JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

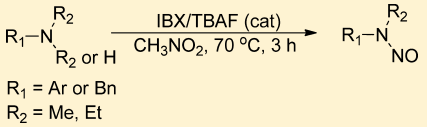
Nitromethane with IBX/TBAF as a Nitrosating Agent: Synthesis of Nitrosamines from Secondary or Tertiary Amines under Mild Conditions

Hima K. Potturi, Ras K. Gurung, and Yuqing Hou*

Meyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry and Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901, United States

Supporting Information

ABSTRACT: Aliphatic or aromatic *N,N*-disubstituted nitrosamine was generated in fair to excellent yield from the reaction of a secondary or tertiary amine with *o*-iodoxybenzoic acid (IBX) or *o*-iodosylbenzoic acid (IBA)/R_4NX (X = halide) and nitromethane. The product yield was strongly influenced by both the halide of R_4NX and iodanes. IBX gave a higher yield than IBA, while the halides follow $F^- > Cl^- > Br^- \sim I^-$. Nitrous acid formed in situ from nitromethane and IBX (or IBA)/halides is likely responsible for the observed reaction.



INTRODUCTION

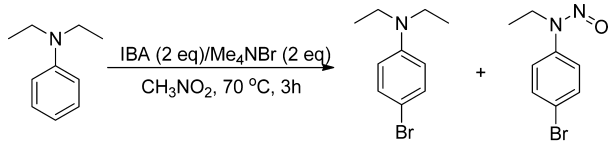
N-Nitrosamines have been known as potent carcinogens and mutagens in lab animals.[1,2] Human exposure to such compounds mainly comes from processed meat products,[3] beverages,[4] cosmetic products,[5] and tobacco smoking.[6] The carcinogenicity and/or mutagenicity of *N*-nitrosamines are believed to stem from the DNA-alkylation reactions of their diazonium metabolites through cytochrome P450 enzymes.[7]

Additionally, *N*-nitrosamines are potential nitric oxide donors, exhibiting intriguing biological activities.[8] *N*-Nitrosamines are also important intermediates for other useful organic compounds, such as hydrazines,[9] and biologically active compounds, such as sydnones.[10] They are conventionally synthesized through reactions of amines with either sodium nitrite/acid[11−16] or alkyl nitrites.[17,18] Sodium nitrite/acid method usually requires the use of a strong acid, such as HCl, limiting the use of this method when there is an acid-labile group on the substrate. These methods often lead to unwanted ring nitration and ipso-substitution reactions as well.[17,19] Various other nitrosating agents, such as lithium amides/NO,[20] nitrosonium tetrafluoroborate,[21] oxyhyponitrite,[22] trichloronitromethane,[23] and Fremy's salt,[24] have been reported earlier. However, an efficient synthetic protocol for nitrosamines with easily available reagents under mild conditions will be a useful addition to the existing methods.

Hypervalent iodine compounds are becoming increasingly popular synthetic tools in organic chemistry because of their low toxicity, ready availability, and ease in handling.[25,26] Particularly, *o*-iodoxybenzoic acid (IBX, **1**) has quickly become the reagent of choice for selective oxidation of alcohols to aldehydes and ketones. Lately, IBX/tetraethylammonium bromide (TEAB) has been reported to brominate activated aromatic compounds.[27]

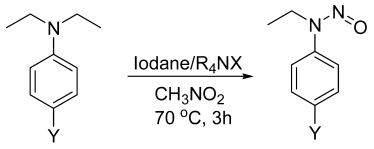
However, *o*-iodosylbenzoic acid (IBA, **2**) has not attracted much attention from synthetic organic chemists, primarily because it is much less reactive than IBX. We reasoned that since IBA is a much weaker oxidant than IBX, the combination of IBA and a quaternary ammonium bromide may provide a better regioselectivity than the corresponding IBX combination. Thus, treating *N,N*-diethylaniline (**3**) with two equivalents of IBA/TMAB in nitromethane produced the expected *p*-bromo-*N,N*-diethylaniline (**4**) at 80%. Surprisingly, an *N*-nitrosation−dealkylation product, 4-bromo-*N*-ethyl-*N*-nitrosoaniline (**5**), was also observed (Scheme 1). The reaction also turned all IBA into *o*-iodobenzoic acid. A search in the literature showed that only two brief reports of *N*-nitrosation of secondary amines by trichloronitromethane[23] or bromonitromethane[28] appeared almost two decades ago. The first reported reaction, however, was a result of decomposition of trichloronitromethane into nitrosyl chloride, which was believed to be the active nitrosating agent,[23] while the nitrosation by bromonitromethane was a result of substitution of the bromine by a secondary amine followed by nitrite formation.[28] To our best knowledge, nitromethane itself has never been reported as the source of nitroso group for *N*-nitrosation reaction. We have, therefore, explored the scope of this *N*-nitrosamine formation reaction and found that this is an effective, fair to high yield, and selective method to make *N*-nitrosamine under mild conditions.

