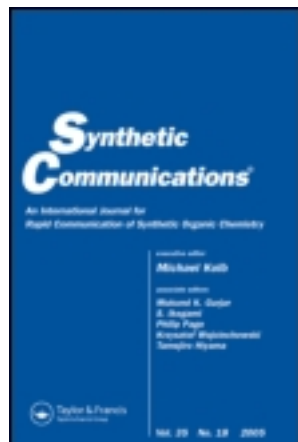


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Sodium Lauryl Sulfate-Catalyzed Oxidative Chlorination of Aromatic Compounds

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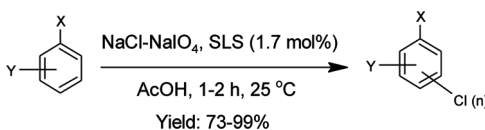
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SODIUM LAURYL SULFATE-CATALYZED OXIDATIVE CHLORINATION OF AROMATIC COMPOUNDS

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GRAPHICAL ABSTRACT



X = OH, NH₂, NHCOMe, NHCOPh, COOH, CHO

Y = H, OH, Br, Cl, NO₂

Abstract Chlorination of commercially important aromatic compounds using sodium chloride as chlorine source and sodium periodate as oxidant in acidic medium catalyzed by sodium lauryl sulfate (SLS) led to the chloro-substituted aromatics in good yields and purity. Addition of sodium lauryl sulfate led to increased chlorination rate, better yield, excellent purity, and better quality of end product. The advantages of the present method are greater yield, excellent purity, and shorter reaction time at room temperature. Also dichlorinated product can be obtained by increasing the amount of sodium chloride and sodium periodate at slightly higher temperature (40 °C).

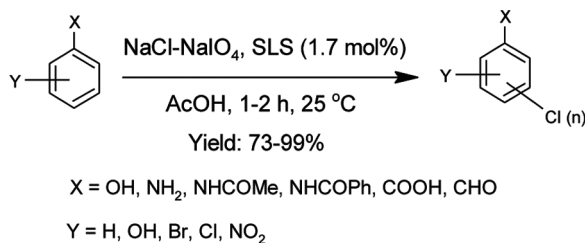
Keywords Chlorination; chloroarenes; regioselectivity; sodium lauryl sulfate; sodium periodate

INTRODUCTION

Chlorinated organic compounds play very important roles in chemistry; they are essential in organic syntheses as starting compounds and synthetic intermediates, designer molecules for material science, industrial chemicals, and bioactive compounds.^[1-4] The classical synthetic procedure involves the use of molecular chlorine, which is hazardous, difficult to store, and hard to handle.^[5] A range of new methods has been published lately, and the development of new chlorination protocols focused on environmentally acceptable techniques and materials. Although use of halogenating enzymes^[6-8] could be the most effective from an environmental point of view, large-scale halogenations using enzymes have not been commercialized.

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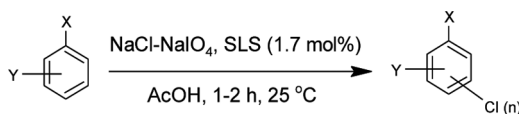
Scheme 1. SLS-catalyzed oxidative chlorination of aromatics using NaCl and NaIO₄.

Here we report the chlorination of some commercially important aromatic substrates that are widely used in pharmaceutical, agricultural, and dye industries, for production of various drugs, insecticides, herbicides, and dyestuffs.^[9,10] Chlorination reported so far has been extensively described using many reagents such as KCl/oxone,^[11] *t*-butylhypochlorite,^[12] HCl/H₂O₂,^[13] NaCl/H₂O₂/HNO₃,^[14] NCSac,^[15] HCl/*m*-CPBA/DMF,^[16] SnCl₄/Pb(OAc)₄,^[17] Cl₂/1°,2°,3° amines,^[10] and TBACl₃/CH₃COOH/CH₂Cl₂.^[18] However, these methods have some drawbacks such as use of strong,^[12] nonselective,^[16] toxic, and expensive reagents,^[17] poor yield, and long reaction times.^[13,11] Also efforts are being directed toward carrying out the chlorination of aromatic substrates using aluminosilicate catalyst especially zeolites.^[19] However, a stumbling block to this is damage caused to the zeolites, and hence industrial applications are still rare.

