Regioselective copper-catalysed amination of halobenzoic acids using aromatic amines

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Copper dipyridine dichloride ($CuPy_2Cl_2$) has been found to be an efficient catalyst for the synthesis of *N*-arylanthranilic acids from ortho halobenzoic acids and aromatic amines under microwave irradiation. Some of the advantages of this method are high chemoselectivity, ease of operation, less reaction times and high yields. (61–98%).

Keywords: copper dipyridine dichloride, 2-halobenzoic acids, aromatic amines, ethylene glycol, microwave irradiation

Microwave-assisted organic synthesis (MAOS) continues to affect synthetic chemistry significantly by enabling rapid, reproducible, and scalable chemistry development.[1] Numerous reactions have been explored under microwave conditions, some of which have been applied to medicinal chemistry and the total synthesis of natural products.[2] Microwave irradiation is a convenient procedure for conducting reactions in minutes that otherwise would require hours under traditional heating.[3] The exploration of microwave chemistry has been of particular interest to us. Here, we report a regioselective copper-catalysed amination of halobenzoic acids using aromatic amines under microwave irradiation. The method eliminates the need for acid protection and produces N-arylanthranilic acid derivatives in up to 98% yield. N-Arylanthranilic acids have received considerable attention in recent years.[4,5] The first direct synthesis of N-arylanthranilic acids from 2-chlorobenzoic acid was accomplished by Ullmann.[6] Since then, various copper-catalysed amination procedures suitable to ortho-chlorobenzoic acids have been used by others.[7] The palladium-catalysed amination of aryl halides exhibiting free carboxylic acid groups in the *meta* or *para* position has also been explored.[8] N-Arylanthranilic acids are usually prepared from 2-chlorobenzoic acids or via coupling of anthranilic acid and arylhalides.[9] A wide range of 2-bromobenzoic acid derivatives are readily available, by the oxidation of 2-alkyl-1-bromobenzenes[10] or lithiation of dibromobenzenes and subsequent treatment with carbon dioxide.[11] The drawbacks of cross-coupling procedures using bromobenzoic acids are due to their limited tolerance of functional groups to very high reaction temperatures and low yields were reported with sterically hindered arylamines.[12] Recently, Cu/Cu_2O, $CuPy_2Cl_2$ catalysed amination procedures suitable for ortho-halobenzoic acids have been described under high temperature,[13] and long reaction times. Microwave irradiation gives good yields and shorter reaction times.

Results and discussion

We report a highly regioselective synthetic procedure providing convenient access to a range of N-aryl anthranilic acids containing various functional groups through the Cu-catalysed amination of 2-halobenzoic acids. Initially, we employed $CuPy_2Cl_2$ as the catalyst in the reaction of 2-bromobenzoic acid, and 1-aminopyrene, using *n*-butanol, 2-ethoxyethanol and ethylene glycol as solvent. Further screening of bases (Na_2CO_3, K_3PO_4, K_2CO_3) showed that the best results for the synthesis of N-(1-pyrenyl) anthranilic acid, were obtained in the presence of potassium carbonate and catalytic amounts of dipyridine copper chloride in ethylene glycol under microwave irradiation at 300 W for 20 min. Ethylene glycol acts as a ligand in stabilising or solubilising the copper complex. A control experiment revealed that no reaction was observed in the absence of ethylene glycol. The yields were significantly less when 2-methoxyethanol, diethyleneglycol, ethoxyethanol and glycerol were employed. The optimised amination procedure was then applied to a variety of arylamines and halobenzoic acids to evaluate the synthetic potential of this method (Table 1). Reaction of halobenzoic acid with aromatic amines gave the corresponding N-arylanthranilic acids in 61–98% yields. Importantly, the copper-catalysed amination proceeds with remarkable chemo- and regioselectivity because only the bromide adjacent to the carboxylic acid moiety is replaced. The most striking advantage of this method is that this reaction can be conducted at ordinary pressure in the presence of air. No inert atmosphere is needed for conducting the experiment which is easy to operate and shorter. We also observed that the yields are higher with ortho-iodobenzoic acids. Amination of dibromobenzoic acid with aniline yielded N-phenyl-5-bromo-anthranilic acid. Aryl halide bonds located in the aniline ring are also not affected. N-(3-Chlorophenyl)- and N-(3-bromophenyl) anthranilic acids were obtained through cross-coupling of halobenzoic acids with 3-chloro and 3-bromo-anilines. Comparison of the results obtained with 4-substituted anilines reveals that incorporation of electron-donating groups facilitates the amination reaction. In particular, the formation of N-(4-nitrophenyl)anthranilic acid, proved to be slow and substantial amounts of starting materials were recovered after 24 h.

