

Bright red-orange solid; mp 174–176 °C.

IR (KBr): 3468, 3363, 1654, 1617, 1597, 1555, 1456, 1359, 1332, 1233, 1026, 824, 764 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 5.0 Hz, 1 H), 7.30 (t, *J* = 5.3 Hz, 1 H), 7.03 (t, *J* = 5.0 Hz, 1 H), 6.86 (d, *J* = 6.3 Hz, 1 H), 6.74 (d, *J* = 4.5 Hz, 1 H), 6.45 (d, *J* = 6.5 Hz, 1 H), 5.12 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.03, 153.66, 148.39, 142.92, 132.98, 129.47, 129.43, 127.63, 126.02, 121.21, 114.79, 104.36.

MS (FAB): *m*/*z* = 356.8 [M + H$^+$].

Anal. Calcd for $C_{12}H_8Br_2N_2O$: C, 40.48; H, 2.26; N, 7.87. Found: C, 40.32; H, 2.38; N, 7.62.

2-Amino-5-bromo-(1,4)-benzoquinone-4-(4-bromo)phenylimide (8b)

Bright red-orange solid; mp >300 °C.

IR (KBr): 3477, 3375, 1648, 1621, 1582, 1477, 1218, 1065, 1002, 875, 833 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 5.3 Hz, 2 H), 7.19 (s, 1 H), 6.73 (d, *J* = 5.5 Hz, 2 H), 5.88 (s, 1 H), 4.66 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.82, 154.77, 149.28, 143.27, 142.88, 133.57, 131.92, 121.53, 117.94, 95.86.

MS (FAB): *m*/*z* = 356.8 [M + H$^+$].

Anal. Calcd for $C_{12}H_8Br_2N_2O$: C, 40.48; H, 2.26; N, 7.87. Found: C, 40.31; H, 2.31; N 7.72.

2-Amino-5-iodo-(1,4)-benzoquinone-4-(4-iodo)phenylimide (9b)

Bright red-orange solid; mp >300 °C.

IR (KBr): 3469, 3366, 1648, 1612, 1581, 1468, 1411, 1296, 1215, 998, 872, 833 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 5.3 Hz, 2 H), 7.58 (s, 1 H), 6.61 (d, *J* = 5.3 Hz, 2 H), 5.91 (s, 1 H), 4.58 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.46, 155.18, 150.30, 143.34, 141.48, 138.25, 126.67, 122.47, 94.86, 88.84.

MS (FAB): *m*/*z* = 450.8 [M + H$^+$].

Anal. Calcd for $C_{12}H_8I_2N_2O$: C, 32.03; H, 1.79; N, 6.23. Found: C, 32.00; H, 1.65; N, 6.18.

1-Amino-5-aza-10,11-dithiadibenzo[*a*,*d*]cyclohepten-2-one (10b)

Purple solid; mp 157–159 °C.

IR (KBr): 3465, 3359, 1647, 1602, 1584, 1450, 1432, 1294, 1215, 872, 833, 678 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.0 Hz, 1 H), 7.39–7.43 (m, 2 H), 7.18 (d, *J* = 10.0 Hz, 1 H), 7.10 (t, *J* = 7.6, 7.2 Hz, 1 H), 6.63 (d, *J* = 10.0 Hz, 1 H), 5.21 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.43, 155.71, 149.47, 149.12, 141.90, 134.83, 133.52, 131.45, 129.95, 128.25, 126.89, 109.13.

MS (FAB): *m*/*z* = 260.8 [M + H$^+$].

Anal. Calcd for $C_{12}H_8N_2OS_2$: C, 55.36; H, 3.10; N, 10.76. Found: C, 55.31; H, 2.89; N, 10.43.

4,4′-Diazenediylbisaniline (11b)

Bright yellow solid; mp 266–268 °C.

IR (KBr): 3475, 3376, 3204, 1617, 1591, 1504, 1300, 1152, 837 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 5.8 Hz, 4 H), 6.73 (d, *J* = 5.3 Hz, 4 H), 3.93 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.56, 145.87, 124.31, 114.73.

MS (FAB): *m*/*z* = 212.8 [M + H$^+$].

Anal. Calcd for $C_{12}H_{12}N_4$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.78; H, 5.59; N, 26.24.

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