The present communication reports a versatile reaction for the chlorination of aromatics, giving good to excellent yields (73–99%) of chlorinated products using NaIO₄ as oxidant and NaCl as chlorine source. A perusal of the literature revealed that an earlier method reported by Dewkar et al.^[20,21] has limitations of long reaction time (6–18 h), high temperature (80 °C), and poor yield (20–83%) as well as nonselectivity. The present method overcomes all these limitations and method has advantages of good yield (73–99%), low reaction time (1–2 h), and good selectivity or purity at room temperature. When a solution of substrate (0.01 mol) in AcOH was stirred at room temperature in the presence of NaIO₄ (0.005 mol), NaCl (0.03 mol), SLS (50 mg), and H₂SO₄ (1 mL), the chlorinated product was obtained in excellent yield (Scheme 1) and purity.

RESULTS AND DISCUSSION

To optimize the best reaction conditions, 4-bromoacetanilide was used as a model substrate. Reaction was performed at room temperature using NaIO₄ (0.005 mol), NaCl (0.03 mol), and SLS (50 mg) with respect to the substrate (0.01 mol). A wide variety of aromatic substrates were subjected to chlorination to test the generality of this method, and results are summarized in Table 1. The results of Table 1 show that all substrates were chlorinated within 1–2 h, and 4-bromoacetanilide was chlorinated within 1 h at room temperature, having the maximum yield (99%, Table 1, entry 1) and excellent purity (99%, Table 6, entry 1) of 4-bromo-2-chloroacetanilide. This compound finds application as an intermediate in research and development.^[22] In the case of benzanilide (**3**), *para*-substituted product was obtained

Table 1. Oxidative chlorination of aromatics using NaCl and NaIO₄

Entry	Substrate	Time (h)	Product	Yield (%)	Mp (°C) (lit.)
1		1		99 ^a	152 (151–152 ^[28a])
2		1		98 ^a	145 (143–146 ^[18])
3		2		98 ^a	198 (199–201 ^[29])
4		1		95 ^a	107 (107–110 ^[24])
5		2		97 ^b	190 (190–194 ^[9])
6		1		90 ^a	175 (175–177 ^[25])
7		1		92 ^b	101 (101–103 ^[28b])
8		2		85 ^a	83 (85–87 ^[28b])
9		2		93 ^b	121 (120–125 ^[28b])
10		2		80 ^a	130 (128–132 ^[30])
11		2		73 ^a	138 (138–139 ^[31])

(Continued)

Table 1. Continued

Entry	Substrate	Time (h)	Product	Yield (%)	Mp (°C) (lit.)
12		2		85 ^a	172 (171–173 ^[26])
13		2		89 ^b	221 (220–222 ^[28b])

^aReaction conditions: substrate, 0.01 mol; NaCl, 0.03 mol; NaIO₄, 0.005 mol; AcOH, 10 mL; H₂SO₄, 1.0 mL; SLS, 50 mg; temp 25 °C.

^bReaction conditions: substrate, 0.01 mol; NaCl, 0.05 mol; NaIO₄, 0.01 mol; AcOH, 10 mL; H₂SO₄, 1.0 mL; SLS, 50 mg; temp 40 °C.

within 2 h in 98% yield and 96.23% purity (Table 2, entry 2), which is also an industrially important compound.^[23] 2-Chloro-4-nitroaniline was synthesized by monochlorination of 4-nitroaniline (**4**) within 1 h at room temperature (Table 1, entry 4). It is used in organic synthesis and also as a dye intermediate.^[24] Another industrially important compound, 2,6-dichloro-4-nitroaniline, was obtained by dichlorination of 4-nitroaniline (**5**) in 97% yield and 98.8% purity (Table 2, entry 3) within 2 h at 40 °C. This compound is known to be active against certain soil, foliar, and fruit pathogens on ornamental and agricultural crops. Earlier its synthesis has been reported by Smythe et al.^[9] using Cl₂ gas. 2-Bromo-6-chloro-4-nitroaniline, which

Table 2. Product selectivity in chlorination of various aromatic substrates

Entry	Substrate	Product	Yield ^a (%)	Product purity ^b (%)	
				Main product	Others
1			99 ^c	99.2	0.8
2			98 ^c	96.23	3.77
3			97 ^d	98.8	1.2

^aIsolated yield.