In conclusion, we have shown that amination of halobenzoic acids using aromatic amines proceeds microwave irradiation with copper dipyridine dichloride ($CuPy_2Cl_2$) as a catalyst. The best results were obtained by heating the reaction mixture to 300 W and holding this power for 20 min. It is also possible to perform the reaction at a lower power of 200 W but to the slight detriment of yield. The experimental procedure is very simple and the yields are relatively high.

Experimental

General

All materials were obtained from commercial suppliers and used without further purification. Standard distilled water was used throughout the study. Melting points were measured on Electrothermal 9100. NMR spectra were recorded at 293 K on a 300 MHz spectrometer (^{1}H NMR) and 75 MHz (^{13}C NMR). All reactions were carried out in air. All products are known and were characterised by comparison of NMR data with that in the literature.[13]

General procedure for amination of halobenzoic acids using copper dipyridine dichloride ($CuPy_2Cl_2$) as a catalyst under microwave irradiation.

A mixture of 1-aminopyrene (2.0 g, 9.3 mmol), 2-bromobenzoic acid (1.75 g, 8.8 mmol), K_2CO_3 (9.3 mmol), copper dipyridine dichloride ($CuPy_2Cl_2$) (1.0 mmol), and 3 ml of 2-ethylene glycol was placed in a 10 ml glass tube. The vessel was then sealed with a septum and placed in microwave cavity. Initial microwave temperature of 75°C was used and a power of 300 W. Once this was reached, the reaction mixture was held at this temperature for 20 min. The reaction mixture was stirred continuously during the reaction. After allowing the mixture to cool to room temperature, the reaction vessel was opened and

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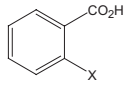
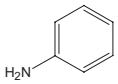
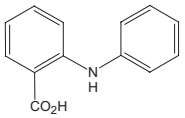
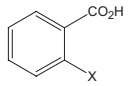
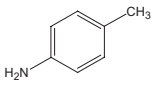
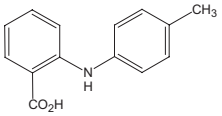
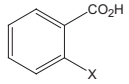
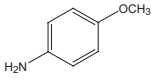
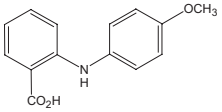
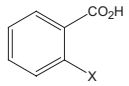
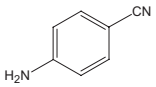
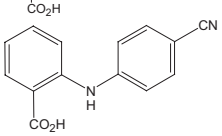
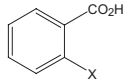
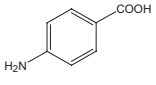
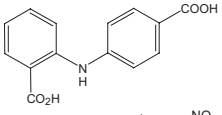
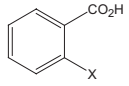
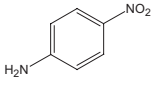
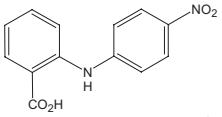
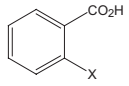
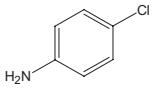
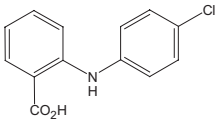
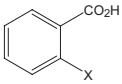
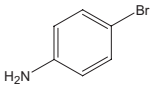
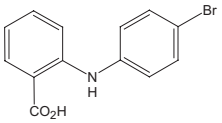
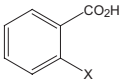
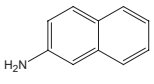
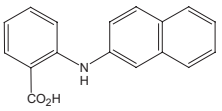
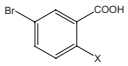
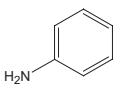
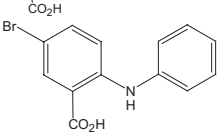
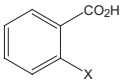
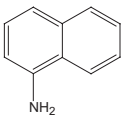
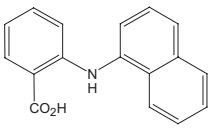
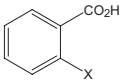
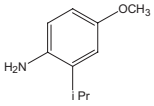
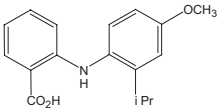
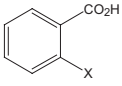
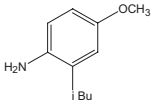
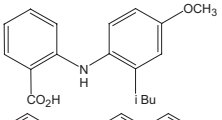
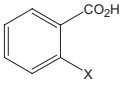
Table 1 $CuPy_2Cl_2$ catalysed amination of 2-halo bezoic acids using aromatic amines under microwave irradiation

Entry	Halobezoic acid	Amine	Product	Yield/%		
				a	b	c
1				70	71	88
2				80	91	86
3				89	90	94
4				64	75	89
5				61	72	88
6				62	82	81
7				80	94	96
8				83	91	93
9				88	91	94
10				79	91	96
11				72	87	98
12				67	79	90
13				84	90	94
14				89	93	96

(a) X =Cl, (b) X = Br, (c) X = I

the contents were poured into 30 ml of water to which decolourised charcoal was added. The mixture was filtrated through Celite. The crude product was obtained by precipitation upon acidification of the filtrate with diluted HCl. The residue was dissolved in 100 ml of 5% aqueous Na_2CO_3. The solution was filtered through Celite, and *N*-(1-pyrenyl)anthranilic acid **14** (2.75 g, 8.2 mmol) was obtained in 93% yield as an off-white solid by precipitation as described above.

