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A New, Simple, and General Synthesis of *N*-Oxides of Iodopyridines and Iodoquinolines via the Diazotization–Iodination of Heterocyclic Amino *N*-Oxides in the Presence of *p*-Toluenesulfonic Acid in Water

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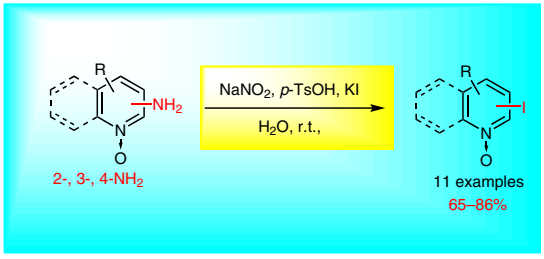

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Abstract The diazotization of a series of *N*-oxides of aminopyridines and aminoquinolines under the action of sodium nitrite in the presence of KI and *p*-TsOH in water at room temperature leads to the formation of the corresponding *N*-oxides of iodopyridines and iodoquinolines in high yields. The method has a general character and can be used for the preparation of 3-, 2-, and 4- *N*-oxides of iodopyridines.

Key words diazo compounds, pyridines, quinolines, halogenation, iodine

N-Oxides of iodinated heterocyclic compounds with a pyridine moiety (pyridines, quinolines) are important intermediates in the synthesis of new heterocyclic scaffolds,[1] biologically active molecules,[2] and drugs.[3,4] In addition, these compounds can be easily converted into iodopyridines and iodoquinolines,[5] which are widely used in organic synthesis, medicinal chemistry, and for the production of modern materials. Moreover, such compounds are valuable themselves as drugs and diagnostics.[6]

Diazotization-iodination of anilines is one of the most common methods for the synthesis of iodoaromatic compounds. However, this method is not widely used for obtaining iodopyridines and iodoquinolines and has lower efficiency in this case.[7] Whereas diazotization-iodination of 3-aminopyridines using the same reagents as for diazotization of anilines ($NaNO_2$ or AlkONO in the presence of HCl, H_2SO_4, *p*-TsOH and KI, NaI, HI) gives moderate to good yields of 3-iodopyridines,[8] the diazotization-iodination of 2- and 4-aminopyridines requires the use of such systems as *t*-BuONO/CH_2I_2/CuI/I_2, KNO_2/HI/DMSO/CuI, and the yields of 4- and, especially, 2-iodopyridines rarely exceed 50%.[4,9] The highest yield of 4-iodopyridine (70%) was achieved via diazotization of 4-aminopyridine by $NaNO_2$ in HBF_4 at –10 °C followed by the reaction with KI in aqueous acetone.[9e] Thus, there is no a general method for obtaining 2-, 3-, and 4-iodopyridines via diazotization-iodination reactions. Diazotization-iodination of aminoquinolines for the preparation of quinolines with iodine in the pyridine moiety was described only for the synthesis of 3-iodoquinolines, but not for 2- and 4- derivatives.[10]

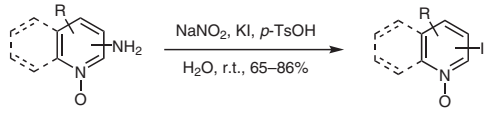
It was shown previously that the diazotization of anilines in the presence of *p*-TsOH and other sulfonic acids leads to stable aryldiazonium sulfonates, which readily undergo iodination with the formation of iodoarenes.[11] In contrast, it turned out that aminopyridines, when being diazotized in the presence of *p*-TsOH or TfOH do not form the diazonium salts, but the corresponding pyridyl tosylates PyOTs and pyridyl triflates PyOTf.[12] This fact as well as the unsatisfactory results of diazotization-iodination of aminopyridines mentioned above could be explained by the instability of pyridinediazonium salts, especially with the diazonium group at the positions 4 and 2.

