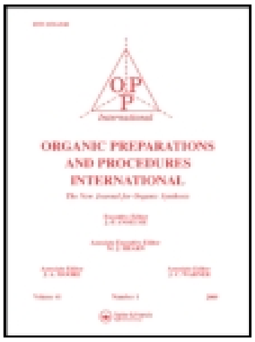

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Iodination of Anilines with Sodium Dichloroiodate

Shire Elmi,[1] Per Heggen,[1] Bjarte Holmelid,[1]
Didrik Malthe-Sørensen,[2] and Leiv K. Sydnes[1]

[1]Department of Chemistry, University of Bergen, Allégt. 41, NO-5007 Bergen, Norway
[2]GE Healthcare, Lindesnes Site, NO-4510 Spangereid, Norway

Iodinated aromatic compounds have been synthetic targets for decades,[1–6] and a number of methods have been developed for iodination of arenes.[2–25] The simplest and mildest are those relying on the electrophilicity of iodine in dichloroiodate salts.[15–25] At least one such reagent, sodium dichloroiodate, is utilized on an industrial scale to obtain triply iodinated benzenes,[26,27] which constitute the key structural motif in several X-ray contrast agents.[1–6] Since this process has to be very carefully controlled to minimize the formation of by-products (in particular azoarenes[26,27]), this inspired us to study the iodination of some anilines with sodium dichloroiodate in greater detail.

In order to evaluate the sensitivity of the industrial process to pH, exploratory experiments were performed using 2,4-dimethylaniline (**1a**). Under acidic conditions (pH 1–2) iodination of **1a** with sodium dichloroiodate proceeded smoothly to give a clean product mixture from which pure 2-iodo-4,6-dimethylaniline[28] (**2a**) was isolated in 88% yield. However, under basic conditions **2a** was not formed at all and a complex product mixture was obtained from which the only reasonably pure product isolated in low yield (4%) was 2,2′,4,4′-tetramethylazobenzene (**3a**).[29]

The iodination of benzene derivatives is influenced by the nature of the substituents.[6–25] It was therefore of interest to investigate the reaction of some activated and deactivated aniline derivatives under the conditions applied to **1a** (room temperature; acidic and basic conditions; variable amounts of sodium dichloroiodate).

Dimethylanilines **1b**–**1d** (*Scheme 1* and *Table 1*) gave relatively simple reaction mixtures under acidic conditions; in order for all the starting materials to be consumed, an excess of sodium dichloroiodate had to be utilized. Under these conditions 2,3-dimethylaniline (**1b**) gave a 44% yield of **2b** but also afforded 4,6-diiodo-2,3-dimethylaniline (19%) with the use of a 60% molar excess of the reagent. Under the same conditions but with a 3.8 molar excess of the reagent, 3,5-dimethylaniline (**1c**) gave a complex mixture; use of a much larger excess of sodium dichloroiodate (4.8 molar) led to 2,4,6-triiodo-3,5-dimethylaniline (78%) as the sole isolatable product (*Table 1*). 2,6-Dimethylaniline (**1d**) exhibited a third type of reactivity; while iodination still occurred to afford 4-iodo-2,6-dimethylaniline (**2d**) in 21% yield, the main product was 2,6-dimethyl-*p*-benzoquinone-4-(2′,6′-dimethyl)anil in 28% yield.[32] Under basic conditions (KOH in methanol/H_2O),

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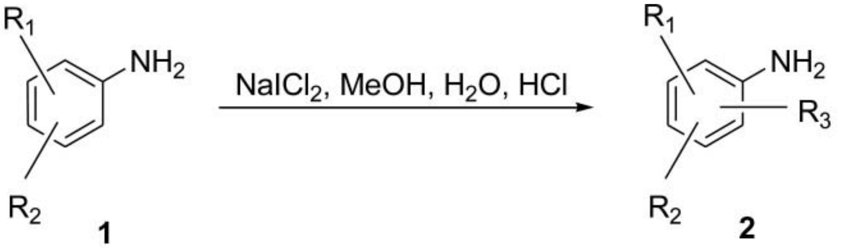
Address correspondence to Leiv K. Sydnes, Department of Chemistry, University of Bergen, Allégt. 41, NO-5007 Bergen, Norway. E-mail: leiv.sydnes@uib.no