^bPurity determined by HPLC.

^cReaction conditions: substrate, 0.01 mol; NaCl, 0.03 mol; NaIO₄, 0.005 mol; AcOH, 10 mL; H₂SO₄, 1.0 mL; SLS, 50 mg; temp 25 °C.

^dReaction conditions: substrate, 0.01 mol; NaCl, 0.05 mol; NaIO₄, 0.01 mol; AcOH, 10 mL; H₂SO₄, 1.0 mL; SLS, 50 mg; temp 40 °C.

Table 3. Effect of amount of NaCl on the yield and melting point of 4-bromo-2-chloroacetanilide in chlorination of 4-bromoacetanilide (**1**)

Entry	Moles of NaCl	Yield (%)	Mp (°C) (lit. ^[28a] 151–152)	Appearance
1	0.01	79.3	148	Yellowish white
2	0.02	92.59	152	White crystals
3	0.03	99	152	White crystals
4	0.04	98.2	152	White crystals

Notes. Reaction conditions: substrate, 0.01 mol; NaIO₄, 0.005 mol; AcOH, 10 mL; H₂SO₄, 1.0 mL; SLS, 50 mg; temp 25 °C.

is used as dye, as well as intermediate for dye,^[25] was also synthesized within 1 h starting from 2-bromo-4-nitroaniline (**6**). 2,6-Dichloro-4-nitrophenol, which is a valuable chemical intermediate useful in agrochemistry that can be used as enzyme inhibitor, was obtained in 93% yield from 4-nitrophenol (**9**) within 2 h at 40 °C. Earlier this compound was synthesized by Desmurs et al.^[10] at high temperature (120 °C) using molecular chlorine as chlorinating agent. 5-Chlorosalicylic acid^[26] (Table 1, entry 12), which is used in pesticides, medicines, and as dye intermediates was synthesized in 85% yield within 2 h.

Because chlorination reactions are less selective than bromination and chlorine has a lower oxidation potential than bromine, in case of chlorination reactions we needed a 3-fold molar excess of NaCl for each introduced chlorine atom.^[27] Results of Table 3 show that decreasing the concentration of NaCl from 0.03 mol to 0.01 mol reduced the yield of 4-bromo-2-chloroacetanilide from 99% to 79.3% and also depressed the melting point. Increasing the concentration from 0.03 to 0.04 mol makes the yield of the product become static and there is no further increase in yield. It is quite obvious from Table 4 that the yield and quality of the product is strongly dependent on the concentration of NaIO₄. With the decrease in amount of NaIO₄ from 0.005 to 0.0025 mol, the yield of the product drops to 78.1% and the melting point also lowers to 149 °C (not within the required standards). When we further increased the amount of NaIO₄ from 0.005 to 0.01 mol, there was no effect on yield. It has also been observed from Table 5 that use of 50 mg of SLS gives the best yield (99%) and also improves the texture of the product. In the absence of SLS the yield was 85%, purity was 90.6% (Table 6, entry 1), and yellowish white product was obtained. As we increased the amount of SLS up to 50 mg, the yield of product increased from 85 to 99%, purity of product increased from 90.6 to 99.2%

Table 4. Effect of amount of NaIO₄ on the yield and melting point of 4-bromo-2-chloroacetanilide in the chlorination of 4-bromoacetanilide (**1**)

Entry	Moles of NaIO ₄	Yield (%)	Mp (°C) (lit. ^[28a] 151–152)	Appearance
1	0.0025	78.1	149	Yellowish
2	0.005	99	152	White shiny crystals
3	0.01	98.8	152	White

Notes. Reaction conditions: substrate, 0.01 mol; NaCl, 0.03 mol; AcOH, 10 mL; H₂SO₄, 1.0 mL; SLS, 50 mg; temp 25 °C.

Table 5. Effect of amount of SLS on the yield of 4-bromo-2-chloroacetanilide in chlorination of 4-bromoacetanilide (**1**)

Entry	Amount of SLS (mg)	Yield (%)	Mp (°C) (lit. ^[28a] 151–152)	Appearance
1	—	85	149	Yellowish white
2	10	94.2	151	Yellowish white
3	30	94.6	152	White
4	50	99	152	White shiny crystals
5	70	97.4	152	White
6	100	97	152	White

Notes. Reaction conditions: substrate, 0.01 mol; NaCl, 0.03 mol; NaIO₄, 0.005 mol; AcOH 10 mL; H₂SO₄ 1.0 mL; temp 25 °C.

