and ȮH,[33] the selectivities are considerably small.

Experimental Section

Materials. Methyl-substituted dienes were commercially available. Chloro-substituted dienes were donated from Denki Kagaku Kogyo Co. Ltd. Diaryl disulfides which are the arylthiyl radical sources for the flash photolysis were prepared from the corresponding thiols.[34] Cyclohexane used as a solvent is of spectroscopic grade.

Apparatus and Procedure. The flash photolysis apparatus was a standard design with two xenon flash lamps (Xenon Corp. N-810C; half duration of 5 μs and input energy of 100 J).[35] Diaryl disulfide (< ca. 10^{-4} M in cyclohexane) was filled in a cylindrical quartz flash cell 10 mm in diameter and 100 mm long with optical flat windows at both ends. All rate constants were determined at room temperature (23 °C). For each flash, a fresh solution containing disulfide with diene in different concentration was prepared.

Acknowledgment. We are thankful to the Grant-in-Aid (No. 60540271/62540314) for Scientific Research from the Ministry of Education, Science and Culture. We also express our deep thanks to Mr. Y. Asada and Mr. Y. Miyata of Denki Kagaku Kogyo Co. Ltd. for their kind donation of chlorobutadienes.

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Hydrolysis and Fe^{2+}-Induced Reduction of *N*-Aryl-*O*-pivaloylhydroxylamines: Aqueous Solution Chemistry of Model Carcinogens

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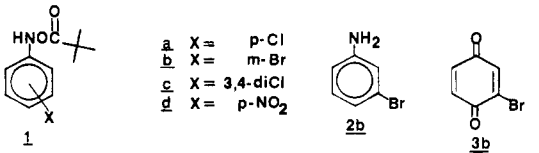
The *N*-aryl-*O*-pivaloylhydroxylamines, **1a–d**, which serve as models for the carcinogenic metabolites of aromatic amines, decompose in aqueous media by heterolysis of the N–O bond. Substituent effects on rates of reaction and products of the decomposition of **1a–c** are entirely consistent with the intermediacy of a singlet nitrenium ion. The least reactive compound in the series *N*-(4-nitrophenyl)-*O*-pivaloylhydroxylamine (**1d**) yields 4-nitroaniline (**2d**) as its major decomposition product. This material may be formed through H• abstraction by a triplet ion, but a nitrene reaction appears to be more likely. In the presence of Fe^{2+} **1a–d** undergo rapid reduction to the corresponding anilines **2a–d**. This reaction requires complexation of the ester with Fe^{2+} and proceeds with heterolysis of the N–O bond since nearly quantitative yields of pivalic acid are isolated. The radical cations **25a–d** appear to be the most likely precursors to the reduction products.

A significant number of polycyclic aromatic amines and amides, including 2-aminofluorene and *N*-acetyl-2-aminofluorene, are known to be metabolized into potent carcinogens in laboratory animals.[1] These materials are metabolized, in part, via N-hydroxylation, and there is good evidence that sulfuric and carboxylic acid esters of the resulting *N*-arylhydroxylamines and *N*-aryl-*N*-hydroxyamides are among the more important carcinogenic metabolites of these compounds.[1] We have previously reported on the chemistry of sulfuric and carboxylic acid esters of *N*-hydroxyacetanilides, which are analogues of the metabolites of the polycyclic amides.[2] In aqueous solution these compounds undergo heterolysis of the N–O bond to yield *N*-acyl-*N*-arylnitrenium ion–sulfate ion or carboxylate ion pairs, which can undergo internal return or be attacked by nucleophiles and reducing agents.[2]

We are now investigating the chemistry of *N*-aryl-*O*-pivaloylhydroxylamines, **1**, which serve as models for the deacylated metabolites of the polycyclic amines. In a preliminary account of our work with **1b**, we interpreted the detection of significant amounts of 3-bromoaniline (**2b**) and 2-bromo-1,4-benzoquinone (**3b**) in terms of competition between heterolysis and homolysis of the N–O bond.[3]



However, our more recent work, reported in this paper, shows that both of these products arise because of reactions involving trace amounts of Fe^{2+} or Fe^{3+} in the aqueous

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solutions. In demetalized aqueous solutions in the pH range 1.0–7.0 at 40 °C **1a–c** yield products entirely consistent with heterolysis of the N–O bond. Under the same conditions the very unreactive **1d** does yield *p*-nitroaniline (**2d**) as its major decomposition product. This may be due to a singlet to triplet spin inversion of the nitrenium ion as originally suggested by Gassman and co-workers,[4] but H• abstraction by a nitrene may be more likely. Proton or metal ion induced homolysis of the N–O bond, for which Hoffman and co-workers have provided some evidence in aliphatic systems,[5] can be ruled out since pivalic acid is isolated in high yield during the hydrolysis of **1d**.

Our investigations into the mechanism of the Fe^{2+}-induced reduction of **1a–d** show that this reaction does not involve nitrenium ion intermediates but requires complexation of Fe^{2+} and **1**. Homolysis of the N–O bond can again be ruled out on the basis of recovery of pivalic acid from the reaction mixtures. The mechanism of this reduction and the implications of our results with respect to the carcinogenicity of polycyclic analogues of **1** are discussed herein.

Experimental Section

All solvents used in synthetic procedures were reagent grade and were purified, in necessary, by standard methods. Me_4Si was used as an internal standard for all NMR spectra.

Synthesis and Characterization of 1a–d. The synthesis and characterization of **1b** and **1d** have been described.[3,6] The 3,4-dichloro ester, **1c**, was made in a manner identical with that reported for **1b**.[3] After initial purification by column chromatography on silica gel (CH_2Cl_2 eluent), the fractions containing **1c** were combined and recrystallized from hexanes as slightly grayish needles: mp 62.5–65.5 °C; IR (KBr) 3200, 2975, 1745, 1595, 1470, 1110 cm^{-1}; ^1H NMR (90 MHz, CD_2Cl_2) δ 1.30 (9 H, s), 6.89 (1 H, dd, J = 8.80, 2.20 Hz), 7.12 (1 H, d, J = 2.20 Hz), 7.38 (1 H, d, J = 8.80 Hz), 8.75 (1 H, s, broad). Anal. Calcd for $C_{11}H_{13}NO_2Cl_2$: C, 50.40; H, 5.00; N, 5.34. Found: C, 50.48; H, 5.01; N, 5.24.

***N*-(4-Chlorophenyl)-*O*-pivaloylhydroxylamine (1a).** This ester was made by an adaptation of the method of Lobo et al.[7] *N*-(4-Chlorophenyl)hydroxylamine[2a] (71.8 mg, 0.50 mmol) was added to 5 mL of dry benzene stirred under N_2 at room temperature. Dry *N*-ethylmorpholine (58.3 μL, 0.50 mmol) was added, followed by pivaloylcyanide[8] (62 μL, 0.50 mmol). The mixture was stirred for 20 min and then extracted twice with cold (5 °C) 1 N NaOH (5 mL), twice with cold 5% $NaHCO_3$ (5 mL), and once with ice-cold H_2O (5 mL). The organic phase was then dried over Na_2SO_4 at 5 °C for ca. 2 h, filtered, and evaporated under a dry vacuum to yield a yellowish waxy solid (85 mg, 75%). ^1H NMR and HPLC indicated that this material was >98% pure. Attempts at further purification led to decomposition: IR (benzene) 3240, 2975, 1735, 1485, 1125 cm^{-1}; ^1H NMR (90 MHz, C_6D_6) δ 1.04 (9 H, s), 6.50 (2 H, d, J = 8.80 Hz), 6.97 (2 H, d, J = 8.80 Hz), 8.79 (1 H, s, broad). Benzene or CH_3CN solutions of **1a** kept at −25 °C were stable for several weeks, but the neat compound decomposed in a few days at the same temperature.