1a–**1d** behaved similarly to the anisidines (*vide infra*); only the corresponding azo compounds were generated in low yields. The reactivity of 2,6-dimethylaniline (**1d)** is also different from that of **1a**–**1c**: nearly no azo compound was formed and only the anil was isolated in 34% yield.



a) R_1 = 2-Me, R_2 = 4-Me
b) R_1 = 2-Me, R_2 = 3-Me
c) R_1 = 3-Me, R_2 = 5-Me
d) R_1 = 2-Me, R_2 = 6-Me

a) R_1 = 4-Me, R_2 = 6-Me, R_3 = 2-I
b) R_1 = 2-Me, R_2 = 3-Me, R_3 = 4-I
c) ------------ ------------------------
d) R_1 = 2-Me, R_2 = 6-Me, R_3 = 4-I

Scheme 1. Iodination of Dimethylanilines with $NaICl_2$.

Table 1
Iodination of Anilines (1) Using Sodium Dichloroiodate under Acidic Conditions[a]

Aniline	Ratio of Reagent to Aniline	Product (% Yield[b])	Other products[c] (% Yield[b])
2,4-Dimethyl (**1a**)	1.1	**2a** (88)	—
2,3-Dimethyl (**1b**)	1.6	**2b** (44)	4,6-Diiodo-**1b** (19)
3,5-Dimethyl (**1c**)	4.8	—	2,4,6-Triiodo-**1c** (78)
2,6-Dimethyl (**1d**)	3.8	**2d** (21)	Anil[d] (28)
2-Chloro (**1e**)	2.5	**2e** (61)	4,6-Diiodo-**1e** (27)
3-Chloro (**1f**)	3.6	—	2,4-Diiodo-**1f** (12) 4,6-Diiodo-**1f** (61) 2,4,6-Triiodo-**1f** (18)
4-Chloro (**1g**)	2.5	**2g** (75)	2,6-Diiodo-**1g** (24)
2-COOMe (**1h**)	2.5	**2h** (57)	4,6-Diiodo-**1h** (41)
3-COOMe (**1i**)	2.5	—	2,4-Diiodo-**1i** (38) 4,6-Diiodo-**1i** (47)
4-COOMe (**1j**)	2.5	**2j** (75)	2,6-Diiodo-**1j** (23)

[a] Treatment for 3 hrs in methanol/H_2O/HCl at room temperature.

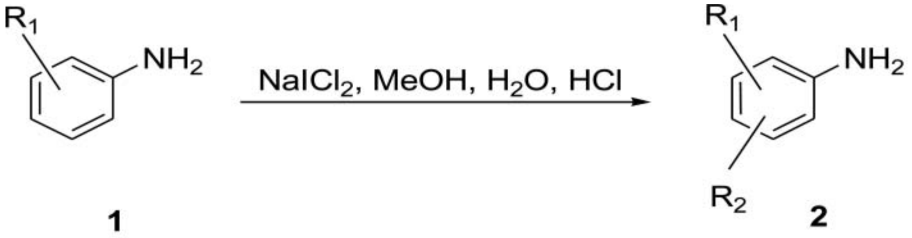
[b] Isolated yield.

[c] With the exception of the anil formed from **1d**, all compounds are regarded as aniline derivatives when abbreviated in this table,and the positions of the iodo substituents are given the numbers that follow from the numbering of **1**. For instance, 6-chloro-2,4-diiodoaniline is called 4,6-diiodo-**1e** because positions 4 and 6 in **1e** have been iodinated.

[d] 2,6-Dimethyl-*p*-benzoquinone-4-(2′,6′-dimethyl)anil.

All three anisidines gave black, tarry mixtures (possibly aniline oligomers, polymers as judged from the spectroscopic data.[30,31]) under acidic conditions. The use of basic conditions also led to poor results, the corresponding azobenzenes being the only compounds isolated from *m*- and *p*-anisidines (1% and 5%).

