Studies on Sulfenamides. XIII.[1] Reaction of 2-Nitrobenzene-sulfenanilides with *N*-Bromosuccinimide

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The reaction of *N*-alkyl 2-nitrobenzenesulfenanilides (1a—3a) with *N*-bromosuccinimide (NBS) gave the corresponding monobrominated 2-nitrobenzenesulfenanilides (1b—3b) in good yields. The initial step of this reaction is the attack of NBS on the nitrogen atom of 1a—3a. The intermediate of this reaction is considered to be a cation radical of the sulfenanilides. A similar reaction of *N*-unsubstituted 2-nitrobenzenesulfenanilides (5a—10a) with NBS gave mono- or di-brominated 2-nitrobenzenesulfenanilides in low yields.

Keywords bromination; *N*-bromosuccinimide; sulfenamide; 2-nitrobenzenesulfenanilide

In this paper the bromination of the aromatic ring in the aniline moiety of sulfenanilides is reported. As shown in previous papers,[1,2] the oxidation of sulfenanilides involves various reactive intermediates, but neither their reactivity nor their fate in the oxidation process is known. 2-Nitrobenzenesulfenanilides [*N*-Me-4′-OMe (**1a**), *N*-Me (**2a**), *N*-Et (**3a**), 4′-Me (**5a**), 4′-COOEt (**6a**), unsubstituted (**7a**), 3′-OMe (**8a**), 3′-Me (**9a**), and 2′-COOEt (**10a**)] and *N*-(2-nitrophenylthio)-1,2,3,4-tetrahydroquinoline (**4a**) were subjected to reaction with *N*-bromosuccinimide (NBS) to elucidate the reactivity of the reactive intermediates derived from **1a**—**10a**. The feasibility of applying the method to the preparation of bromoanilines was also investigated, because a mild and facile synthesis of bromoanilines is still required.[3] The 2-nitrobenzenesulfenyl group, which is frequently used for protection of the amino group, can be easily removed by hydrogen chloride.[4]

Results and Discussion

The reaction of *N*-substituted 2-nitrobenzenesulfenanilides (**1a**—**4a**) with NBS in dry CH_2Cl_2 at room temperature gave the corresponding brominated compounds (**1b**—**4b**) in good yields as shown in Table I.

The *para* position to nitrogen in **2a**—**4a** was brominated selectively and almost quantitatively, but **1a**, which contains 4′-OMe, gave the 2′-brominated compound (**1b**). The oxidation mechanism of **1a**—**4a** has been reported in detail, base on the results of cyclic voltammetry and electron spin resonance (ESR) spectrometry.[2h] The conclusion in the previous paper suggests that the 4′-position of the cation radicals derived from sulfenanilides is the most reactive site. Chart 1 shows the bromination mechanism of **2a** as a typical example.

The electrophilic attack of NBS or Br^+ must take place at the position which has the highest electron density in the molecule of **2a**, that is, the lone pair of the nitrogen atom. Homolysis of the N–Br bond gives the cation radical B and a bromine atom, and the latter attacks the 4′-position of B to give C. A similar mechanism of generation of the cation radical was reported in the oxidation of triethylamine.[5] Subsequent deprotonation gives **2b** as the final product.

Compounds **5a** and **6a** did not give good results, as shown in Table I. Unreacted **5a** (29%) still remained in the reaction mixture, though the oxidation potential of **5a**[2d] was slightly lower than that of **2a**.[2h] When two equivalents of NBS was used, no unreacted **5a** was detected in the reaction mixture but the yield of **5b** was reduced to 3.4%. These facts suggest that the bromination of **5a** and **6a** proceeds *via* an alternative mechanism and the N–H bond must play an important role in it. In order to elucidate this phenomenon, **1a** and **5a**—**10a** were treated with NBS under basic conditions. The results are shown in Table II.

