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Hypochlorite-Induced Substitution of Chlorine for Iodine in Aromatic Compounds and the Role of Iodyl Intermediates

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Aqeuous hypochlorite, with a phase-transfer catalyst, effects exchange of chlorine for bromine bonded to aromatic rings in reactions that are influenced by the electronic effects of substituents[1] and with rates significantly enhanced by Ni(II) catalyst systems.[2] In contrast with bromoaromatic starting materials, only modest yields (5-10%) of chloroaromatics were achieved when iodoaromatic substrates were employed.

In preliminary work,[3] a rapid reaction of iodobenzene (PhI, 1) was noted with aqueous hypochlorite at pH 8-9, using dichloromethane and the phase-transfer catalyst (PTC) tetra-*n*-butylammonium bisulfate. In this simple, two-phase system (without Ni(II) catalyst), a heavy white precipitate formed, but only if stirring was halted after 15-30 min. The solid dissolved upon further mixing of the two phases, with further precipitation occurring more sluggishly, upon cessation of stirring, as reaction times extended to several hours. The identity of the precipitate as iodylbenzene ($PhIO_2$, formerly iodoxybenzene, **2**) was deduced from its explosive decomposition upon heating[4] and by infrared analysis. Gas chromatography indicated chlorobenzene (PhCl, **3**) to be a slow-developing product of longer term reactions.

The present study focuses on the overall course of phase-transfer catalyzed reactions of iodoaromatics with hypochlorite and elucidates factors governing formation and subsequent hypochlorite-induced reactions of iodylbenzenes.

Short-term exposure of a series of iodobenzenes to pH 8.2-9.2 aqueous hypochlorite in two-phase reaction mixtures with PTC resulted in formation of precipitates that on continued treatment reacted further to give the corresponding substituted chlorobenzenes (see Table I). As with other hypochlorite-induced transformations,[1,5] reactions proceeded with some facility at pH 8-9, but at pH >11, iodobenzene was inert.

Table I[a]

substrate (QPhI) Q	yield (%) of QPhCl	reaction time[b] (h)
H	44-50[c]	4-6
3-CF_3	41-77	19-72
4-Cl	85-100	23-28
4-F	72-95	24-70

[a] See Experimental Section for general procedure. [b] A second portion of hypochlorite and catalyst was added for reactions with periods over 6 h. [c] 82% in 4 d reaction, without pH control.

These results, coupled with the isolation of iodylbenzene from short-term reactions of compound 1, indicate that the phase-transfer-catalyzed interaction of iodoaromatics with aqueous hypochlorite leading to chloroaromatics involves iodyl compounds as intermediates. Iodylbenzenes have been synthesized from iodobenzenes using acidified hypochlorite solutions[6] as well as other oxidizing agents.[7]

$$\mathrm{ArI} \xrightarrow{\text{hypochlorite/PTC}} \mathrm{ArIO_2} \xrightarrow{\text{hypochlorite/PTC}} \mathrm{ArCl}$$

When the interaction of iodylbenzene with aqueous hypochlorite/CH_2Cl_2 with a phase-transfer catalyst was followed closely for extended periods of time, two significant observations were made. A. A suspension of iodylbenzene dispersed in the organic phase rapidly disappeared, due to its higher solubility in the aqueous phase[8] (where it would not be subject to phase transfer catalysis). B. Substantial yields (63-79%) of chlorobenzene from iodylbenzene were realized.

Poor yields of chloroaromatics from iodocompounds in Ni(II)-catalyzed reactions with hypochlorite have been attributed to competing pathways leading to iodobenzene dichlorides,[2] which are iodine(III) compounds.[9] No direct evidence for formation of the latter has been observed in the present work. However, iodobenzene diacetate, a readily available iodine(III) substrate, reacted relatively rapidly with hypochlorite/PTC to produce approximately 80% yields of chlorobenzene under conditions described for reactions in Table I. The reaction of iodobenzene dichloride with NaOCl/acetic acid previously has been used to synthesize the iodine(V) product, iodylbenzene.[10]