Both *o*- and *p*-chloroanilines (**1e** and **1g**) and the methyl esters of *o*- and *p*-aminobenzoic acids (**1h** and **1j**) underwent iodination with $NaICl_2$ under acidic conditions to give reasonable yields (57–75%) of the monoiodo compounds (*Scheme 2*). However, since a 2.5–3.6 molar excess of dichloroiodate had to be used to achieve complete conversion, significant amounts (>20%) of polyiodinated anilines were generated as well (*Table 1*). Under these conditions, the *meta* isomers (**1f** and **1i**) gave no monoiodinated products. Under basic conditions, very poor results were obtained: the chloroanilines gave small amounts (<10%) of the corresponding azobenzenes[29] and the aminobenzoates did not react at all.



e) R_1 = 2-Cl	**e**) R_1 = 2-Cl, R_2 = 4-I
f) R_1 = 3-Cl	**f**) ----------- ---------
g) R_1 = 4-Cl	**g**) R_1 = 4-Cl, R_2 = 2-I
h) R_1 = 2-CO_2Me	**h**) R_1 = 2-CO_2Me, R_2 = 4-I
i) R_1 = 3-CO_2Me	**i**) ----------------- ---------
j) R_1 = 4--CO_2Me	**j**) R_1 = 4-CO_2Me, R_2 = 2-I

Scheme 2. Iodination of Chloroanilines and Methyl Aminobenzoate.

In conclusion, the article describes a simple method for the iodination of some aniline derivatives using sodium dichloroiodate. Although the reaction gives some mono-iodinated anilines in 75–88% yields under acidic conditions, the results are quite sensitive to the nature of the substituents and their position relative to the amino group. Under basic conditions iodination does not occur.

Experimental Section

All melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer or Spectrum One FT-IR ATR (Attenuated Total Reflection) spectrophotometer. The IR spectra were obtained as liquid films by the attenuated total reflection technique (ATR) or as KBr discs. The molecular absorptions frequencies are given in wave numbers (cm^{-1}) and indicated as strong (s), medium (m), weak (w) or broad (b). NMR spectra were acquired on a Bruker Spectrospin AC 200F or a Bruker Spectrospin DMX 400 with the field strengths of 200 MHz and 400 MHz, respectively. Chemical shifts are reported in δ (ppm) using either TMS (for ^{1}H) or $CDCl_3$ (for ^{13}C) as the internal standard for shift calibration (7.28 ppm for ^{1}H and 77.8 ppm for ^{13}C). All coupling constants (J) are given in Hertz (Hz), and the multiplicity are reported as (s) for singlet, (d) for doublet, and (bs) for broad singlet. Mass spectra and high resolution mass spectra were determined on a JEOL Accu-TOF T100GC which was operated in the DART mode. All new compounds were also analysed in the CHN-mode on a VarioEL III Element Analyser using helium a carrier gas. Due to the low contents of hydrogen in all the samples, the results of the analyses for this element are close to the detection limit for the instrument and within a range where it operates with poor accuracy. Consequently, the hydrogen values were calibrated against the response of several blank combustions and given as the mean of two replicates.

Iodination of Anilines under Acidic Conditions

To a solution of the aniline (**1**, 20.0 mmol) in a mixture of H_2O (100 mL) and MeOH (300 mL), was added conc. hydrochloric acid was added until pH was 1–2 (pH strip). Then an aqueous solution of $NaICl_2$ (50% w/w 1.1–4;.8 molar equiv; for amount, see *Table*) was added dropwise and the resulting mixture was stirred with a stirring bar at room temperature for 3–4 h. Saturated aqueous $NaHSO_3$ was added until negative starch test was obtained and the product was worked up.

When no precipitate was clearly visible in the product mixture, the mixture was made slightly basic (pH strip) by dropwise addition of an aqueous solution of NaOH (1 M) and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under vacuum to give a solid.