***N*-(Pivaloyloxy)-3-bromoacetanilide (4b).** This material was synthesized as previously described for *N*-(pivaloyloxy)-acetanilide.[6] Purification by column chromatography on silica gel (CH_2Cl_2 eluent) led to a colorless oil: IR (neat) 2980, 1780, 1690, 1590, 1475, 1370, 1330, 1070 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.31 (9 H, s), 2.10 (3 H, s), 7.2–7.7 (4 H, m). Anal. Calcd for $C_{13}H_{16}NO_3Br$: C, 49.70; H, 5.13; N, 4.46. Found: C, 49.56; H, 5.20; N, 4.39. Spectral data for this compound are similar to those previously reported for the unsubstituted ester and other ring-substituted derivatives.[6]

Kinetic Measurements. Kinetics were performed in 5% CH_3CN–H_2O solutions. General procedures for solvent purification and monitoring kinetics by UV and HPLC methods have been described.[2] Kinetics were performed at 40.0 ± 0.1 °C in the pH range 1.0–7.0 in HCl solutions and in acetate or phosphate buffers (0.01 M total buffer). All solutions were maintained at an ionic strength of 0.50 M with KCl. All pH measurements were taken at room temperature with an Orion Model 701A pH meter equipped with a Radiometer GK 2402 C combination electrode.

Care was taken to remove contaminating metals from all solutions. All glassware and plasticware was soaked in saturated Na_2EDTA solutions overnight before rinsing with deionized (18.0 MΩ cm) H_2O. All H_2O used in this study was distilled, deionized (18.0 MΩ cm), and distilled again into high-density polyethylene (HDPE) bottles for storage. Solutions were made in glass volumetrics and then stored in HDPE bottles. All buffer salts were of the highest purity available, and KCl solutions (1 N) were demetalized as follows.[9] The KCl solution (1 L) was brought to pH 9.0 by small amounts of 40% NaOH solution and then extracted with ca. 50 mL of diphenylthiocarbazone solution in CCl_4 (0.25 g/L) until the green color of the diphenylthiocarbazone was undiminished. The KCl solution was then washed with CCl_4 (ca. 50 mL) until no color could be observed in the organic phase. Residual CCl_4 was removed by bubbling H_2O-saturated N_2 (supplied via a Teflon tube) through the KCl solution overnight. Atomic absorption analyses of buffer solutions prepared by using these procedures showed no detectable Fe (detection limit ca. 10^{-7} M).

All reaction solutions were outgassed with N_2 as described elsewhere[2b] and were kept in an inert atmosphere (N_2) box until used. Buffers used for HPLC kinetics (50 mL) were incubated at 40 °C for at least 0.5 h in HDPE bottles fitted with rubber septa. Reactions were initiated by injection of 250 μL of ca. 1.5×10^{-2} M solutions of **1** in CH_3CN into the buffers. This gave an initial concentration of **1** of ca. 7.5×10^{-5} M. Aliquots (20 μL) were removed and analyzed by HPLC methods described previously.[2a] Column and conditions were as follows: μ-Bondapak C-18 reverse-phase column, MeOH/H_2O (50/50, 60/40, or 70/30 depending on the ester under analysis), 1 mL/min, UV absorbance monitored at 250 nm. Peak area vs time data for **1b–d** and several hydrolysis products of **1c** were fit to the standard first-order rate equation. The hydrolysis of **1a** was too fast to monitor by HPLC methods, so absorbance vs time data at 233 nm (λ for maximum absorbance change) were fit to the first-order rate equation in this case. Procedures for monitoring kinetics in thunberg cuvettes under N_2 are described elsewhere.[2b]

Product Analyses. Product studies were performed under conditions identical with those described above for the kinetic studies. Reactions were allowed to proceed for five hydrolysis half-lives before they were quenched by immersion in an ice–salt bath. Product peak areas were determined by triplicate HPLC runs (UV detector set at 250 or 380 nm). Yields were subsequently determined from peak area data and molar extinction coefficients, which were determined for the products after purification and identification. Products were isolated by extraction into CH_2Cl_2 or EtOAc and were separated and purified as described elsewhere.[2,3] Products were identified by comparison with commercially available samples (**2a–d**, **7a**, **7c**, **7d**, **8c**, **9d**, **16**) by comparison with samples available from other studies in this laboratory[3,10,11] (**3b**, **9b**, **9c**, **10b**, **10c**, **11d**, **18b**, **19b**) or by independent syntheses and spectral data (**3c**, **5a–d**, **6b**, **6c**, **9a**).[12]

Appropriate concentrations of Fe were achieved by adding $FeCl_2$, $FeCl_3$, or $K_4Fe(CN)_6$ to buffer solutions prepared as described above. Reactions run in the presence of Fe were treated as described above. The reactions of *N*-(4-chlorophenyl)-

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(12) Details of synthesis and/or isolation and characterization of **3c**, **5a-d**, **6b**, **6c**, and **9a** are available. See supplementary material.

hydroxylamine (**20a**),[2a] *N*-(4-nitrophenyl)hydroxylamine (**20d**),[6] *N*-(pivaloyloxy)-3-bromoacetanilide (**4b**), and *N*-(sulfonatooxy)-3-bromoacetanilide (**26b**)[3] were treated as described above for **1a–d**.

Analysis for Pivalic Acid. After five hydrolysis half-lives, reaction mixtures were adjusted to pH <3.0 if necessary and were extracted (4 × 25 mL) with CH_2Cl_2. After being dried over Na_2SO_4, the CH_2Cl_2 extracts were fractionally distilled to a small volume (<5 mL). The remaining solvent was removed by short-path distillation. The residue that remained was then either directly analyzed by NMR spectroscopy for pivalic acid (AcOH used as internal concentration standard) or was treated with CH_2N_2 in the usual manner to generate methyl pivalate. The concentration of methyl pivalate was determined by gas chromatography (10% OV-101 on Chromosorb W-HP, 30 °C, 75 mL/min, FID detector). Calibration was done with authentic methyl pivalate. Some of the relatively volatile pivalic acid was lost with this procedure, so solutions of known concentration of pivalic acid in the same range as the reaction mixtures were analyzed with each experimental determination. Experimental yields were then corrected by the percent recovery from solutions of known concentration. The recovery yields from the known solutions were in the range of 45–55%.

Analysis for Isobutane. Gas chromatographic analysis of the headspace above reaction mixtures was performed in an attempt to detect isobutane. Headspace samples (1 mL) were injected onto a 10 ft column of 5-Å molecular sieves, 60–80 mesh, at a flow rate of 75 mL/min and a temperature of 30 °C (FID detector). Known samples were prepared by injecting appropriate amounts of 1 N *tert*-butyllithium into the reaction buffers.