The active agents specifically responsible for conversion of iodobenzene to iodylbenzene and the latter to chlorobenzene in the present study may be hypochlorous acid, hypochlorite ion, or an agent, such as Cl_2O, derived from these species under the conditions employed.[11,12] Evidence has been found for involvement of free-radical reactions of Cl_2O in phase-transfer-catalyzed systems involving hypochlorite, with and without Ni(II) catalysts.[2,11b]

This work extends the scope of halogen replacement reactions by hypochlorite/PTC to include iodo compounds as substrates. Under mild conditions, comparable to those

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[1] Arnold, J. T.; Bayraktaroglu, T. O.; Brown, R. G.; Heiermann, C. R.; Magnus, W. W.; Ohman, A. B.; Landolt, R. G. *J. Org. Chem.* **1992**, *57*, 391.

[2] O'Connor, J. K.; Burrows, C. J. *J. Org. Chem.* **1991**, *56*, 1344.

[3] Bayraktaroglu, T. O.; Landolt, R. G. Paper U-13, 24th Annual Meeting-In-Miniature of the Dallas/Fort Worth Section of the American Chemical Society, April 26, 1991.

[4] Iodylaromatics (iodoxycompounds) *characteristically are explosive, especially when heated*, and care should be exercised in their handling. See: Plumb, J. B.; Harper, D. J. *Chem. Eng. News* July 16, 1990. Beringer, F. M.; Bodlaender, P. *J. Org. Chem.* **1968**, *33*, 1968. The latter report "violent decomposition of dry samples may be initiated by the scraping action of a spatula."

[5] Elmore, P. R.; Reed, R. T.; Terkle-Huslig, T.; Welch, J. S.; Young, S. M.; Landolt, R. G. *J. Org. Chem.* **1989**, *54*, 970 and references cited therein.

[6] Barton, D. H. R.; Godfrey, C. R. A.; Morzycki, J. W.; Motherwell, W. B.; Vey, S. V. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1947.

[7] (a) Iodylbenzene from iodobenzene/Caro's Acid: Gakovic, Z.; Morgan, K. J. *J. Chem. Soc. B* **1967**, 416 and references cited therein. (b) Iodylbenzene from iodobenzene and other oxidizing agents: Sharefkin, J. G.; Saltzman, H. Organic Syntheses; John Wiley and Sons: New York, 1973; Collect. Vol. V, pp 665-667 and references cited therein.

[8] Iodylbenzene water solubility is >12 mmol/L at ambient temperature: Mason, I.; Race, E.; Pounder, F. E. *J. Chem. Soc.* **1935**, 1669. Finely powdered iodylbenzene in quantities employed in the present effort efficiently is extracted from the organic phase by neutral or pH 9 buffered water as well as aqueous hypochlorite.

[9] Banks, D. F. *Chem. Rev.* **1966**, *66*, 243.

[10] Formo, M. W.; Johnson, F. R. *Organic Syntheses*; John Wiley and Sons: New York, 1955; Collect. Vol. III, pp 486-487.

[11] (a) The p*K*′ = 7.537 (25 °C) for HOCl: Morris, J. C. *J. Phys. Chem.* **1966**, *70*, 3798. (b) Fonouni, H. E.; Krishnan, S.; Kuhn, D. G.; Hamilton, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 7672 and references cited therein.

[12] At the suggestion of a reviewer, reactivity of iodylbenzene with hypochlorite without phase-transfer catalyst was investigated, and chlorobenzene was produced in yields comparable to reactions conducted with catalyst.

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required to convert bromoaromatics more or less directly to chloro compounds,[1] it is a multistep process that gives rise first to oxidation at iodine followed by cleavage of the aromatic–iodine bond and replacement by chlorine.