The following points are noteworthy. First, **1a** gave good results even under these conditions. Second, **5b**—**10b** also reacted with NBS. Although unreacted substrates were recovered from the reactions of **7a**, **8a**, and **9a**, only the dibrominated compounds were obtained without formation of the monobrominated compounds. This fact suggested

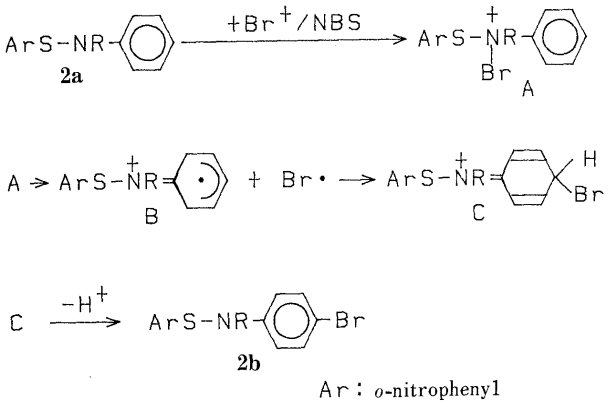

Chart 1

TABLE I. Results of Reaction of *N*-Substituted 2-Nitrobenzenesulfenanilides with NBS

Compd. no.	Sulfenanilide	Products identified (comp. no.)	Yields
1a	$ArSN(Me)C_6H_4$-4′-OMe	$ArSN(Me)C_6H_3$-2′-Br-4′-OMe (**1b**)	Quantitative
2a	$ArSN(Me)C_6H_5$	$ArSN(Me)C_6H_4$-4′-Br (**2b**)	98%
3a	$ArSN(Et)C_6H_5$	$ArSN(Et)C_6H_4$-4′-Br (**3b**)	Quantitative[a]
4a	*N*-ArS-1,2,3,4-tetrahydroquinoline	*N*-ArS-1,2,3,4-tetrahydro-6-Br-quinoline (**4b**)	99%
5a	$ArSNHC_6H_4$-4′-Me	$ArSNHC_6H_4$-2′-Br-4′-Me (**5b**)	40%
6a	$ArSNHC_6H_4$-4′-COOEt	$ArSNHC_6H_4$-2′-Br-4′-COOEt (**6b**)	44%

Ar: 2-nitrophenyl. *a*) One and half equivalents of NBS was used.

TABLE II. Results of Reaction of 2-Nitrobenzenesulfenanilides with NBS under Basic Conditions

Compd. no.	Sulfenanilides	Products identified (compd. no.)	Yield[a]	
			1 h	2 h[b]
1a	$ArSN(Me)C_6H_4$-4′-OMe	$ArSN(Me)C_6H_3$-2′-Br-4′-OMe (**1b**)	78% (44%)	96% (18%)
5a	$ArSNHC_6H_4$-4′-Me	$ArSNHC_6H_3$-2′-Br-4′-Me (**5b**)	26% (20%)	42% (10%)
6a	$ArSNHC_6H_4$-4′-COOEt	$ArSNHC_6H_3$-2′-Br-4′-COOEt (**6b**)	49% (53%)	35% (19%)
7a	$ArSNHC_6H_6$	$ArSNHC_6H_3$-2′,4′-Br_2 (**7b**)	11% (24%)	17% (8%)
8a	$ArSNHC_6H_4$-3′-OMe	$ArSNHC_6H_2$-2′,4′-Br_2-3′-OMe (**8b**)	74% (39%)	67% (24%)
9a	$ArSNHC_6H_4$-3′-Me	$ArSNHC_6H_2$-2′,4′-Br_2-3′-Me (**9b**)	20% (23%)	19% (2%)
10a	$ArSNHC_6H_4$-2′-COOEt	$ArSNHC_6H_3$-4′-Br-2′-COOEt (**10b**)	56% (55%)	33% (37%)

a) Yield based on the amount of consumed substrate. The amount of recovered substrate is shown in parentheses. Determined by HPLC. *b*) After 1 h, the same amounts of NBS and K_2CO_3 were added to the solution again.

that the monobrominated products were much more reactive than the starting materials.