When a visible precipitate was obtained, the solid was isolated by gravity filtration (each case specified below) and the filtrate was then made slightly basic (pH strip) by addition of an aqueous solution of NaOH (1 M) and extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated under vacuum to afford a solid.

All the solids were analysed by TLC (silica gel; varying mixtures of hexanes/ethyl acetate). When a solid consisted of several products, the compounds were separated and purified by flash chromatography (silica gel; hexanes/ethyl acetate 9:1 when not otherwise stated).

The products obtained were characterized by mps (and comparison with *lit.* mps), IR, MS, ^{1}H- and ^{13}C-NMR spectra as well as elemental analysis for all new compounds. The anisidines gave no products that could be characterized. Anilines **1a**–**1j** gave products as summarized below; most of them are known from the literature.

2,4-Dimethylaniline (**1a**) afforded 2-iodo-4,6-dimethylaniline (**2a**), mp 65–66°C (*lit.*[28] 65°C).

2,3-Dimethylaniline (**1b**) gave 4-iodo-2,3-dimethylaniline (**2b**), mp 55–56°C (*lit.*[18] 56°C), and 4,6-diiodo-2,3-dimethylaniline (4,6-diiodo-**1b**), mp 91–92°C (*lit.*[18] 89–90°C).

3,5-Dimethylaniline (**1c**) gave 2,4,6-triiodo-3,5-dimethylaniline (2,4,6-triiodo-**1c**), mp. 188–190°C (*lit.*[15] 192°C).

2,6-Dimethylaniline (**1d**) furnished 4-iodo-2,6-dimethylaniline (**2d**), mp 49–50°C (*lit.*[28] 52–5;3 °C), and 2,6-dimethyl-*p*-benzoquinone-4-(2’,6’-dimethyl)anil, mp 74–76°C (*lit.*[32] 76–77°C).

2-Chloroaniline (**1e**) gave 2-chloro-4-iodoaniline (**2e**), mp 67–69°C (*lit.*[21] 68–70°C), and 6-chloro-2,4-diiodoaniline (4,6-diiodo-**1e**) (isolated by filtration), mp 125–126°C (*lit.*[12] 126–127°C).

3-Chloroaniline (**1f**) gave a mixture of two diiodoanilines, 3-chloro-2,4-diiodoaniline (2,4-diiodo-**1f**) and 5-chloro-2,4-diiodoaniline (4,6-diiodo-**1f**), as well as one triiodoaniline, 3-chloro-2,4,6-triiodoaniline (2,4,6-triiodo-**1f**), which were separated by flash chromatography (silica gel; hexanes/ethyl acetate 85:15). 2,4-Diiodo-**1f**, gray powder, mp 116–118°C; IR (KBr): 3405s, 3305s, 3054w, 2922w, 1601s, 1587s, 1569s, 1447m, 1373m, 1297w, 1269w, 1111m, 1080s, 940w, 878m, 839m, 808s, 715s, 697s cm$-^1$; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.56 (d, $J = 8.4$, 1 H), 6.36 (d, $J = 8.4$, 1 H), 4.38 (bs, 2 H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 149.1 (C), 149.0 (C), 139.4 (CH), 113.6 (CH), 86.9 (C), 80.4 (C); DART-MS: 381 (30), 379 (100, [M + H]+), 251 (20); HR-MS: 379.8208 ([M + H]+, $C_6H_5{}^{35}ClI_2N+$; calc. 379.8200).

Anal. Calcd for $C_6H_4{}^{35}ClI_2N$: C, 19.00; H, 1.06; N, 3.69. Found: C, 18.94; H, 1.10; N, 3.67.

4,6-Diiodo-**1f**, off-white powder, mp 117.5–119.5°C; IR (KBr): 3378w, 3303m, 3171m, 2923w, 2918w, 1612s, 1567s, 1441m, 1358m, 1288m, 1256w, 1112m, 1020m, 908w, 877s, 841m, 802s, 715s, 704m, 697s, 655m cm−1; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.00 (s, 1 H), 6.87 (s, 1 H), 4.19 (bs, 2 H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 147.8 (C), 139.4 (CH), 139.1 (C), 114.2 (CH), 82.8 (C), 81.9 (C); DART-MS: 381 (30), 379 (100, [M + H]+), 251 (8); HR-MS: 379.8213 ([M + H]+, $C_6H_5{}^{35}ClI_2N+$; calcd. 379.8200).