Scheme 1. Unexpected Formation of *N*-Nitrosation−Dealkylation Product, 5



Received: November 3, 2011
Published: December 7, 2011

Table 1. Effect of Halides and Iodanes on *N*-Nitrosation−Dealkylation



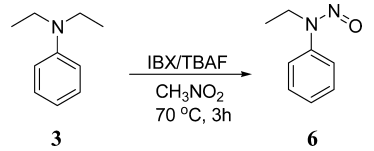
3, Y = H
4, Y = Br

6, Y = H
5, Y = Br

entry	substrate	iodane/R_4NX (equiv)	product	yield (%)
1	**3**	IBA/$(CH_3)_4NBr$ (2)	**5**	20
2	**4**	IBA/$(CH_3)_4NBr$ (2)	**5**	26
3[a]	**4**	IBA/$(CH_3)_4NBr$ (2)	**5**	26[b]
4	**4**	IBA/$(CH_3)_4NBr$ (4)	**5**	45
5	**4**	IBA/$(CH_3)_4NBr$ (8)	**5**	67
6	**4**	PhI=O/$(CH_3)_4NBr$ (2)	**5**	7
7	**4**	PhI(OH)(OTs)/$(CH_3)_4NBr$ (2)	none	0
8	**4**	$PhI(CO_2CF_3)$/$(CH_3)_4NBr$ (2)	none	0
9	**4**	none/$(CH_3)_4NBr$ (2)	none	0
10	**4**	IBA/none	none	0
11	**3**	IBA/$(n\text{-}Bu)_4NPF_6$	none	0
12	**3**	IBA/$(n\text{-}Bu)_4NBF_4$	none	0
13	**3**	IBA/$(CH_3)_4NI$ (2)	**6**	19
14	**3**	IBA/$(C_2H_5)_4NCl{\cdot}H_2O$ (2)	**6**	46
15	**3**	IBA/$(C_2H_5)_4NCl{\cdot}H_2O$ (8)	**6**	NA[c]
16	**3**	IBA/$(n\text{-}C_4H_9)_4NF$ (2)	**6**	53
17	**3**	IBA/$(n\text{-}C_4H_9)_4NF$ (4)	**6**	87
18	**3**	IBX/$(n\text{-}C_4H_9)_4NF$ (2)	**6**	91
19[d]	**3**	IBX/$(n\text{-}C_4H_9)_4NF$ (2)	none	0
20	**3**	IBX/$(n\text{-}C_4H_9)_4NF$ (1)	**6**	59
21	**3**	IBX/$(n\text{-}C_4H_9)_4NF$ (1)	**6**	58[e]
22	**3**	IBX/$BnMe_3NOH$	none	0

[a]Mixture of IBA and $(CH_3)_4NBr$ was added in small portions over a period of 6 h. [b]A substantial increase in the yield (15%) of aromatic bromination product, 2,4-dibromo-*N*,*N*-diethylaniline (**30**), was observed. [c]A complex mixture of products was observed. No isolation of **6** was attempted. [d]Reaction was performed at room temperature. [e]THF from the solution of TBAF was evaporated prior to the addition of other reagents.