2-(Benzylimino)-5-chlorophenyl Pivalate (17a). This material was synthesized by esterification of the corresponding phenol. Benzaldehyde (0.75 g, 7.0 mmol) and 2-amino-5-chlorophenol (**9a**)[13] (1.01 g, 7.0 mmol, see the supplementary material for synthesis) were combined with stirring. After the reaction mixture had cooled, EtOH (ca. 4 mL) was added, and recrystallization led to brownish platelets, which were recrystallized a second time from EtOH to yield slightly yellow platelets (1.20 g, 75% yield) of 2-(benzylimino)-5-chlorophenol: mp 106–107 °C; IR (KBr) 3320, 1620, 1575, 1480 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 7.0–8.2 (9 H, m), 8.80 (1 H, s). Anal. Calcd for $C_{13}H_{10}NOCl$: C, 67.40; H, 4.35; N, 6.04. Found: C, 67.34; H, 4.45; N, 6.01. This material was esterified as follows. An 80% dispersion of NaH in mineral oil (0.015 g, 5.0 mmol) was washed three times with 1 mL of dry pentane in a three-necked 25-mL round-bottom flask under a N_2 atmosphere. Dry Et_2O was then added (2 mL), and a solution of 0.100 g (4.3 mmol) of 2-(benzylimino)-5-chlorophenol in 3 mL of dry Et_2O was added over a period of ca. 1 min with rapid stirring. A bright yellow precipitate formed instantly, and 0.053 mL of pivaloyl chloride (4.3 mmol) was then added over a period of about 45 s. After ca. 15 min of stirring, the yellow precipitate had been replaced by a white solid, and the mixture was filtered into a 25-mL pear-shaped flask. The Et_2O was removed by rotary evaporation, and the oil that remained was taken up into 2 mL of dry pentane. A small amount of precipitate was removed by filtration, and the pentane was removed by rotary evaporation to yield 0.105 g (77% yield) of a yellow oil, which decomposed on both silica gel and alumina: IR (neat) 3060, 2965, 1745, 1625, 1570, 1475, 1105 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.34 (9 H, s), 7.1–8.1 (8 H, m), 8.45 (1 H, s). Anal. Calcd for $C_{18}H_{18}NO_2Cl$: C, 68.46; H, 5.74; N, 4.43. Found: C, 68.18; H, 5.77; N, 4.44. The hydrolysis of this compound was monitored at pH 4.7 and 1.0 by HPLC and UV methods as described above for **1a–d**. Nonvolatile hydrolysis products were isolated and purified as described above. Kinetic data were obtained at 270 and 233 nm.

Results and Discussion

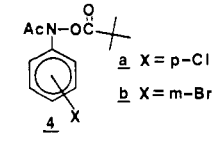
Hydrolysis Kinetics. Since it was determined that Fe^{2+} has a marked effect on the chemistry of **1a–d** in an aqueous environment (see below), all studies were performed in demetalized solutions as described in the Experimental Section. Since some reaction products (aminophenols) were also subject to oxidation by O_2, all reactions were also performed in N_2-saturated solutions which were protected from the atmosphere.

Table I. Rate Constants for the Decomposition of 1a–d at 40 °C[a]

ester	pH[d]	k_{obsd},[e] s^{-1}
1a[b]	1.0	(2.17 ± 0.06) × 10^{-2}
1a[b]	4.7	(1.59 ± 0.05) × 10^{-2}
1a[b]	6.8	(1.29 ± 0.03) × 10^{-2}
1b[c]	1.0	(1.1 ± 0.1) × 10^{-4}
1b[c]	4.6	(0.9 ± 0.1) × 10^{-4}
1b[c]	6.8	(1.0 ± 0.1) × 10^{-4}
1c[c]	4.6	(3.2 ± 0.3) × 10^{-4}
1d[c]	4.6	(9.9 ± 0.7) × 10^{-7}

[a] Conditions: 5 vol % CH_3CN–H_2O, μ = 0.50 M (KCl); T = 40.0 ± 0.1 °C. [b] Monitored at 233 nm by UV spectrophotometry. [c] Peak area of ester monitored as a function of time by HPLC. UV detector set at 250 nm. [d] pH was measured at room temperature, values reported are rounded to nearest 0.1. HCl, HOAc/KOAc, and KH_2PO_4/K_2HPO_4 were used to maintain pH. [e] All rate constants are averages of two runs.

Kinetics of the decomposition of **1** at 40 °C were monitored by UV spectroscopy (**1a**) or HPLC methods (**1b–d**). Rate data were fit well by the first-order rate equation, and the derived rate constants, k_{obsd}, are given in Table I. Rate constants for the appearance of several of the hydrolysis products (see below) of **1c** were also measured by HPLC methods at pH 4.6. These were in substantial agreement (ranging from 1.9 × 10^{-3} to 3.5 × 10^{-3} s^{-1}) with the rate constant for the disappearance of **1c** under the same conditions. The rate constants for **1a** and **1b** show that there is little, if any, pH dependence of the rate of decomposition of these esters. A correlation of the hydrolysis rate constants measured at pH 4.6 vs Brown's σ^+ parameter, gave a slope of −6.0 ± 1.1 (r = 0.96). This slope is comparable to those previously observed for the hydrolysis of *N*-(sulfonatooxy)acetanilides[2a] (−4.4 ± 0.9), and *N*-(pivaloyloxy)acetanilides[2b] (−5.6 ± 0.8), and the ethanolysis of *N*-*tert*-butyl-*N*-chloroanilines[4] (−6.35). The magnitude of the slope is consistent with the development of a significant positive charge in the aromatic ring during the rate-determining step of the reaction; however, **1d** may not decompose in aqueous solution via a nitrenium ion path (see below). The average rate constant for the decomposition of **1a** at 40 °C is approximately 4 × 10^3 larger than the rate constant for the decomposition of *N*-(pivaloyloxy)-4-chloroacetanilide (**4a**) measured at 70 °C.[2b] This large difference in reactivity is in accord with the difference in electronic effects of hydrogen and the acetyl group.



Hydrolysis Products. Results of product analyses performed under various conditions in demetalized solutions for **1a**, **1c**, and **1d** are reported in Table II. The hydrolysis products of **1a** and **1c** are similar to those previously reported for the hydrolysis of *N*-(sulfonatooxy)- and *N*-(pivaloyloxy)acetanilides,[2] and the alcoholysis of *N*-*tert*-butyl-*N*-chloroanilines.[4,14] These products and the substituent effects on the kinetics are certainly consistent with a nitrenium ion process. Scheme I presents a mechanism for the decomposition of **1a**. The pivalanilide **5a** is probably formed by intramolecular rearrangement