Experimental Section

Materials and General Procedures. All compounds employed, except for iodylbenzene, were secured from commercial suppliers. Aqueous hypochlorite ("5.25%") was obtained in the form of commercial Clorox. In all cases, the phase-transfer catalyst (PTC) used was tetra-*n*-butylammonium hydrogen sulfate. Gas chromatographic (GC) analyses were accomplished with a Tracor 540 system with a 6-ft × 1/4-in. 3% SP2100 packed column and a Waters Dimension I gas chromatograph with a 15-m DB-5 Megabore capillary column. Both GC's employed flame ionization detectors. Infrared spectra were obtained with a Perkin-Elmer 1420 spectrophotometer. A Mel-Temp melting point apparatus was used, with minimum samples in glass capillary tubes, to derive melting/decomposition data. The pH of top, aqueous layers of biphasic systems was set and maintained at desired levels by addition of aqueous NaOH or HCl, and pH was monitored with Orion 501 pH meters equipped with gel-filled plastic combination electrodes. Progress of reactions was followed by GC using internal standards, such as fluorobenzene, chlorobenzene, or dichlorobenzene, which were determined to be stable to reaction conditions and with retention times not interfering with reactants or products.

Reactions of Iodobenzenes. General. Two-phase systems, consisting of equal molar amounts of substrate iodobenzenes and internal standards (2.5×10^{-3} mol) dissolved in 50 mL of CH_2Cl_2 and 100 mL of hypochlorite containing 0.20 g of PTC, adjusted to pH 8.2–9.2, were stirred magnetically. In all cases, a white precipitate began to form in the organic layer within 10–30 min, if stirring was discontinued. (Filtration of the precipitate from iodobenzene reactions yielded crude iodylbenzene. See below for characterization.) Yields of chloroaromatic products (characterized by GC) in longer-term, stirred biphasic reactions are given in Table I for reactions run at pH 8.2–9.2. Even after 22 h at pH >11, no loss of iodobenzene or formation of chlorobenzene was observed in reactions employing PTC.

Synthesis of Iodylbenzene (2). CAUTION: See Ref 4. A. From Caro's Acid Method. Authentic samples of iodylbenzene were prepared by the procedure of Gakovic and Morgan[7a] which provided an infrared spectrum and melting/decomposition data for comparison with material isolated from iodobenzene–hypochlorite–PTC reactions.

B. From Hypochlorite/PTC Reactions. Iodobenzene, 1.01 g (4.9×10^{-3} mol), was dissolved in 75 mL of CH_2Cl_2 and stirred vigorously with 200 mL of pH 8.2 hypochlorite for 45 min. After stirring was interrupted for 60 min, filtration of two crops of precipitates gave crude iodylbenzene (0.69–0.94 g, $2.9–4.1 \times 10^{-3}$ mol, with melting/decomposition at 215 and 225 °C, 59–81% yield). Crystallization from water or acetic acid provided material with infrared spectrum[13] coincident and melting/decomposition points (231, 233, and 240 °C (lit.[7a,6] mp 236 and 250 °C) comparable to iodylbenzene prepared by the Caro's acid method. (Reactions at pH >11 with PTC gave no trace of iodylbenzene.)

Iodylbenzene/Hypochlorite/PTC Reaction. Crude iodylbenzene (from hypochlorite/PTC reaction of iodobenzene), 0.25 g (1.1×10^{-3} mol) mixed with 0.1 g of PTC and 50 mL of aqueous hypochlorite at pH 8.8–9.2 and 50 mL of CH_2Cl_2 for 2 h, showed 24–32% yield of chlorobenzene by GC. After addition of a second 50-mL portion of hypochlorite and 0.1 g of PTC and stirring for a total of 22–30 h, chlorobenzene yields of 63–79% were observed.

Iodobenzene Diacetate/Hypochlorite/PTC Reaction. Iodobenzene diacetate (0.80 g, 2.5×10^{-3} mol), dissolved in 50 mL of CH_2Cl_2 with 0.21 g of PTC and stirred with 100 mL of pH 8.8–9.2 aqueous hypochlorite, lost all starting material and began to show substantial chlorobenzene within 2 h. Addition of 1,4-dichlorobenzene as internal standard (delayed because the standard has same retention time as substrate) along with 100 mL of fresh hypochlorite and 0.21 g of PTC revealed chlorobenzene yields of 79–84% within 16–20 h.

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(13) The infrared spectrum also corresponded peak-for-peak with that of iodylbenzene, no. 6703, Sadtler Standard Spectra, Midget Edition, Sadtler Research Laboratories, Philadelphia, PA, 1962.