Table 2. Effect of Varying Amounts of TBAF on the Yield of 6



3 **6**

entry	molar ratio of **3**, IBX, and TBAF	yield (%) of **6**
1	1:2:2	91
2	1:2:1	86
3	1:2:0.5	82
4	1:2:0.25	53[a]
5	1:2:0.25	80[b]

[a]*N*,*N*-diethylaniline was recovered in 24%. [b]The reaction time was prolonged to 8 h.

RESULTS AND DISCUSSION

Replacing nitromethane with acetonitrile as the reaction medium under identical conditions eliminated the formation of **5**, although the bromination went as expected, confirming that nitromethane is not only a solvent but also a reactant in the formation of **5**. The reaction was further explored with different substrates, iodanes, and quaternary ammonium salts.

While the ratio of iodane to quaternary ammonium salt was maintained at 1:1, the ratio of substrate to iodane/quaternary ammonium salt was varied to see the effect of such alterations (Table 1). The use of compound **4**[29] as the starting material or portionwise addition of IBA and TMAB did not increase the yield of **5** significantly (Table 1, entries 2 and 3). Higher yield of **5** was achieved when increased amount of IBA/Me_4NBr was used (Table 1, entries 4 and 5). When a large excess of IBA/TMAB was used, a number of unidentified side products were also produced.

Replacing IBA with iodosobenzene, PIFA, or Koser's reagent yielded little or no **5** (Table 1, entries 6−8), and no **5** was observed in the absence of IBA, TMAB, or halide (Table 1, entries 9−12). Little difference in the yield was observed with TMAI (Table 1, entry 13), possibly because of the fast oxidation of iodide to iodine by IBA, consequently leading to low product yield. Much better yields were obtained when

dx.doi.org/10.1021/jo202276x | J. Org. Chem. 2012, 77, 626−631

TEAC or TBAF were used (Table 1, entries 14 and 16), with IBA/TBAF providing a much cleaner reaction. Surprisingly, 2 equiv of IBX/TBAF was sufficient to induce a clean *N*-nitrosation−dealkylation reaction with an excellent yield at 70 °C (Table 1, entry 18), although no reaction was observed at room temperature (Table 1, entry 19). A small amount of THF from the commercial TBAF solution did not affect the yield of **6** (Table 1, entries 20 and 21). Thus, the yield of nitrosamine is greatly affected by the nature of the halides, following this order: $F^- > Cl^- > Br^- \approx I^-$. This might be attributed to the nucleophilicity or basicity of the halides. When **3** was treated with IBX/benzyltrimethylammonium hydroxide in nitromethane, no reaction was observed (Table 1, entry 22). Thus, it is reasonable to believe that the superiority exhibited by fluoride is due to its strongest ability to form a complex with IBX while not being oxidized easily.

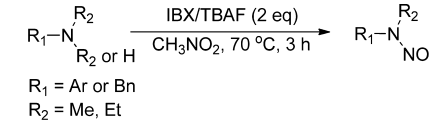
To determine if fluoride is functioning as a catalyst, a series of experiments with varying amounts of TBAF were carried out (Table 2). The results clearly show that fluoride is acting as a catalyst in the reaction, although a stoichiometric amount of fluoride provided a slightly better yield.

Experiments were also performed on different amines to evaluate the scope of the reaction (Table 3). While **7**, **9**, and **10** reacted with IBX/TBAF to provide the expected products in good yield (Table 3, entries 1, 2, and 3), the treatment of **11**−**13** with IBX/TBAF generated complex mixtures (Table 3, entries 4−6). No nitrosamines were detected by NMR, although all the starting materials were all consumed. Our attempt to detect *n*-decylbenzene in the case of **12** also failed. A low yield of 4-(*N*-methyl-*N*-nitrosoamino)pyridine (**15**) was isolated when **14** was subjected to the same treatment (Table 3, entry 7). An interesting observation was that no reaction occurred when **16** was used as the substrate (Table 3, entry 8), indicating that this method should exhibit regioselectivity between simple amines and amides. Indeed, treating 4-acetamido-*N*,*N*-diethylaniline (**17**) with IBX/TBAF yielded **18** in 41% with no nitrosation of the amide functionality. When **19** was subjected to the same treatment, 29% of **20** and 23% of benzaldehyde were obtained, indicating a competition between the demethylation and debenzylation of the intermediate (Table 3, entry 10; see also mechanism below). Lastly, the reaction may also be initiated with other 1° nitroalkanes as shown by our test reaction with 1-nitropropane (Table 3, entry 11).