Product characterisation data[13]

N-Phenylanthranilic acid (**1**): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.75 (dd, *J* = 7.9 Hz, 8.3 Hz, 1H), 7.13 (dd, *J* = 7.3 Hz, 8.6 Hz, 1H), 7.20–7.50 (m, 5H), 8.05 (d, *J* = 7.6 Hz, 1H), 9.33 (bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 111.0, 114.7, 117.8, 123.8, 124.7, 130.0, 133.2, 135.8, 140.9, 149.5, 174.3. M.p. 182°C

N-(4-Methyl phenyl)anthranilic acid (**2**): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.22 (s, 3H), 6.75 (dd, *J* = 7.9 Hz, 8.3 Hz, 1H), 7.13 (dd, *J* = 7.3 Hz, 8.6 Hz, 1H), 7.20–7.50 (m, 5H), 8.05 (d, *J* = 7.6 Hz, 1H), 9.33 (bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 19.5, 111.4, 112.8, 114.8, 116.3, 125.1, 131.9, 133.0, 134.2, 148.9, 156.1, 170.2. M.p. 191°C

N-(4-Methoxyphenyl)anthranilic acid (**3**): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.83 (s, 3H), 6.68 (dd, *J* = 7.3 Hz, 7.3 Hz, 1H), 6.93 (dd, *J* = 8.6 Hz, 8.6 Hz 3H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.26–7.32 (m, 1H), 8.0 (d, *J* = 8.6 Hz, 1H)), 9.60 (bs, 1H). ^{13}C NMR (75 MHz, DMSO-d6) δ = 55.2, 111.4, 112.8, 114.8, 116.3, 125.1, 131.9, 133.0., 134.2, 148.9, 156.1, 170.2. M.p. 207°C

N-(4-Cyanophenyl)anthranilic acid (**4**): ^{1}H NMR (300 MHz, DMSO-d6) δ = 7.13 (ddd, *J* = 2.0 Hz, 7.1 Hz, 7.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.61–7.68 (m, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 7.3 Hz, 1H), ^{13}C NMR (75 MHz, CD_3OD) δ = 104.4, 117.9, 119.5, 120.7, 121.5, 133.7, 135.1, 145.8, 147.9, 171.9. M.p. 201°C

N-(4-Carboxyphenyl)anthranilic acid (**5**): ^{1}H NMR (300 MHz, CD_3OD) δ = 7.00–7.06 (m, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.56–7.59 (m, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.3 Hz, 1H), 9.91 (bs, 1H). ^{13}C NMR (75 MHz, CD_3OD) δ = 115.3, 116.2, 117.9, 119.6, 123.5, 131.2, 132.0, 134.1, 144.6, 145.6, 167.1, 169.7. M.p. 229°C

N-(4-Nitrophenyl)anthranilic acid (**6**): ^{1}H NMR (300 MHz, CD_3OD) δ = 7.22 (dd, *J* = 7.1 Hz, 7.8 Hz, 1H), 7.50 (m, 2H), 7.68–7.78 (m, 2H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.36–8.36 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD) δ = 118.1, 118.2, 118.8, 122.2, 127.1, 133.7, 135.3, 142.6, 145.4, 150.0, 171.5. M.p. 220°C

N-(4-Chlorophenyl)anthranilic acid (**7**): ^{1}H NMR (300 MHz, CD_3OD) δ = 6.81 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.97–7.01 (m, 2H), 7.08 (dd, *J* = 1.2 Hz, 8.8 Hz, 1H), 7.21–7.27 (m, 2H), 7.43 (ddd, *J* = 1.7 Hz, 7.7 Hz, 7.9 Hz, 1H), 8.11 (dd, *J* = 1.7 Hz, 8.1 Hz, 1H). ^{13}C NMR (75 MHz, CD_3OD) δ = 112.5, 114.4, 117.2, 117.3, 127.4, 133.4, 134.0, 135.4, 151.7, 156.0, 172.4. M.p. 198°C