However, it is known that *N*-oxide groups slightly stabilize diazonium salts, and aminopyridine 1-oxides can behave similar to anilines in the diazotization reaction.[13] Nevertheless, only rare examples of diazotization-iodination of aminopyridine 1-oxides are known. In particular, 4-aminopyridine 1-oxide and some of its derivatives are diazotized-iodinated in the presence of HCl, H_2SO_4, or HBF_4 with the formation of corresponding iodopyridines in 14–45% yields.[3,5a,b,14]

We have found that *N*-oxides of aminopyridines **1–8** and aminoquinolines **9–11** under the action of sodium nitrite, KI, and *p*-TsOH in water at room temperature undergo successive diazotization and iodination with the formation

of corresponding hetaryl iodides **1a–11a** in 65–86% yields (Table 1). The following optimum molar ratio of reagents was found: substrate/ *p*-TsOH/$NaNO_2$/KI = 1:4.25:3.3:3.25. Under these conditions, the reactions proceed with complete conversion of the starting amines and without side products. Even low-basic 2-amino-5-nitropyridine 1-oxide (**5**) undergoes diazotization-iodination in the presence of *p*-TsOH. However, due to its low solubility in water, the reaction was carried out in acetonitrile in this case.

Table 1 Diazotization-Iodination of *N*-Oxides of Aminopyridines **1–8** and Aminoquinolines **9–11**[a]



1–11 **1a–11a**

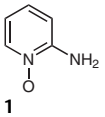
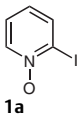
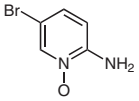
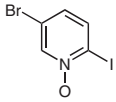
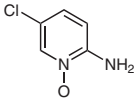
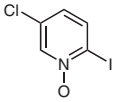
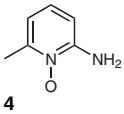
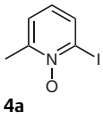
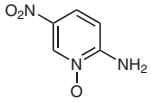
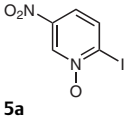
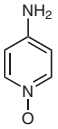
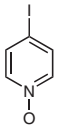
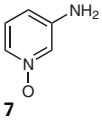
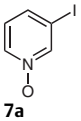
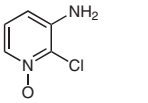
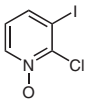
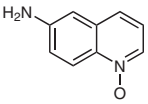
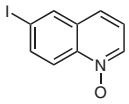
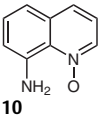
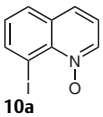
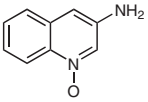
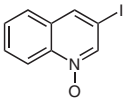
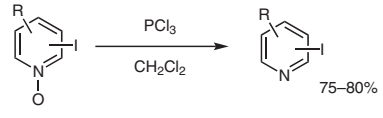
Starting substrate	Product	Yield (%)[b]	Time (h)	Mp (°C) (Lit. mp)
 **1**	 **1a**	78	3	119–121 (120–121.5)[15]
 **2**	 **2a**	72	3	167–170
 **3**	 **3a**	74	3	192–194
 **4**	 **4a**	86	3	142–144 (142–143)[16]
 **5**	 **5a**	80[c]	8	182–184
 **6**	 **6a**	68	5	170–171 (170–171)[14]
 **7**	 **7a**	75	3	130–132 (130–131)[17]

Table (continued)

Starting substrate	Product	Yield (%)[b]	Time (h)	Mp (°C) (Lit. mp)
 **8**	 **8a**	70	3	162–164 (162–164)[17]
 **9**	 **9a**	74	6	168–170 (168–170)[18]
 **10**	 **10a**	65	6	158–160 (158–160)[19]
 **11**	 **11a**	70	6	137–139 (137–140)[2]

[a] Reaction carried out under the action of system $NaNO_2$/KI/*p*-TsOH in H_2O.
[b] Isolated yields.
[c] In MeCN solution.

As shown in Table 1, the developed method has a general character, since it can be used for obtaining *N*-oxides of pyridines with iodine at positions 2, 3, and 4, and is also applicable to *N*-oxides of aminopyridines with both electron-donating and electron-withdrawing substituents in the pyridine moiety. Taking into account that the *N*-oxide group in N-oxidized pyridines can be readily removed,[5] it can be assumed that the proposed procedure is the first general method for obtaining 2-, 3-, and 4-iodopyridines via diazotization-iodination. To further confirm this possibility we have shown on three examples that *N*-oxide groups of iodides **2a**, **3a**, and **7a** can be reduced by a known method under the action of PCl_3[5c] without an appreciable reduction of C–I bonds (Scheme 1).