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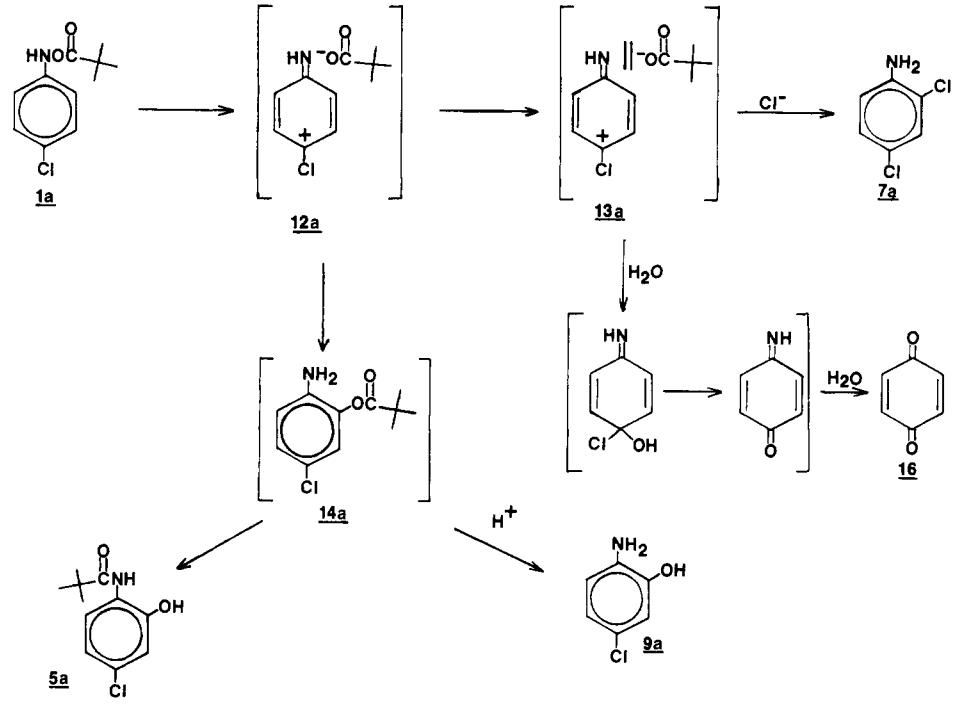
Table II. Yields of Hydrolysis Products of 1 in 5% CH_3CN-H_2O at 40 °C[a]

product	0.1 N HCl, μ 0.5 M (KCl), pH 1.0	1:1 HOAc/KOAc[b] μ 0.5 M (KCl), pH 4.7	1:1 KH_2PO_4/K_2HPO_4,[b] μ 0.5 M (KCl), pH 6.7
from **1a**:			
4-chloro-2-hydroxypivalanilide (**5a**)	8.3 ± 0.9	26.2 ± 2.3	24.1 ± 1.0
2,4-dichloroaniline (**7a**)	53.2 ± 2.5	49.6 ± 3.0	47.4 ± 2.0
2-amino-5-chlorophenol (**9a**)	3.6 ± 0.6		
1,4-benzoquinone (**16**)	3.8 ± 0.3	7.0 ± 1.4	1.0 ± 0.5
from **1c**:			
2-chloro-1,4-benzoquinone (**3c**)		2.9 ± 0.5	
4,5-dichloro-2-hydroxypivalanilide (**5c**)		23.7 ± 2.5	
3,4-dichloro-2-hydroxypivalanilide (**6c**)		14.5 ± 1.3	
2,4,5-trichloroaniline (**7c**)		5.4 ± 0.8	
2,3,4-trichloroaniline (**8c**)		12.8 ± 1.3	
4,5-dichloro-2-aminophenol (**9c**)		10.6 ± 1.2	
5,6-dichloro-2-aminophenol (**10c**)		3.5 ± 1.0	
3,4-dichloroaniline (**2c**)		3.2 ± 1.3	
from **1d**:[c]			
2-hydroxy-4-nitropivalanilide (**5d**)		trace[d]	
2-chloro-4-nitroaniline (**7d**)		trace[d]	
2-amino-5-nitrophenol (**9d**)		trace[d]	
4-nitroaniline (**2d**)		70 ± 10[e]	
4,4'-dinitroazoxybenzene (**11d**)		10 ± 3[e]	

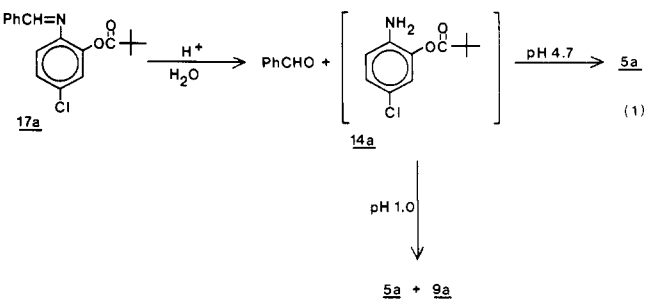
[a] Initial concentration of 1 was ca. 7.5×10^{-5}M. Yields reported with respect to 1 initially present were determined from HPLC peak areas except where indicated. All reactions were run under a N_2 atmosphere. [b] Total buffer concentration 0.01 M. [c] Yields determined after ca. 50% completion are corrected for unreacted **1d** still present. [d] Less than 0.2%. [e] Determined from NMR peak integration.

Scheme I



of the pivalic acid ester **14a**. Rearrangement products similar to **14a** are produced in the hydrolysis reactions of *N*-(sulfonatooxy)acetanilides and *N*-(pivaloyloxy)acetanilides,[2] the alcoholysis of *N*-*tert*-butyl-*N*-chloroanilines,[4,14] and the decomposition of methanesulfonic acid esters of *N*-hydroxyacetanilides in $CDCl_3$.[15]

A previous attempt to synthesize a compound similar to **14a**, 2-aminophenyl acetate, led only to products (including the isomeric amide) apparently formed by intramolecular participation of the amino group.[16] It was not possible to isolate **14a** in this study either, but a precursor, 2-(benzylimino)-5-chlorophenyl pivalate, **17a**, was synthesized. The hydrolysis of this compound at pH 4.7 and 40 °C led exclusively to benzaldehyde and the pivalanilide **5a** (90 ± 4%) (eq 1). Both HPLC and UV studies showed



(1)

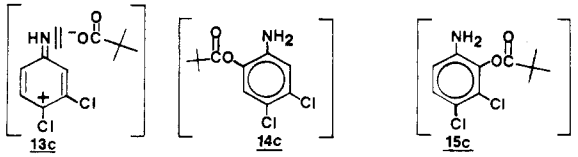
(15) Gassman, P. G.; Granrud, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1498–1499.
(16) Takeuchi, H.; Koyama, K. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1269–1273.

that the hydrolysis was biphasic in nature. At very short reaction times (<1 min), it was possible to detect an intermediate by HPLC (retention time 8.5 min, MeOH/H_2O:70/30). This is apparently **14a**. Two pseudo-first-order rate constants of $(5.3 \pm 0.5) \times 10^{-2}$ s^{-1} and $(1.8 \pm 0.2) \times 10^{-2}$ s^{-1} were obtained from UV data. HPLC results indicate that the smaller of the two rate constants is associated with the hydrolysis of **17a** and the larger rate constant is associated with the decomposition of the intermediate. The half-life of this intermediate (13 s) is such that it should be detectable during the decomposition of **1a** ($t_{1/2}$ = 44 s). In fact, an HPLC peak with a retention time identical with that of the intermediate observed during the hydrolysis of **17a** can also be observed at early reaction times (<1 min) during the hydrolysis of **1a** at this pH. These studies also confirmed that the half-life of **1a** under these conditions is ca. 40 s, which is in good agreement with the kinetic results obtained by UV spectroscopy. The decomposition of the apparent intermediate **14a** into **5a** does not significantly interfere with the measurement of the rate of decomposition of **1a** by UV spectroscopy because of the short half-life of the intermediate and the rather small absorbance changes associated with the **14a** → **5a** process.