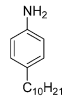
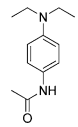
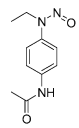
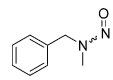
To further understand the mechanism, two more experiments were carried out. (1) Treating α-nitrotoluene (**21**) with IBX/TBAF in acetonitrile in the absence of amine produced benzaldehyde (isolated as its 2,4-dinitrophenylhydrazone (**22**) in 17% yield). (2) Benzylamine (**23**) reacted with IBX/TBAF in nitromethane to afford benzyl 2-iodobenzoate (**24**) in 22% yield.[30,31] These results indicate that the α-position of the 1° nitroalkane was oxidized and nitrous acid is a side product of the oxidation.

Previously, Barton et al. reported that *m*-iodoxybenzoic acid and *N*,*N*,*N*′,*N*′-tetramethyl-*N*″-*t*-butyl-guanidine induced the conversion of secondary nitroalkane into a ketone.[32] During the reaction, a nitrite ion was released through the oxidation of the conjugate anion of nitroalkanes by *m*-iodoxybenzoic acid.[32] Loeppky et al. have studied *N*-nitrosation−dealkylation reaction of tertiary amines with nitrous acid in great detail and proposed that a radical cation was involved in the dealkylation step.[33−35] Our observations agree with the mechanisms proposed in these reports. However, fluoride does not act as a base in the *N*-nitrosation−dealkylation but more likely forms a complex with IBX to induce the reaction. Based on the observations discussed above and literature reports, a plausible mechanism is proposed for this reaction (Scheme 2), illustrated with IBX/fluoride as an example. At stage 1, fluoride and IBX form a complex, **25**, which then reacts

Table 3. Effect of Substrates on the Yield of Nitrosamines



R_1 = Ar or Bn
R_2 = Me, Et

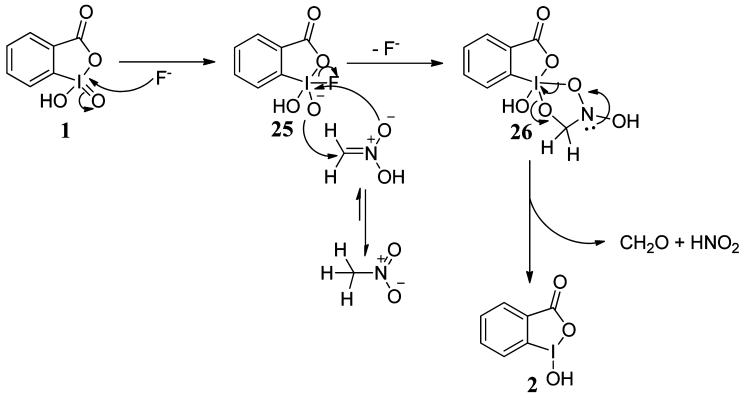
Entry	Substrate	Product	Yield%
1	 **7**	 **8**	90
2	 **9**	 **6**	93
3[a]	 **9**	 **6**	82
4	 **10**	 **8**	93
5	 **11**	NA[b]	0
6	 **12**	NA[b]	0
7	 **13**	NA[b]	0
8	 **14**	 **15**	27
9	 **16**	NR[c]	0
10	 **17**	 **18**	41
11	 **19**	 **20**	29[d]
12	 **3**	 **6**	85[e]

[a]Only 1.2 equiv of IBX/TBAF was used. [b]Starting material was all consumed, but *N*-nitrosamine was not detected with NMR. [c]Starting material was recovered. [d]Benzaldehyde was also observed by ^{1}H NMR in the crude product. [e]1-Nitropropane was used as the solvent.