2a,3a,7a **2b,3b,7b**

Scheme 1 Reduction of some iodopyridine *N*-oxides

In conclusion, for the first time we have shown that the diazotization of a series of *N*-oxides of aminopyridines and aminoquinolines under the action of sodium nitrite in the presence of KI and *p*-TsOH in water at room temperature is an efficient and general method for the synthesis of iodinated *N*-oxides with a pyridine moiety.

All starting aminoheterocycles were ACS grade and used without further purification (Sigma-Aldrich). *N*-Oxides of aminoheterocycles **1**–**11** were obtained by the literature procedure.[20] Control over the reaction and determination of the the purity of the resulting products were carried out by TLC on Sorbfil-AF 254 plates, eluent benzene/EtOH (8:2). Detection of the spots was done by UV light at 254 nm. GC/MS measurements were obtained with an Agilent 7890/5975C instrument, ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-400 (400 MHz) instrument, internal standard TMS. Melting points were obtained with a melting point system MP50 Mettler Toledo. Flash chromatography was carried out on silica gel (Sigma Aldrich, 40–60 microns for flash chromatography).

Iodopyridine 1-Oxides 1a–8a and Iodoquinoline 1-Oxides 9a–11a; General Procedure

To a solution of *p*-TsOH·H_2O (1.47 g, 7.7 mmol) in H_2O (15 mL) was added the respective *N*-oxide of heteroaromatic amine **1**–**11** (2 mmol). The resulting suspension of amine salt was cooled to 10–15 °C and to this was added, gradually, a solution of $NaNO_2$ (0.55 g, 6.5 mmol) and KI (1.04 g, 6.5 mmol) in H_2O (2 mL). The reaction mixture was stirred for 10 min at 10–15 °C, then allowed to come to 20 °C, and stirred until the total time indicated in Table 1 had elapsed. To the reaction mixture was then added 20% aq K_2CO_3 (8–10 mL, until pH 9–10) and 30% aq $Na_2S_2O_3$ (8 mL). The precipitated heteroaromatic iodide *N*-oxide was extracted with EtOAc (4 × 30 mL) and the solvent was evaporated. Purification of compounds **1a**–**11a** was carried out by flash chromatography over silica gel with CH_2Cl_2 or recrystallization from a mixture of hexane/EtOAc (3:1).

2-Iodopyridine *N*-Oxide (1a)

Yield: 0.345 g (78%); white solid; mp 120–121 °C (Lit.[15] mp 120–121.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86–6.90 (m, 1 H), 7.20–7.22 (m, 1 H), 7.83 (d, *J* = 8 Hz, 1 H), 8.35 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.1, 125.4, 125.8, 137.4, 139.

5-Bromo-2-iodopyridine *N*-Oxide (2a)

Yield: 0.432 g (56%); white solid; mp 168–170 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (dd, *J* = 8, 4 Hz, 1 H), 7.75 (d, *J* = 8 Hz, 1 H), 8.53 (d, *J* = 4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.3, 120.3, 128.5, 136.9, 140.2.

MS (EI): *m*/*z* (%) = 299 (100, $[M]^+$), 283 (49), 157 (84), 96 (11), 76 (54), 50 (29).

5-Chloro-2-iodopyridine *N*-Oxide (3a)

Yield: 0.377 g (75%); white solid; mp 192–194 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.96 (dd, *J* = 8, 4 Hz, 1 H), 7.79 (d, *J* = 8 Hz, 1 H), 8.42 (d, *J* = 4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.5, 125.8, 133.4, 136.6, 138.3.

MS (EI): *m*/*z* (%) = 255 (16, $[M]^+$), 239 (57), 112 (100), 76 (53), 50 (19).

2-Iodo-6-methylpyridine *N*-Oxide (4a)

Yield: 0.404 g (80%); white solid; mp 142–144 °C (Lit.[18] mp 142–143 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.59 (s, 3 H), 6.84–6.88 (m, 1 H), 7.25 (d, *J* = 8 Hz, 1 H), 7.79 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 111.4, 125.3, 126.1, 135.1, 149.6.

2-Iodo-5-nitropyridine *N*-Oxide (5a)

Yield: 0.427 g (80%); yellow solid; mp 182–184 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 8 Hz, 1 H), 7.49 (d, *J* = 8 Hz, 1 H), 8,68 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.5, 126, 128.6, 138.3, 145.9.