At pH 1.0 and 40 °C, **17a** has a half-life of much less than 5 s. The intermediate can be observed easily by HPLC under these conditions, and it decomposes into **5a** (78 ± 4%) and **9a** (15 ± 1%) with a rate constant of $(2.2 \pm 0.2) \times 10^{-2}$ s^{-1} (eq 1). At this pH, HPLC results show that the formation of benzaldehyde is not associated with the decomposition of the intermediate but occurs almost instantly as **17a** undergoes hydrolysis. This provides support for our assignment of structure **14a** to the intermediate. The hydrolysis of **14a** may interfere more strongly in the measurement of the rate of decomposition of **1a** at this pH because of its longer lifetime, and examination of the rate data in Table I indicates that this may be the case at this pH, although the absorbance changes associated with the two processes at 233 nm (the wavelength chosen to monitor the decomposition of **1a**) are quite different and such that the hydrolysis of **1a** must dominate the observed absorbance changes.

The strong pH dependence of the yield of **5a** observed in the hydrolysis of **1a** may be due to protonation of the pivalate ion within the ion pair **12a** at low pH. The low yield of the phenol **9a** observed only at pH 1.0 is apparently due to hydrolysis of **14a** under these pH conditions and not due to attack of H_2O on the solvent separated ion pair **13a**.

The ion pair **13a** may be attacked by external nucleophiles to yield **7a** and **16**. The latter product is also observed during the hydrolysis of *N*-(sulfonatooxy)-*p*-chloroacetanilide.[2a] The products of the hydrolysis of **1c**, except **2c**, which is discussed below, can be explained by a similar mechanism. The aminophenols **9c** and **10c** may be formed either by attack of H_2O on the ion pair **13c** or by hydrolysis of the undetected esters **14c** and **15c**, but

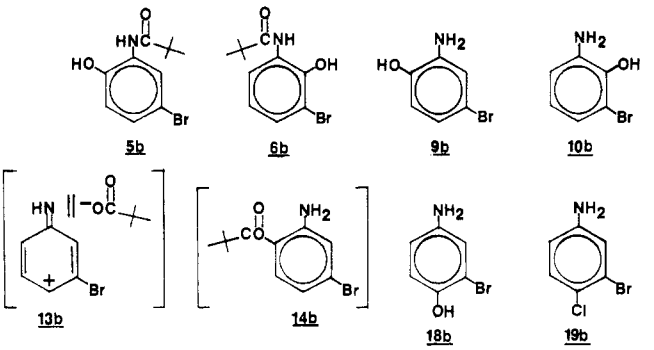


13c **14c** **15c**

they are not produced by hydrolysis of the pivalanilides **5c** and **6c**, which are stable to the reaction conditions. The relative yields of the two trichloroanilines **7c** and **8c** are somewhat surprising and certainly indicate that steric effects do not govern the formation of these products.

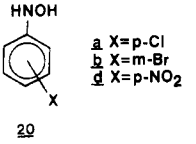
Previously we reported that the hydrolysis of **1b** yielded large amounts of **2b** (ca. 30%) and 2-bromo-1,4-benzoquinone, **3b** (ca. 15%).[3] Since **1b** does not have a good leaving group at the para position, as **1a** and **1c** do, **3b** cannot be formed by the mechanism of Scheme I, but must be produced in a redox process. We proposed a mechanism involving competitive homolysis and heterolysis of the N–O bond in which the amino radical formed by homolysis abstracted H• from one of the expected products of the heterolytic reaction, 4-amino-2-bromophenol (**18b**). Two successive H• abstractions would convert **18b** into a quinonimine, which would hydrolyze to form **3b**.[3] However, in demetalized buffers the yield of **2b** is reduced to ca. 3%, which is similar to the yield of **2c** obtained from **1c**, and **3b** is not detected at all under these conditions. It can be shown that both **2b** and **3b** are produced by a reaction involving trace amounts of metal ions. The effects of added Fe^{2+} and Fe^{3+} are discussed below.

The major hydrolysis products of **1b** in demetalized solutions include **18b** (19.4 ± 1.2% at pH 4.7, and 20.3 ± 0.7% at pH 1.0) and the two isomeric pivalanilides **5b** and **6b** (16.8 ± 1.0% and 6.9 ± 1.0%, respectively, at pH 4.7, 6.3 ± 0.3% and 4.2 ± 0.2% at pH 1.0). Minor products include 3-bromo-4-chloroaniline (**19b**) (ca. 2% yield), 2-amino-4-bromophenol (**9b**) (0.6 ± 0.2% at pH 4.7, 1.0 ± 0.1% at pH 1.0), and 2-amino-6-bromophenol (**10b**) (traces at both pH). The relative yields of **18b**, **9b**, and **10b** at



5b **6b** **9b** **10b** **13b** **14b** **18b** **19b**

pH 4.7 are consistent with the relative yields of the same three products derived from the Bamberger rearrangement of *N*-(3-bromophenyl)hydroxylamine (**20b**),[3] a reaction that is thought to involve a nitrenium ion intermediate.[17] The



a X=p-Cl
b X=m-Br
d X=p-NO_2

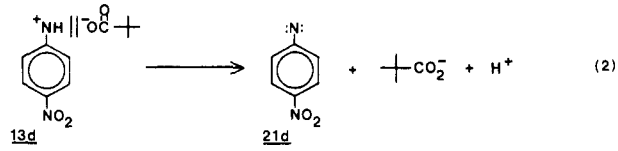
20

increased yield of **9b** at pH 1.0 indicates that some of this product is formed by hydrolysis of the undetected rearrangement product **14b** at this pH. It is now apparent that **1b** undergoes hydrolysis in demetalized solution via a heterolytic process, and there is no evidence for a significant homolytic process as we previously suggested.[3] The changes in the relative proportions of chlorinated and phenolic products observed for **1a–c** are consistent with the expected decrease in selectivity of the ion pairs **13a–c** toward attack by Cl^- and H_2O as these ions become more reactive. The predominant attack of external nucleophiles at the para position of **13b** was also noted for the corresponding *N*-acetylnitrenium ion[3] and appears to be a general characteristic of simple *N*-arylnitrenium ions in

(17) Bamberger, E. *Chem. Ber.* **1894**, *27*, 1347–1350, 1548–1557; **1895**, *28*, 245–251; **1900**, *33*, 3600–3622. Sone, T.; Tokuda, Y.; Sakai, T.; Shinkai, S.; Manabe, O. *J. Chem. Soc., Perkin Trans. 2* **1981**, 298–302.

which the para position is not blocked by a substituent.[2a]