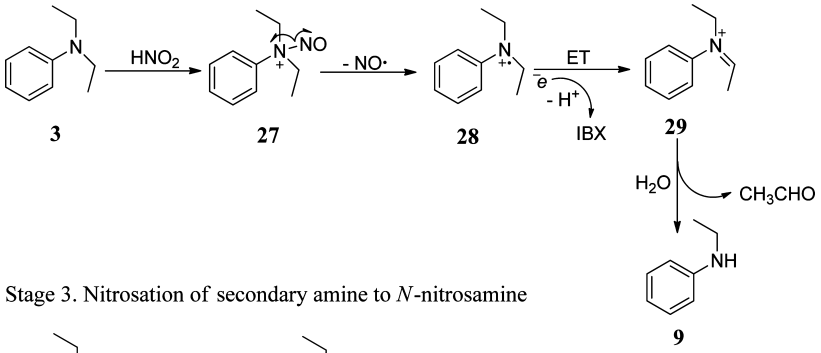
dx.doi.org/10.1021/jo202276x | *J. Org. Chem.* 2012, 77, 626−631

Scheme 2. Plausible Reaction Mechanism for the Observed *N*-Nitrosation−Dealkylation

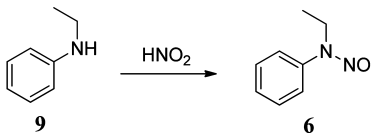
Stage 1. Generation of nitrous acid



Stage 2. Generation of secondary amine through *N*-nitrosation and oxidative dealkylation



Stage 3. Nitrosation of secondary amine to *N*-nitrosamine



with nitromethane's tautomer to form cyclic intermediate **26**. The decomposition of **26** generates formaldehyde, nitrous acid, and IBA. At stage 2, nitrous acid reacts with **3** to form a quaternary *N*-nitrosammmonium ion (**27**), which goes through a homolytic bond cleavage to release an NO radical and a radical cation, **28**. Radical cation **28** can be further oxidized by IBX through an electron transfer mechanism to form iminium ion, **29**. Hydrolysis of **29** leads to the formation of a secondary amine, **9**. At stage 3, **9** reacts with another molecule of nitrous acid to form the final product, **6**. This mechanism in Scheme 2 calls for 2 equiv of in situ generated nitrous acid to complete the reaction with a tertiary amine as the substrate, whereas only 1 equiv of nitrous acid is needed for a secondary amine. This is also supported by our observation (Table 3, entry 3).

CONCLUSIONS

Nitromethane is an inexpensive, stable solvent for organic reactions. However, under certain conditions, it acts as an excellent, regioselective nitrosating reagent for amines. Secondary or tertiary amines reacted with IBX (or IBA)/R_4NX (X = halide) and nitromethane to form nitrosamines in fair to excellent yields, whereas primary amines produced complex mixtures. The yield of the product was strongly influenced by both the halide of R_4NX and the structures of the iodanes. IBX gave a higher yield than IBA, whereas other iodanes gave very low to zero yield of *N*-nitrosamines. For the halides, the following order has been observed: $F^- > Cl^- > Br^- \sim I^-$. Fluoride is acting as a catalyst in this reaction. While this reaction occurs on amines, it does not nitrosate amides, thus providing a good regioselectivity between amines and amides. The reaction likely follows the mechanism of oxidative Nef reaction by generating nitrous acid in situ, which subsequently reacts with secondary or tertiary amines to provide the final product.

EXPERIMENTAL SECTION

All the reagents, solvents, and starting materials were used as received from commercial suppliers without further purification. ^{1}H NMR or ^{13}C NMR spectra were recorded on a Varian Mercury 400 spectrometer at 400 or 100 MHz, respectively, in $CDCl_3$, unless otherwise indicated. Iodosobenzene,[36] Koser's reagent,[37] IBA,[38] IBX,[39] 4-bromo-*N*,*N*-diethylaniline,[29] and *N*-(4-Diethylamino-phenyl)-acetamide[40] were synthesized by following previously reported procedures in the literature and characterized with ^{1}H NMR.

Typical Procedure for the Formation of *N*-Nitrosamine. In a 50 mL round-bottom flask, *N*,*N*-diethylaniline (1 mmol), IBX (2 mmol), and TBAF (2 mmol, in 1 M THF solution) were mixed with nitromethane (15 mL). The reaction mixture was heated to 70 °C and maintained at this temperature for 3 h. The mixture was cooled to room temperature, and 20 mL of saturated sodium bicarbonate solution was added. The crude product was extracted with ethyl ether, evaporated, and chromatographed to afford the pure product.