MS (EI): *m*/*z* (%) = 264.9 (100, $[M]^+$), 250 (7), 207 (8), 92 (57), 80 (6), 65 (37), 49 (17).

4-Iodopyridine *N*-Oxide (6a)

Yield: 0.300 g (65%); white solid; mp 170–171 °C (Lit.[16] mp 170–171 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.84 (d, *J* = 4 Hz, 2 H), 8.3 (d, *J* = 4 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 106.95, 133.4, 150.7.

3-Iodopyridine *N*-Oxide (7a)

Yield: 0.331 (70%); brown solid; mp 131–132 °C (Lit.[17] mp 130–131 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.12 (m, 1 H), 8.00 (d, *J* = 8 Hz, 1 H), 8.54 (d, *J* = 4 Hz, 1 H), 8.84 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 93.6, 125.3, 144.3, 148.2, 155.9.

2-Chloro-3-iodopyridine *N*-Oxide (8a)

Yield: 0.357 (68%); brown solid; mp 162–164 °C (Lit.[17] mp 163–164 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.97 (dd, *J* = 8 Hz, 1 H), 8.16 (d, *J* = 8 Hz, 1 H), 8.38 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 94.96, 123.2, 148.8, 148.9, 154.5.

6-Iodoquinoline *N*-Oxide (9a)

Yield: 0.379 (68%); white solid; mp 168–170 °C (Lit.[19] mp 168–170 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (d, *J* = 4 Hz, 1 H), 7.33 (d, *J* = 4 Hz, 2 H), 7.69 (dd, *J* = 4, 4 Hz, 1 H), 7.8 (s, 1 H), 8.07 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 94.67, 122.8, 130.9, 131.1, 134.5, 136.3, 136.8, 143, 149.7.

8-Iodoquinoline *N*-Oxide (10a)

Yield: 0.352 g (65%); brown solid; mp 158–160 °C (Lit.[19] mp 158–160 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.04–7.01 (m, 1 H), 7.2–7.23 (m, 1 H), 7.75 (d, *J* = 8 Hz, 1 H), 7.81 (d, *J* = 8 Hz, 1 H), 7.86 (m, 1 H), 8.63 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 93.8, 119.6, 127.6, 128.2, 128.7, 137.4, 140.9, 142.1, 148.6.

3-Iodoquinoline *N*-Oxide (11a)

Yield: 0.370 g (75%); white solid; mp 137–139 °C (Lit.[2] mp 137–140 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.60–7.64 (m, 1 H), 7.76–7.80 (m, 1 H), 7.85 (d, *J* = 8 Hz, 1 H), 7.99 (d, *J* = 8 Hz, 1 H), 8.84 (s, 1 H), 9.02 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 91.4, 127.7, 127.9, 129.3, 130, 130.6, 144, 146.2, 155.8.

Iodopyridines 2b, 3b, and 7b; General Procedure

A solution of iodopyridine 1-oxide **2a**, **3a**, or **7a** (2 mmol) in CH_2Cl_2 (20 mL) was added dropwise to PCl_3 (0.5 mL) at 0 °C. The resulting solution was refluxed for 1 h, poured onto ice (10 g), and basified with aq 10 N NaOH (100 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic extracts were dried (Na_2SO_4), filtered, and concentrated.

5-Bromo-2-iodopyridine (2b)

Yield: 0.43 g (75%); white solid; mp 112–113 °C (Lit.[21] mp 112.5–113.5 °C).

MS (EI): *m*/*z* (%) = 282 (100, $[M]^+$), 156 (98), 127 (26), 76 (61), 50 (32).

5-Chloro-2-iodopyridine (3b)

Yield: 0.37 g (78%); yellow solid; mp 85–86 °C (Lit.[22] mp 85–87 °C).

MS (EI): *m*/*z* (%) = 238 (70, $[M]^+$), 127 (20), 112 (100), 76 (53), 50 (19).

3-Iodopyridine (7b)

Yield: 0.35 g (80%); red solid; mp 52–53 °C (Lit.[23] mp 52–53 °C).

MS (EI): *m*/*z* (%) = 205 (100, $[M]^+$), 127 (15), 78 (48), 50 (27).

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591738.

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