Although the rate of decomposition of **1d** in demetalized solutions appears to be normal compared to the other members of the series, the reaction products are very different. Only traces of the "normal" hydrolysis products are observed. The major product is 4-nitroaniline, **2d**. Gassman and Campbell previously observed a similar tendency for *N*-*tert*-butyl-*N*-chloroanilines para substituted with strong electron-withdrawing groups to yield the corresponding anilines under ethanolysis conditions.[4] They suggested that a spin inversion from the singlet to triplet ion may be enhanced by increasing the positive charge on nitrogen and that the triplet ion then abstracted hydrogen from the solvent.[4] More recently, Ford and Scribner have reported MNDO calculations, which indicate that the singlet ions are the ground states (by >20 kcal) for most *N*-arylnitrenium ions.[18] Their results do indicate that the singlet–triplet energy difference does depend on the charge on nitrogen. However, recent measurements of the lifetimes of nitrenium and carbenium ions in aqueous solution suggest that the ion pairs **12d** and **13d** will not have a finite lifetime under our reaction conditions.[19] An alternative species that could lead to **2d** is the nitrene **21d**, which is the conjugate base of **13d** (eq 2). Hydrogen abstraction



(2)

by triplet aryl nitrenes is a well-documented reaction.[20] The minor azoxy product **11d** may also be formed by a nitrene reaction. Such compounds are often generated during the deoxygenation of nitro and nitroso aromatics.[21] Trapping studies indicate that triplet nitrenes are involved in the formation of these species.[22] Unlike aryl nitrenium ions, the triplet state is the ground state of most aryl nitrenes, including **21d**.[23] If **21d** is responsible for the observed products, it is not likely to be formed by deprotonation of **13d**, which is not expected to exist in aqueous media, but it may be generated directly from **1d** by either concerted or stepwise α-elimination processes. We are currently investigating the nature of this reaction.

The homolysis of the N–O bond of **1d**, a process suggested by Hoffman and co-workers to explain similar results in aliphatic systems,[5] appears to be ruled out by the available data. Such a process would yield the pivaloxy radical, which should rapidly lose CO_2 to generate the *tert*-butyl radical, which would then abstract hydrogen from the solvent.[24] In fact, a yield of pivalic acid of 70 ± 15% was observed under these conditions. Hydride abstraction from solvent by the singlet nitrenium ion[4] would also appear unlikely since this process would not be expected to be competitive with internal return of the tight ion pair to form the rearranged product **5d**. The minor yields of **2b** and **2c** observed in the hydrolysis reactions of **1b** and **1c** may be due to the same process that produces **2d** from **1d**, but it is not possible to rule out reduction by trace metal ions in these cases (see below).

Table III. Yields of Anilines 2 in Fe^{2+} Solutions at 40 °C[a]

ester	conditions	% yield of 2[b]
1a	pH 4.7, 10^{-3} M Fe^{2+}	39.7 ± 2.2
1b	pH 1.0, 10^{-3} M Fe^{2+}	70.7 ± 1.9
1b	pH 1.0, 10^{-4} M Fe^{2+}	55.9 ± 1.5
1b	pH 1.0, 10^{-5} M Fe^{2+}	30.3 ± 1.1
1b	pH 1.0, 10^{-6} M Fe^{2+}	9.4 ± 0.5
1b	pH 4.6, 10^{-3} M Fe^{2+}	57.0 ± 1.4
1b	pH 6.8, 10^{-3} M Fe^{2+}	51.0 ± 1.6
1c	pH 4.6, 10^{-3} M Fe^{2+}	55.5 ± 3.4
1c	pH 4.6, 10^{-3} M $K_4Fe(CN)_6$	10.9 ± 0.5
1c	pH 4.6, 10^{-3} $K_4Fe(CN)_6$ and 5×10^{-3} M KCN	6.5 ± 0.4
1d	pH 4.6, 10^{-3} M Fe^{2+}	95.0 ± 1.2

[a] Conditions, except for Fe^{2+} concentrations, were identical with those reported in Table II. $FeCl_2$ was used except when indicated. [b] Determined from HPLC peak integration.

Fe^{2+}-Induced Reduction. The decomposition of **1a–d** is remarkably changed by the addition of Fe^{2+}. In 10^{-3} M Fe^{2+} solutions, all four esters (initial concentration ca. 7.5×10^{-5} M) decompose completely in less than 1 min at 40 °C, and the corresponding anilines **2a–d** are the major decomposition products. Although **1d** yields **2d** as its major decomposition product both in the presence and absence of Fe^{2+}, the 3.0×10^4 rate acceleration in 10^{-3} M Fe^{2+} indicates that a new reaction has occurred. The rate accelerations observed in the presence of Fe^{2+} rule out mechanisms involving reduction by Fe^{2+} of intermediates generated in the hydrolysis reactions described above. The yields of the reduction products obtained in Fe^{2+} solutions under various conditions are given in Table III. Since the yields of **2** are considerably less than quantitative in some cases, we examined the reduction of **1a** more closely. No other characterizable product was detected, although a considerable amount of tarry residue was found.

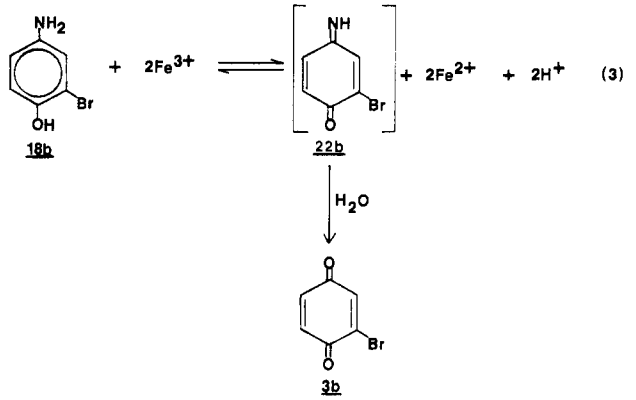
The data for **1c** indicate that strongly complexed Fe^{2+} does not cause reduction. The modest amount of reduction (10.9 ± 0.5%) observed in the presence of 10^{-3} M $K_4Fe(CN)_6$ is apparently caused by free Fe^{2+} formed by dissociation of $Fe(CN)_6^{4-}$. When excess KCN is added, the yield of **2c** drops to 6.5 ± 0.4%, which is only slightly larger than the yield of **2c** observed in the absence of Fe (3.2 ± 1.3%). The yields of **5c** and **8c** obtained in $K_4Fe(CN)_6$ solution (23.7 ± 0.8% and 12.5 ± 0.2%, respectively) and in $K_4Fe(CN)_6$ with excess KCN (26.5 ± 1.6% and 12.8 ± 0.4%, respectively) are comparable to the yields of **5c** and **8c** obtained in the absence of Fe (Table II). Similar results were obtained for other hydrolysis products. All measured rate constants for the decomposition of **1c** in the presence of $K_4Fe(CN)_6$ and in the absence of Fe are comparable and fall in the range $(3.0–3.5) \times 10^{-4}$ s^{-1}. Since we were unable to observe electrochemical reduction of **1** in cyclic voltammetric experiments and the oxidation potential of $Fe(CN)_6^{4-}$ is more favorable than that of Fe^{2+},[25] it appears that reduction of **1** occurs only after complexation of the ester with Fe^{2+}.