Anal. Calcd for $C_6H_4{}^{35}ClI_2N$: C, 19.00; H, 1.06; N, 3.69. Found: C, 18.91; H, 1.09; N, 3.67.

2,4,6-Triiodo-**1f**, gray powder, mp 141–143°C. IR (KBr): 3398m, 3308s, 2924w, 1597s, 1569m, 1512w, 1414s, 1397w, 1333w, 1293w, 1277w, 1114m, 1073m, 936w, 871m, 842m, 812s, 712m, 704m cm−1; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.08 (s, 1 H), 4.94 (bs, 2 H); ^{13}C-NMR (50 MHz, $CDCl_3$): 147.9 (C), 147.4 (CH), 142.3 (C), 84.4 (C), 80.3 (C), 78.7 (C); DART-MS: 507 (30), 505 (100, [M + H]+), 379 (5), 377 (15); HR-MS: 505.7142 ([M + H]+, $C_6H_4{}^{35}ClI_3N+$; calcd. 505.7166).

Anal. Calcd for $C_6H_3{}^{35}ClI_3N$: C, 14.26; H, 0.60; N, 2.77; found: C, 14.35; H, 0.88; N, 2.69.

4-Chloroaniline (**1g**) gave 4-chloro-2-iodoaniline (**2g**), mp 43–44°C (*lit.*[21] 42–43°C), and 4-chloro-2,6-diiodoaniline (2,6-diiodo-**1g**) (isolated by filtration), mp 127–128°C (*lit.*[20] 128–130°C).

Methyl 2-aminobenzoate (**1h**) gave methyl 2-amino-5-iodobenzoate (**2h**), mp 78–80°C (*lit.*[35] 83–85°C), and methyl 2-amino-3,5-diiodobenzoate (4,6-diiodo-**1h**) (isolated by filtration), mp 106–109°C (*lit.*[36] 110 °C).

Methyl 3-aminobenzoate (**1i**) afforded two diiodoanilines, methyl 3-amino-2,6-diiodobenzoate (2,6-diiodo-**1i**) and methyl 5-amino-2,4-diiodobenzoate (4,6-diiodo-**1i**), which were separated by flash chromatography (silica gel; hexanes/ethyl acetate 85:15). (2,6-Diiodo-**1i**): off-white powder, mp 140–144°C; IR (KBr): 3405m, 3318s, 3148w, 2948w, 1709s, 1618s, 1579m, 1489w, 1431m, 1291s, 1255s, 1188w, 1119m, 1031w, 963m, 906w, 825w, 761s, 706w, 674m cm$-^1$; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.47 (d, $J = 8.4$, 1 H), 6.48 (d, $J = 8.4$, 1 H), 4.08 (bs, 2 H), 3.88 (s, 3 H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 168.5 (C=O), 147.1 (C), 138.9 (CH), 116.2 (CH), 114.9 (C), 80.9 (C), 74.8 (C), 52.9 (OC_3); DART-MS: 403 (100, [M + H]+), 343 (30); HR-MS: 403.8657 ([M + H]+, $C_8H_8I_2NO_2+$; calcd. 403.8639).

Anal. Calcd for $C_8H_7I_2NO_2$: C, 23.85; H, 1.75; N, 3.48; found: C, 23.94; H, 1.89; N, 3.51.