N-(4-Bromophenyl)anthranilic acid (**8**): ^{1}H NMR (300 MHz, CD_3OD) δ = 6.81 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.99–7.04 (m, 2H), 7.12 (dd, *J* = 1.2 Hz, 8.8 Hz, 1H), 7.29–7.32 (m, 2H), 7.48 (ddd, *J* = 1.7 Hz, 7.7 Hz, 7.9 Hz, 1H), 8.11 (dd, *J* = 1.7 Hz, 8.1 Hz, 1H). ^{13}C NMR (75 MHz, CD_3OD) δ = 112.5, 114.4, 117.2, 117.3, 127.4, 133.4, 134.0, 135.4, 151.7, 156.0, 172.4. M.p. 211°C

N-(2-Naphthyl)anthranilic acid (**9**): ^{1}H NMR (300 MHz, DMSO-d6) δ = 6.85 (ddd, *J* = 2.0 Hz, 7.0 Hz, 9.0 Hz, 1H), 7.35–7.49 (m, 5H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.79–7.90 (m, 3H), 7.98 (dd, *J* = 1.7 Hz, 7.9 Hz, 1H), 9.90 (bs, 1H). ^{13}C NMR (75 MHz, DMSO-d6) δ = 113.1, 114.2, 115.9, 117.8, 122.2, 124.3, 126.4, 126.8, 127.5, 129.2, 129.7, 131.9, 134.0, 134.2, 138.3, 146.7, 170.0. M.p. 231°C

N-Phenyl-5-bromoanthranilic acid (**10**): ^{1}H NMR (300 MHz, CD_3OD) δ = 7.29–7.33 (m, 2H), 7.38–7.42 (m, 2H), 7.48–7.60 (m, 3H), 8.23 (d, *J* = 2.4 Hz, 1H), ^{13}C NMR (75 MHz, DMSO-d6) δ = 108.3, 116.7, 122.1, 122.6, 124.4, 130.2, 134.3, 137.2, 140.7, 147.0, 169.4. M.p. 241°C

N-(1-Naphthyl)anthranilic acid (**11**): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.73 (dd, *J* = 7.3 Hz, 7.6 Hz, 1H), 6.85(d, *J* = 8.6 Hz, 1H), 7.23–7.29 (m, 1H), 7.46–7.51 (m, 4H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.89–7.92 (m, 1H), 8.08(m, 2H), 9.60 (bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 110.5, 114.2, 117.5, 122.8, 123.5, 126.5, 126.5, 127.1, 129.1, 130.8, 133.1, 135.5, 136.0, 136.9, 151.2, 174.2. M.p. 233°C

N-(2-Isopropylphenyl)anthranilic acid (**12**): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.22 (d, *J* = 6.9 Hz, 6H), 3.21 (sept, *J* = 6.9 Hz, 1H), 4.68 (bs, 1H), 6.68 (dd, *J* = 7.2 Hz, 7.4 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 7.22–7.40 (m, 4H), 8.1 (dd, *J* = 1.7 Hz, 8.2 Hz, 1H), 9.18 (bs, 1H). ^{13}C NMR (75 MHz, DMSO-d6) δ = 23.6, 28.4, 112.0, 113.6, 117.0, 125.7, 126.1, 127.1, 127.3, 132.5. 135.0, 137.9, 143.6, 149.8, 171.0. M.p. 241°C

N-(2-tert-Butylphenyl)anthranilic acid (**13**): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.41 (s, 9H), 6.65 (dd, *J* = 7.0 Hz, 7.9 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 1H), 7.17–7.28 (m, 4H), 7.47–7.50 (m, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 9.21 (bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 31.3, 35.7, 110.0, 114.8, 116.7, 126.6, 127.6, 128.1, 129.8, 133.1, 135.9, 139.4, 147.1, 151.4, 173.7. M.p. 248°C

N-(1-Pyrenyl)anthranilic acid (**14**): ^{1}H NMR (300 MHz, DMSO-d6) δ = 6.94 (dd, *J* = 7.4 Hz, 7.4 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.43 (dd, *J* = 8.0 Hz, 7.4 Hz, 1H), 8.09–8.41 (m, 10H), 10.7 (bs, 1H). ^{13}C NMR (75 MHz, DMSO-d6): δ = 114.2, 118.1, 122.0, 122.1, 124.8, 124.9, 125.4, 125.7, 125.8, 126.4, 126.7, 127.2, 128.0, 128.2, 131.4, 131.7, 133.6, 134.6, 135.2, 148.8, 172.7. EIMS *m/z* 337 (M +). Anal. calcd. for C23H15NO2: C, 81.88; H, 4.48; N, 4.15. Found: C, 81.63; H, 4.74; N, 4.32. M.p. 268°C

Received 19 August 2007; accepted 16 October 2007
Paper 07/4798 doi: 10.3184/030823407X255597

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