4-Bromo-*N*-ethyl-*N*-nitrosoaniline (5). Spectral data: ^{1}H NMR δ 1.09 (t, J = 7.2 Hz, 3H), 3.97 (q, J = 7.2 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H); ^{13}C NMR δ 11.8, 38.8, 120.7, 127.7, 138.6, 140.4. HRMS calculated for $C_8H_{10}N_2OBr$, 228.9976; found, 228.9977.

dx.doi.org/10.1021/jo202276x | J. Org. Chem. 2012, 77, 626−631

***N*-Ethyl-*N*-nitrosoaniline (6).** Spectral data: ^{1}H NMR δ 1.19 (t, J = 7.2 Hz, 3H), 4.08 (q, J = 7.2 Hz, 2H), 7.36 (dd, J = 7.2 Hz, 1.2 Hz, 1H), 7.48 (m, 2H), 7.53 (m, 2H); ^{13}C NMR δ 11.93, 39.42, 119.78, 127.54, 129.73, 141.64. ^{13}C NMR matches with literature report.[41]

***N*-Methyl-*N*-nitrosoaniline (8).** Spectral data: ^{1}H NMR δ 3.46 (s, 3H), 7.36 (m, 1H), 7.48 (m, 2H), 7.53 (m, 2H); ^{13}C NMR δ 31.4, 119.2, 127.3, 129.5. ^{1}H NMR matches with literature report.[12]

4-(*N*-Methyl-*N*-nitrosoamino)pyridine (15). Spectral data: ^{1}H NMR δ 3.40 (s, 3H), 7.54 (dd, J = 4.8 Hz, 1.6 Hz, 2H), 8.76 (dd, 4.8 Hz, 1.6 Hz, 2H); ^{13}C NMR δ 29.0, 111.4, 151.2. HRMS calculated for $C_6H_7N_3O$, 137.05892; found, 137.06048.

***N*-(4-(*N*-Ethyl-*N*-nitrosoamino)phenyl)acetamide (18).** Spectral data: ^{1}H NMR (DMSO-d_6) δ 1.01 (t, J = 8 Hz, 3H), 2.05 (s, 3H), 4.01(q, J = 8 Hz, 2H), 7.52 (d, J = 8 Hz, 2H), 7.71 (d, J = 8 Hz, 2H), 10.11 (s); ^{13}C NMR (DMSO-d_6) δ 11.8, 24.5, 120.1, 121.1, 136.2, 139.2, 168.9. HRMS calculated for $C_{10}H_{14}N_3O_2$ (M + H), 208.10860; found, 208.10733.

***N*-Methyl-*N*-nitrosobenzylamine (20) (*E*/*Z* = 62:38).** Spectral data: ^{1}H NMR δ 2.94 (*E*, s, 3H), 3.68 (*Z*, s, 3H), 4.80 (*Z*, s, 3H), 5.30 (*E*, s, 3H), 7.13 (*Z*, m, 2H), 7.25−7.40 (m, 5H (*E*), 3H (*Z*)); ^{13}C NMR δ 30.2 (*E*), 38.7 (*Z*), 48.0 (*Z*), 128.2 (*Z*), 128.3 (*E*), 128.6 (*Z*), 128.8 (*E*), 129.1 (*Z*), 129.3 (*E*), 134.0 (*Z*), 134.7 (*E*). ^{13}C NMR matches with literature report.[41]