Table 6. Effect of addition of SLS on purity of 4-bromo-2-chloroacetanilide in the chlorination of 4-bromoacetanilide (**1**)

Entry	Amount of SLS (mg)	Yield ^a (%)	Product purity ^b (%)	
			Main product	Others
1	—	85	90.6	9.4
2	50	99	99.2	0.08

^aIsolated yield.

^bPurity determined by HPLC.

Notes. Reaction conditions: substrate, 0.01 mol; NaCl, 0.03 mol; NaIO₄, 0.005 mol; AcOH, 10 mL; H₂SO₄, 1.0 mL; SLS, 50 mg; temp 25 °C.

(Table 6, entry 2), and also white shiny crystals of 4-bromo-2-chloroacetanilide were obtained. On further increase in amount of SLS from 50 to 100 mg, there was no effect on yield. Therefore, it is concluded experimentally that 0.005 mol of NaIO₄, 0.03 mol of NaCl, and 50 mg of SLS under acidic conditions (H₂SO₄, 1 mL) afford best yield and excellent purity of chlorinated product in acetic acid as solvent. Dichlorinated product has been obtained by increasing the amounts of NaCl (0.05 mol) and NaIO₄ (0.01 mol) at 40 °C (Table 1, entries 5, 7, 9, and 13).

CONCLUSIONS

It is concluded that chlorination of commercially important aromatics using NaCl as chlorine source, and NaIO₄ as oxidant in acidic medium can be performed within 1–2 h in AcOH and a small amount of SLS to give good yield and purity of chlorinated product. Monochlorinated product is obtained at room temperature, whereas for dichlorination temperature is raised slightly (40 °C) along with increased amount of NaCl and NaIO₄. When the reaction was catalyzed in the presence of a small amount of SLS, the yield, purity, and reaction rate increased.

EXPERIMENTAL

Starting materials and other reagents were obtained from commercial suppliers and used without further purification. ¹H NMR spectra were recorded on a Bruker

Avance II 400-MHZ spectrometer in CDCl_3 or dimethylsulfoxide (DMSO) using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on Micromass Quattro Micro API triple quadrupole MS equipped with a standard APCI ion source. High-performance liquid chromatographic (HPLC) analyses were conducted using a Waters 2695 instrument with PDA detector, column C_{18} (250 mm \times 4.6 mm \times 5 μm), solvent system of 70% CH_3OH + 30% H_2O , and flow rate of 1 mL/min. HPLC purity is reported by area %.

Monochlorination: Synthesis of 4-Bromo-2-chloroacetanilide (1)

To a solution of 4-bromoacetanilide (2.141 g, 0.01 mol) in AcOH were added SLS (50 mg), NaCl (1.753 g, 0.03 mol), and H_2SO_4 (1 mL), respectively, and the reaction was stirred at room temperature. An aqueous solution of NaIO_4 (1.064 g, 0.005 mol) dissolved in 7 mL of water was added dropwise utilizing a pressure-equalizing funnel. Yellow color appeared after adding aqueous solution of NaIO_4 . Reaction progress was monitored with thin-layer chromatography (TLC). After completion of the reaction, the mixture was poured into water and filtered. The precipitated mass was washed with water, dried, and recrystallized with methanol. White shiny crystals of 4-bromo-2-chloroacetanilide were obtained in 2.465 g (99%) yield having 99% purity and melting point 152 °C. ^1H NMR (400 MHz, CDCl_3) δ 2.23 (s, 3H, CH_3), δ 7.51 (d, 1H, arom), δ 7.39 (dd, 1H, arom), δ 7.59 (br, s, 1H, NH), δ 8.27 (d, 1H, arom) ppm. MS: calcd. for $\text{C}_8\text{H}_7\text{BrClNO}$ $[\text{M}]^+$ 249; found 250 $[\text{M} + 1]^+$.