The yield of pivalic acid produced during the decomposition of **1b** in 0.1 N HCl and 10^{-3} M Fe^{2+} was 78 ± 13%, and the yield of the same product obtained from the de-

(18) Ford, G. P.; Scribner, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 4281–4291.
(19) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 4689–4691 and 4691–4692. Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361–1372. Fishbein, J. C.; McClelland, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 2824–2825.
(20) Smith, P. A. S. In *Azides and Nitrenes*; Scriven, E. F. V., Ed., Academic: New York, 1984; pp 95–204.
(21) Buckler, S. A.; Doll, L.; Lind, F. K.; Epstein, M. *J. Org. Chem.* **1962**, *27*, 794–798. Bunyan, P. J.; Cadogan, J. I. G. *J. Chem. Soc.* **1963**, 42–50.
(22) Abramovitch, R. A.; Challad, S. R. *J. Chem. Soc., Chem. Commun.* **1972**, 964–966.
(23) Wasserman, E. In *Progress in Physical Organic Chemistry*; Wiley: New York, 1971; Vol. 8, pp 319–336. Hebden, J. A.; McDowell, C. A. *J. Magn. Reson.* **1971**, *5*, 115–133.
(24) Kochi, J. K. In *Free Radicals*; Kochi, J. K., Ed., Wiley: New York, 1973; Vol. II, pp 665–710.
(25) Clark, W. M. *Determination of Hydrogen Ions*, 2nd ed.; Williams and Wilkins: Baltimore, 1922; p 387.

composition of **1d** at pH 4.7 and 10^{-3} M Fe^{2+} was 100 ± 15%. No isobutane could be detected by GC analysis of the headspace above reaction mixtures of **1b** containing Fe^{2+}. Control experiments showed that much less than a 5% yield of isobutane could easily have been detected. These experiments show that homolysis of the N–O bond of 1 does not play an important role in the Fe^{2+}-induced reduction.

The data for **1b** shown in Table III indicate that at low concentration of Fe^{2+} a yield of reduction product in considerable excess over the Fe^{2+} concentration can be observed. For example, the ca. 30% yield of **2b** obtained in 10^{-5} M Fe^{2+} is 2.3-fold larger than the initial concentration of Fe^{2+}. This can only happen if Fe^{2+} is regenerated during the reaction. Under these same conditions, a considerable yield of 2-bromo-1,4-benzoquinone (**3b**) is always observed. This product is absent if Fe^{2+} is in excess over **1b**. Control experiments showed that 4-amino-2-bromophenol (**18b**), one of the major hydrolysis products of **1b**, is oxidized by Fe^{3+} to **3b** under our reaction conditions, presumably through the quinoneimine, **22b** (eq 3).

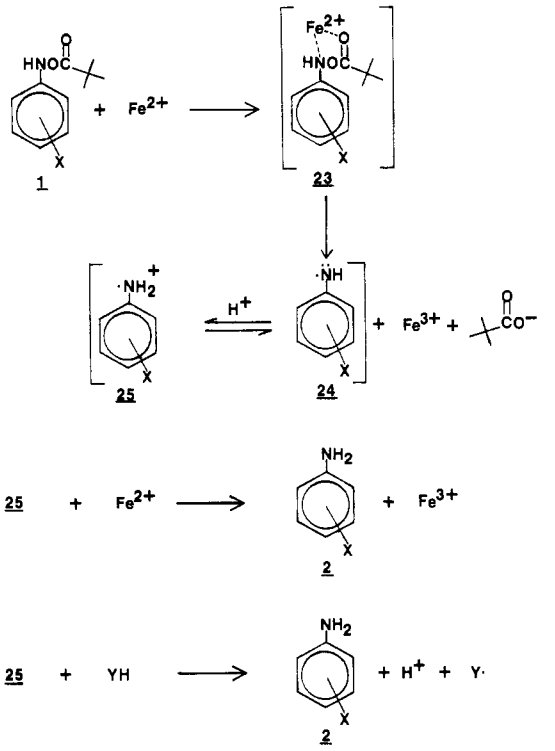


In another control experiment, the incubation of **1b** with 10^{-4} M Fe^{3+} at pH 1.0 led to a 36 ± 2% yield of **2b** with coproduction of **3b** (16 ± 4%). These experiments demonstrate that **18b** generates Fe^{2+} by reaction with Fe^{3+} and that the Fe^{2+} that is generated can then lead to reduction of **1b**. As little as 10^{-5} M Fe would have produced the yields of **2b** and **3b** we previously reported and interpreted in terms of competition between heterolysis and homolysis of the N–O bond.[3]

Pivalic acid can be produced from 1 under these conditions either by heterolysis of the N–O bond or by ester hydrolysis, both accelerated by Fe^{2+}. It is well known that transition metal ions can catalyze ester hydrolysis, particularly in cases in which the metal ion is chelated to the ester.[26] It is also known that hydroxylamine, *N*-alkyl derivatives of hydroxylamine, and *N*-alkyl-*N*-chloroamines are reduced by Fe^{2+} and other metal ions to ammonia and the corresponding amines.[27] However, control experiments show that the hydroxylamines **20a** and **20d**, which would be the products of the ester hydrolyses of **1a** and **1d**, are stable under the reaction conditions and do not undergo reduction in the presence of Fe^{2+}.

A mechanism for the reduction that fits the available data is shown in Scheme II. Complexation of Fe^{2+} and 1 yields an intermediate (**23**) within which electron transfer can occur. Our data do not address the timing of electron

Scheme II



transfer and bond cleavage events, but it is clear that pivalate ion is formed rather than the pivaloxy radical. The neutral arylamino radical **24** will be in equilibrium with the radical cation **25**. The pK_a of the unsubstituted radical cation (**25**, X = H) is 7.0, and this transient species does survive long enough in aqueous media for equilibrium with its neutral form.[28] It is likely that under our reaction conditions **25** is the predominant species at pH 1.0 and 4.6 for all but possibly **25d**, while at pH 6.7 both **25** and **24** are expected to be present in significant concentrations. The neutral radical may also exist in a complex with Fe^{3+}.[27,29] The more electron deficient **25** can be reduced by electron transfer from Fe^{2+} or by H• abstraction from some species in solution. The radical cation of aniline is rapidly reduced by both SO_3^{2-} and HSO_3^- in aqueous solution.[30] The one-electron reduction potentials of SO_3^- to form SO_3^{2-} and HSO_3^- (0.63 and 0.84 V, respectively) bracket that of Fe^{3+} (0.77 V),[31] so reduction of **25** by Fe^{2+} is certainly reasonable, particularly since **25a–d** are expected to be stronger oxidizing agents than the unsubstituted radical cation. The neutral aniline radical (**24**, X = H) was not reduced by either SO_3^{2-} or HSO_3^-.[30] The product yields shown in Table III are consistent with reduction via **25**. At pH 4.6 the highest yield of reduction product was observed for **1d**, the radical cation of which (**25d**) would be the strongest oxidizing agent of the series. The yield of **2b** derived from **1b** in 10^{-3} M Fe^{2+} decreases with increasing pH as would be expected if **25b** is the species reduced. The fate of 1 not reduced to **2** is unknown, but the tarry residue isolated from the product study with **1a** indicates that polymerization competes with reduction.[32]

(26) Sutton, P. A.; Buckingham, D. A. *Acc. Chem. Res.* **1987**, *20*, 357–364 and references therein.