Benzaldehyde 2,4-Dinitrophenylhydrazone (22). In a round-bottom flask, α-nitrotoluene (0.137 g, 1 mmol), IBX (0.56 g, 2 mmol), and TBAF (2 mmol) were mixed with 20 mL of acetonitrile, and the mixture was stirred at 70 °C. After 3 h, the mixture was cooled to room temperature, and 30 mL of saturated sodium bicarbonate solution was added. The crude product was extracted with 40 mL of ether. The ether was evaporated on a rotovap at room temperature under low vacuum to minimize the evaporation of benzaldehyde. The crude product was then dissolved in 20 mL of ethanol. To this solution, 2,4-dinitrophenylhydrazine (0.198 g, 1 mmol) and concentrated HCl (2 mL) were added, and the reaction mixture was refluxed for 3 h. The reaction was stopped and neutralized. The crude product was obtained by evaporating solvent in vacuo. Pure benzaldehyde 2,4-dinitrophenylhydrazone was obtained by recrystallization from ethanol and water (0.048 g, 17%). Spectral data: ^{1}H NMR δ 7.48 (m, 3H), 7.79 (m, 2H), 78.10 (m, 1H), 8.36 (m, 1H), 8.71 (s, 1H), 8.85 (m, 1H), 11.67 (s, 1H), agreeing with literature report.[42]

Benzyl 2-Iodobenzoate (24). Spectral data: ^{1}H NMR δ 5.38 (s, 2H), 7.14 (ddd, J = 7.2 Hz, 1.6 Hz, 2H), 7.32−7.42 (m, 4H), 7.46 (m, 2H), 7.82 (m, 1H), 7.99 (m, 1H); ^{13}C NMR δ 67.6, 94.5, 128.1, 128.7, 128.8, 128.9, 131.3, 132.9, 135.2, 135.7, 141.6, 166.5. ^{1}H NMR and ^{13}C NMR match with literature report.[43]

2,4-Dibromo-*N*,*N*-diethylaniline (30). Spectral data: ^{1}H NMR δ 1.00 (t, J = 7.2 Hz, 6H), 3.07 (q, J = 7.2 Hz, 4H), 6.94 (d, J = 8.4 Hz, 1H), 7.35 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.71 (d, J = 2.4 Hz, 1H); ^{13}C NMR δ 12.4, 47.2, 116.3, 123.3, 125.4, 130.8, 136.2, 148.6. HRMS calculated for $C_{10}H_{13}Br_2N$, 304.9415; found, 304.9398.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for compounds **5**, **15**, **18**, and **30**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: houyq@siu.edu.

■ ACKNOWLEDGMENTS

Financial support for this research from Meyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry, Southern Illinois University Carbondale is gratefully acknowledged.