(4,6-Diiodo-**1i**): off-white powder, mp 142–145°C; IR (KBr): 3407s, 3314s, 3063w, 2948w, 1718s, 1605s, 1530w, 1429m, 1392w, 1297s, 1261s, 1126m, 1052w, 971m, 906w, 760m, 706w cm$-^1$; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.19 (s, 1 H), 7.20

(s, 1 H), 4.22 (bs, 2 H), 3.90 (s, 3 H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 166.2 (C = O), 149.4 (CH), 146.8 (C), 120.2 (C), 116.1 (CH), 88.7 (C), 78.2 (C), 52.3 (OCH_3); DART-MS: 403 ([M + H]+, 100), 343 (20); HR-MS: 403.8666 ([M + H]+, $C_8H_8I_2NO_2$+; 403.8639).

Anal. Calcd for $C_8H_7I_2NO_2$: C, 23.85; H, 1.75; N, 3.48; found: C, 23.89; H, 1.94; N, 3.44.

Methyl 4-aminobenzoate (**1j**) afforded methyl 4-amino-2-iodobenzoate (**2j**), mp 84–86°C (*lit.*[19] 84–87°C), and methyl 4-amino-2,6-diiodobenzoate (2,6-diiodo-**1j**) (isolated by filtration), mp 158–160°C (*lit.*[19] 163–164°C).

Attempted Iodination of Anilines under Basic Conditions

Aniline (**1**) (20.0 mmol) and then KOH (10 g, 0.18 mol) were dissolved in a mixture of H_2O (100 mL) and MeOH (300 mL) under stirring. An aqueous solution of $NaICl_2$ (50% w/w of ICl) (1.1–3.5 molar eq) was added dropwise, and the mixture was stirred at room temperature (stir bar) for 18–24 h. Saturated aqueous $NaHSO_3$ was then added until negative starch test was obtained. The resulting mixture was extracted with Et_2O and the combined organic phases were dried ($MgSO_4$), filtered, and concentrated under vacuum, leaving a semi-solid residue behind. TLC analysis (silica gel; varying mixtures of hexanes/ethyl acetate) gave in most cases one spot. Purification was performed by flash chromatography using a silica-gel column and hexanes/ethyl acetate 97:3 as eluent.

All the anilines were reacted, and **1a**–**1g**, 3-anisidine, and 4-anisidine furnished the corresponding azobenzene (**3**). 2,6-Dimethylaniline (**1d**) gave in addition the same anil that was obtained under acidic conditions. The products were characterized by their IR, MS, ^{1}H- and ^{13}C-NMR spectra as well as melting points.

2,4-Dimethylaniline (**1a**) gave 2,2′,4,4′-tetramethylazobenzene (**3a**), mp 128–129°C (*lit.*[37] 129°C) in 4% yield.

2,3-Dimethylaniline (**1b**) gave 2,2′,3,3′-tetramethylazobenzene (**3b**), mp 109–110°C (*lit.*[37] 110 °C) in 8% yield.

3,5-Dimethylaniline (**1c**) gave 3,3′,5,5′-tetramethylazobenzene (**3c**), mp 136–137°C (*lit.*[37] 136–137 °C) in 25% yield.

2,6-Dimethylaniline (**1d**) gave 2,2′,6,6′-tetramethylazobenzene (**3d**), mp 49–50°C (*lit.*[38] 48°C) in 2% yield, and 2,6-dimethyl-*p*-benzoquinone-4-(2′,6′-dimethyl)anil, mp 75–76°C (*lit.*[32] 76–77°C) in 34% yield.

2-Chloroaniline (**1e**) gave 2,2′-dichloroazobenzene (**3e**), mp 138–139°C (*lit.*[39] 138°C), in 3% yield.

3-Chloroaniline (**1f**) gave 3,3′-dichloroazobenzene (**3f**), mp 103–104 °C (*lit.*[40] 110°C), in 8% yield.

4-Chloroaniline (**1g**) gave 4,4′-dichloroazobenzene (**3g**), mp 189–190°C (*lit.*[40] 189°C), in 10% yield.

***m*-Anisidine** afforded 3,3′-dimethoxyazobenzene, mp 75–76°C (*lit.*[41, 42] 73–75°C), in 1% yield.

***p*-Anisidine** gave 4,4′-dimethoxyazobenzene, mp 162–163°C (*lit.*[43] 160.5–161.9°C), in 5% yield

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