(27) Albisetti, C. J.; Coffman, D. D.; Hoover, F. W.; Jenner, E. L.; Mochel, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 1489–1496. Minisci, F.; Galli, R.; Cecere, M. *Tetrahedron Lett.* **1965**, 4663–4667; **1966**, 3163–3166. Sosnovsky, G.; Rawlinson, D. J. In *Advances in Free Radical Chemistry*; Williams, G. H., Ed.; Academic: New York, 1972; Vol. IV, pp 203–284.

(28) Land, E. J.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2027–2037. Qin, L.; Tripathi, G. N. R.; Schuler, R. H. *Z. Naturforsch., A: Phys. Phys. Chem., Kosmophys.* **1985**, *40A*, 1026–1039.

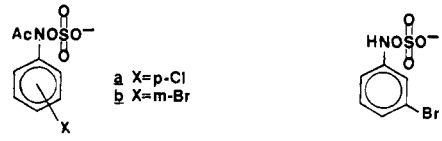
(29) Michejda, C. J.; Campbell, D. H.; Sieh, D. H.; Koepke, S. R. In *Organic Free Radicals*; ACS Symposium Series 69; Pryor, W. A., Ed.; American Chemical Society: Washington, DC, 1978; pp 292–308.

(30) Neta, P.; Huie, R. E. *J. Phys. Chem.* **1985**, *89*, 1783–1787.

(31) Huie, R. E.; Neta, P. *J. Phys. Chem.* **1984**, *88*, 5665–5669.

The second reduction pathway for **25** may not be very important in the presence of sufficient Fe^{2+}. A 5-fold molar excess of thiophenol has a barely discernable effect on the yield of **2a** observed during the reduction of **1a** in 10^{-3} M Fe^{2+} at pH 4.7, increasing the yield from 39.7 ± 2.2% to 42.6 ± 1.9%. This is not unexpected since both neutral and cationic arylamino radicals are relatively poor $H^{\bullet}$ abstracting agents.[33]

N-Acylated materials similar to **1a–d** are not subject to rapid reduction by Fe^{2+}. *N*-(Sulfonatooxy)-4-chloroacetanilide (**26a**) yields only 4.4% of the reduction product 4-chloroacetanilide in 0.25 M $FeCl_2$ at pH 4.6.[2a] *N*-(Pivaloyloxy)-3-bromoacetanilide (**4b**) undergoes little reduction (ca. 2–4%) over a period of 48 h in 10^{-3} M Fe^{2+} at pH 4.7. Neither of these materials undergoes rapid decomposition under these conditions, so competition between Fe^{2+}-mediated reduction and other processes cannot explain their lack of reduction. It is likely that these species do not chelate Fe^{2+} well since the electron pair on N will not be as readily available as in **1**. Surprisingly *N*-(3-bromophenyl)hydroxylamine-*o*-sulfonate (**27b**), which is generated during the hydrolysis of *N*-



26 **27b**

(sulfonatooxy)-3-bromoacetanilide (**26b**) in 0.1 M HCl,[3] is also relatively inert to reduction by Fe^{2+}. At 80 °C in 10^{-3} M Fe^{2+} at pH 1.0, the decomposition of **26b** yields only 4.8 ± 0.8% of **2b**. We have previously shown that >90% of **26b** is converted into **27b** at this pH and temperature.[3] At 40 °C similar yields of **2b** were obtained. In the absence of Fe^{2+} no reduction product is observed.[3] The low yield of **2b** may be due to competition between reduction and unassisted N–O bond heterolysis since **27b** decomposes in aqueous solution about 10^3-fold more rapidly than **1b**. Electron transfer from Fe^{2+} to the anionic sulfate ester may also be more difficult than to the neutral pivalic acid ester. We are continuing our studies on the reduction reactions of **1a–d** with other transition metal ions to test the generality of the reaction.

Our results indicate that the potentially carcinogenic polycyclic analogues[1] of **1a–d** will decompose in aqueous media via heterolysis of the N–O bond to produce nitrenium ion intermediates in the absence of reducing agents. As a result of investigations on a number of related systems including sulfuric, sulfonic, and carboxylic acid esters of *N*-hydroxyacetanilides and *N*-chloroaniline derivatives,[2–4,14,15] it is clear that the predominant mode of reaction of these species is heterolytic formation of *N*-arylnitrenium ions. These electrophilic species remain the most likely candidates for reactions with DNA that lead to cancer. However, we have discovered different modes of reaction, including the Fe^{2+}-mediated reductions demonstrated here, that lead to other reactive species including radicals[6] and quinone imines.[2a,b] Whether these species play a role in the carcinogenic properties of metabolites of aromatic amines and amides is not currently known, but this possibility cannot be dismissed. We have previously pointed out that not all adducts from in vivo and in vitro experiments are easily explainable in terms of the properties of *N*-arylnitrenium ions.[2a]

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Supplementary Material Available: Synthesis, isolation, and characterization of the hydrolysis products **3c**, **5a–d**, **6b**, **6c**, **9a** (4 pages). Ordering information is given on any current masthead page.

(32) A referee has suggested that metal ion catalyzed dismutation of **25** may lead to reduced (anilines) and oxidized products (azo and azoxy products). However, no such oxidation products were detected in the presence of Fe^{2+} in the two cases (**1a**, **1d**) in which such products were sought.

(33) Danen, W. C.; Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 783–789. Nelson, S. F. In *Free Radicals*; Kochi, J. K., Ed., Wiley: New York, 1973; Vol. II, pp 527–593.

Oxidation of *O*-Alkylhydroxylamines with Bis[[(*m*-(trifluoromethyl)phenyl]sulfonyl] Peroxide

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A series of *O*-alkylhydroxylamines was oxidized with [*m*-(trifluoromethyl)phenyl]sulfonyl peroxide to give the corresponding alcohol and carbonyl compound. The evidence presented suggests that these products of N–O cleavage arise from decomposition of a hyponitrite ester intermediate produced by nucleophilic trapping of an *N*-alkoxy nitrenium ion.

In attempts to prepare electrophilic aminating agents, we examined the oxidations of O-substituted hydroxylamines, **1**, with [*m*-(trifluoromethyl)phenyl]sulfonyl peroxide (**2**, *m*-TFBSP). We hoped by this method to access O-substituted *N*-(arylsulfonoxyl)hydroxylamines, **3**, that might be useful as aminating agents toward π-electron donors (eq 1). Early results suggested that the intermediate arylsulfonoxylamines, **3**, were quite reactive. We thus undertook an investigation of the oxidation to learn more of their chemistry.

$$\underset{\mathbf{1}}{2RONH_2} + \underset{\mathbf{2}}{(3\text{-}CF_3C_6H_4SO_2O)_2} \rightarrow \underset{\mathbf{3}}{RONHOSO_2C_6H_4CF_3} + \underset{\mathbf{4}}{RONH_3^+ArSO_3^-} \quad (1)$$

Results and Discussion

O-Benzylhydroxylamine, **1a**, was chosen as a typical *O*-alkylhydroxylamine. Oxidation with **2** in methylene chloride at −30 °C gave benzyl alcohol, **5**, and *O*-benzylbenzaldoxime, **6**, as the major products in addition to the

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