■ REFERENCES

(1) Hecht, S. S. *Proc. Soc. Exp. Biol. Med.* **1997**, *216*, 181−191.
(2) Hildegard, M, S. *Life Sci.* **2007**, *80*, 2274−2280.
(3) Walters, C. L. *Dev. Meat Sci.* **1980**, *1*, 195−217.
(4) Leppänen, O.; Ronkainen, P. *Chromatographia* **1982**, *16*, 219−223.
(5) Anderson, G. A. *Soaps, Deterg. Toiletries Rev.* **1979**, *9*, 19−21.
(6) Serfontein, W. J.; Smit, J. H. *Nature* **1967**, *214*, 169−170.
(7) Ishikawa, S.; Mochizuki, M. *Genes Environ.* **2007**, *29*, 1−10.
(8) Wang, P. G.; Xian, M.; Tang, X.; Wu, X.; Wen, Z.; Cai, T.; Janczuk, A. J. *Chem. Rev.* **2002**, *102*, 1091−1134.
(9) Hartman, W. W.; Roll, L. J. *Org. Synth.* **1933**, *13*, 66−67.
(10) Wagner, H.; Hill, J. B. *J. Med. Chem.* **1974**, *17*, 1337−1338.
(11) Hartman, W. W.; Roll, L. J. *Org. Synth.* **1933**, *13*, 82−83.
(12) Hou, J.-Y.; Wang, Y.-L.; Wang, J.-Y. *J. Chem. Res., Synop.* **2003**, *2003*, 626−627.
(13) Montazerozohori, M.; Karami, B. *Helv. Chim. Acta* **2006**, *89*, 2922−2926.
(14) Zolfigol, M. A.; Ghaemi, E.; Madrakian, E.; Kiany-Borazjani, M. *Synth. Commun.* **2000**, *30*, 2057−2060.
(15) Borikar, S. P.; Paul, V. *Synth. Commun.* **2010**, *40*, 654−660.
(16) Zolfigol, M. A. *Synth. Commun.* **1999**, *29*, 905−910.
(17) Verardo, G.; Giumanini, A. G.; Strazzolini, P. *Tetrahedron* **1990**, *46*, 4303−4332.
(18) Verardo, G.; Giumanini, A. G.; Strazzolini, P. *Tetrahedron* **1991**, *47*, 7845−7852.
(19) Leoppky, R. N.; Tomasik, W. *J. Org. Chem.* **1983**, *48*, 2751−2757.
(20) Nudelman, N. S.; Bonatti, A. E. *Synlett* **2000**, *2000*, 1825−1827.
(21) Oláh, G.; Noszkó, L.; Kuhn, S.; Szelke, M. *Chem. Ber.* **1956**, *89*, 2374−2377.
(22) Chang, S.-K.; Harrington, G. W.; Rothstein, M.; Shergalis, W. A.; Swern, D.; Vohra, S. K. *Cancer Res.* **1979**, *39*, 3871−3874.
(23) Demir, A. S.; Mahasneh, A. S.; Aksoy, H.; Gercek, Z. *Synth. Commun.* **1992**, *22*, 2607−2611.
(24) Castedo, L.; Riguera, R.; Vazquez, M. P. *J. Chem. Soc., Chem. Comm.* **1983**, 301−302.
(25) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523−2584.
(26) Zhdankin, V.; Stang, P. *Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: New York, 1998; pp 327−358.
(27) Bhalerao, D. S.; Mahajan, U. S.; Akamanchi, K. G. *Synth. Commun.* **2008**, *38*, 2814−2819.
(28) Challis, B. C.; Yousaf, T. I. *J. Chem. Soc., Chem. Commun.* **1990**, 1598−1599.
(29) Bhatt, S.; Nayak, S. K. *Synth. Commun.* **2007**, *37*, 1381−1388.
(30) Gurung, R. K.; Hou, Y. *Abstracts of Papers*, 241st ACS National Meeting & Exposition, Anaheim, CA, March 27−31, 2011, ORGN-129.
(31) Wulfman, D. S. *Diazonium and Diazo Groups*; Patai, S., Ed.; John Wiley & Sons, Ltd.: New York, 1978; Vol. *1*, pp 247−339.
(32) Barton, D. H. R.; Motherwell, W. B.; Zard, S. Z. *Tetrahedron Lett.* **1983**, *24*, 5227−5230.
(33) Loeppky, R. N.; Elomari, S. *J. Org. Chem.* **1999**, *65*, 96−103.
(34) Teuten, E. L.; Loeppky, R. N. *Org. Biomol. Chem.* **2005**, *3*, 1097−1108.
(35) Loeppky, R. N.; Singh, S. P.; Elomari, S.; Hastings, R.; Theiss, T. E. *J. Am. Chem. Soc.* **1998**, *120*, 5193−5202.
(36) Blackmond, D. G.; Hodnett, N. S.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 7450−7451.
(37) Merritt, E. A.; Carneiro, V. M. T.; Silva, L. F.; Olofsson, B. *J. Org. Chem.* **2010**, *75*, 7416−7419.
(38) Nicolai, S.; Erard, S.; Gonzalez, D. F.; Waser, J. *Org. Lett.* **2010**, *12*, 384−387.
(39) Giuffredi, G. T.; Purser, S.; Sawicki, M.; Thompson, A. L.; Gouverneur, V. *Tetrahedron: Asymmetry* **2009**, *20*, 910−920.
(40) Hooker, J. M.; Esser-Kahn, A. P.; Francis, M. B. *J. Am. Chem. Soc.* **2006**, *128*, 15558−15559.
(41) Tanno, M.; Sueyoshi, S. *Chem. Pharm. Bull.* **1987**, *35*, 1353−1359.

(42) Largeron, M.; Fleury, M.-B.; Strolin Benedetti, M. *Org. Biomol. Chem.* **2010**, *8*, 3796−3800.
(43) Wang, L.; Prabhudas, B.; Clive, D. L. J. *J. Am. Chem. Soc.* **2009**, *131*, 6003−6012.