Dichlorination: Preparation of 2,6-Dichloro-4-nitroaniline (5)

SLS (50 mg), NaCl (2.922 g, 0.05 mol), and H_2SO_4 (1 mL) were added to a solution of 4-nitroaniline (1.381 g, 0.01 mol) in AcOH and stirred at 40 °C. Dark yellow color appeared on dropwise addition of aqueous solution of NaIO_4 (2.132 g, 0.01 mol) in 7 mL water. Reaction progress was monitored using TLC. After completion of reaction, the reaction mixture was cooled at room temperature and poured into water. The product was filtered, washed with water, and dried in an oven. Yellow powder of 2,6-dichloro-4-nitroaniline was obtained in 2.015 g (97%) yield having 98.8% purity and melting point 190 °C. ^1H NMR (400 MHz; DMSO) δ 8.1 (d, 2H, arom), δ 6.08 (s, 2H, NH_2) ppm. MS (APCI): calcd. for $\text{C}_6\text{H}_4\text{Cl}_2\text{N}_2\text{O}_2$ $[\text{M}]^+$ 207.0; found, 205.0 $[\text{M} - 2]^+$.

Spectroscopic Data of Some Chlorinated Aromatic Compounds

2,4-Dichloroacetanilide (2). White needles; ^1H NMR (400 MHz; CDCl_3) δ 2.23 (s, 3H, CH_3), δ 7.36 (d, 1H, arom), δ 7.25 (dd, 1H, arom), δ 7.64 (br, s, 1H, NH), δ 8.29 (d, 1H, arom) ppm. MS: calcd. for $\text{C}_8\text{H}_7\text{Cl}_2\text{NO}$ $[\text{M}]^+$ 204.06; found, 206.0 $[\text{M} + 2]^+$.

4-Chlorobezanilide (3). White powder; ^1H NMR (400 MHz, CDCl_3) δ 7.19-7.80 (m, 9H, arom) ppm. MS (APCI): calcd for $\text{C}_{13}\text{H}_{10}\text{ClNO}$ $[\text{M}]^+$ 231; found 232 $[\text{M} + 1]^+$.

2-Bromo-6-chloro-4-nitroaniline (6). Yellowish powder; ^1H NMR (400 MHz, DMSO) δ 7.26 (s, 2H, NH_2), δ 8.31 (d, 1H arom), δ 8.19 (d, 1H, arom) ppm. MS (APCI): calcd. for $\text{C}_6\text{H}_4\text{BrClN}_2\text{O}_2$ $[\text{M}]^+$ 251.45; found, 252.5 $[\text{M} + 1]^+$.

2,6-Dichloro-4-nitrophenol (9). Light yellow crystals; ^1H NMR (400 MHz, DMSO) δ 8.22 (d, 2H, arom), δ 6.6 (br, s, 1H, OH) ppm. MS: calcd. for $\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_3$ $[\text{M}]^+$ 208; found, 207 $[\text{M} - 1]^+$.

3-Chloro-4-hydroxybenzaldehyde (10). Light brown powder; ^1H NMR (400 MHz; DMSO) δ 9.78 (s, 1H, CHO), δ 7.81 (d, 1H, arom), δ 7.64 (dd, 1H, arom), δ 7.12 (d, 1H, arom) ppm. MS: calcd. for $\text{C}_7\text{H}_5\text{ClO}_2$ $[\text{M}]^+$ 156.5; found, 157.5 $[\text{M} + 1]^+$.

2-Chloro-4-nitroacetanilide (11). Yellow powder; ^1H NMR (400 MHz, CDCl_3) δ 2.24 (s, 3H, CH_3), δ 8.68 (d, 1H, arom), δ 8.29 (d, 1H, arom), δ 8.16 (dd, 1H, arom), δ 7.91 (br, s, 1H, NH) ppm. MS: calcd. for $\text{C}_8\text{H}_7\text{ClN}_2\text{O}_3$ $[\text{M}]^+$ 214.61; found, 216.8 $[\text{M} + 2]^+$.

5-Chlorosalicylic acid (12). White crystals; ^1H NMR (400 MHz; DMSO) δ 9.05 (s, 1H, OH), δ 7.79 (d, 1H, arom), δ 7.38 (dd, 1H, arom), δ 6.91 (d, 1H, arom) ppm. MS: calcd. for $\text{C}_7\text{H}_5\text{ClO}_3$ $[\text{M}]^+$ 172; found, 173 $[\text{M} + 1]^+$.

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