It has already been reported that the Ep-value of the first anodic wave of **5a—10a** is decreased under basic conditions, because they gave conjugated bases by dissociation of the N–H bond in basic solution.[2f] Therefore, deprotonation of the N–H bond appears to play an important role in the reaction of **5a—10a** with NBS. The reaction of the conjugated bases generated from **5a—10a** gives monobrominated sulfenanilides (MBS). MBS will be oxidized faster than the parent **5a—10a**, because the bromosubstituent attracts electrons in the aromatic ring and increases the acidity of MBS. Oxidation of the conjugated base generated from MBS by NBS gives dibrominated sulfenanilides. However, it is impossible to rule out the existence of *N*-halogenated compounds as intermediates, just as in the chlorination of anilines with *N*-chlorosuccinimide.[6]

In conclusion, the oxidation of **1a—10a** with NBS brought about monobromination of the aniline moiety of the sulfenanilides, and **1b—4b**, with an alkyl group on the nitrogen atom, were not oxidized by NBS any further, whereas the monobrominated products derived from **7a—9a** were oxidized by NBS, because they gave conjugated bases with low oxidation potentials by dissociation of the N–H bond, to give dibrominated compounds **7b—9b**.

Monobromination can be often achieved in good yield but specific conditions are required in each case. NBS–dimethylformanide (DMF)[7] or anilinosilane–NBS[3a] has been reported to be a mild and selective monobromination reagent for reactive aromatic amines. Those reactions need a longer time than the reaction of **1a—10a** with NBS. Preparation of **1a—10a** is easier than that of anilinosilanes because 2-nitrobenzenesulfenyl chloride is commercially available. The oxidation of 2-nitrobenzenesulfenanilides with NBS is a mild and convenient method for their bromination but it is necessary to replace the *N*-hydrogen with an aliphatic substituent in order to increase the yield of monobrominated products.

Experimental

Materials The sulfenanilides were prepared from 2-nitrobenzenesulfenyl chloride and the corresponding amines in dry ether, and purified by recrystallization from ethanol.[2] Each compound gave analysis results consistent with the theoretical values. Dichloromethane was dried over molecular sieves. Methanol was dried with activated magnesium and distilled.

Apparatus Infrared (IR), nuclear magnetic resonance (NMR), and mass spectra (MS) were obtained as previously described.[2h] Melting points are not corrected. High-performance liquid chromatography (HPLC) was carried out as described previously.[2i]

2′-Bromo-4′-methoxy-*N*-methyl-2-nitrobenzenesulfenanilide (1b). Typical Examples of Isolation of Products from the Reaction Mixture a) NBS (0.36 g) was added to the solution of **1a** (576.8 mg) in dichloromethane (10 ml) and the mixture was stirred at room temperature for 1 h. CH_2Cl_2 (30 ml) was added to the reaction mixture, and the whole was washed with 30% aqueous Na_2CO_3 solution twice, and then once with water (30 ml). After being dried over $MgSO_4$, the organic layer was concentrated to dryness, and then the residue was purified on a Silica gel 60 (Merck) column using benzene–hexane (2 : 1) as an eluent to give **1b** (720.0 mg). mp 88—89 °C. (from EtOH). IR ν_{max}^{KBr} cm^{-1}: 1505 (NO_2), 1330 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 3.28 (3H, s, NCH_3), 3.77 (3H, s, OCH_3), 6.82 (1H, dd, J=2.91, 8.85 Hz, aromatic proton), 7.11 (1H, d, J=2.90 Hz, aromatic proton), 7.28 (1H, dt, J=1.34, 7.13 Hz, aromatic proton), 7.42 (1H, d, J=8.84 Hz, aromatic proton), 7.72 (1H, dt, J=1.40, 7.11 Hz, aromatic proton), 8.29 (1H, dd, J=1.33, 8.30 Hz, aromatic proton), 8.37 (1H, dd, J=1.28, 8.29 Hz, aromatic proton). MS *m/z*: 368, 370 (M^+), 214, 216 (H_3C–N^+–$C_6H_3BrOCH_3$), 154 (O_2N–$C_6H_4S^+$). *Anal.* Calcd for $C_{14}H_{13}BrN_2O_3S$: C, 45.54; H, 3.54; N, 7.85. Found: C, 45.42; H, 3.45; N, 7.54.

b) Potassium carbonate (0.4 g) and NBS (714.4 mg) were added to a solution of **1a** (578.8 mg) in dichloromethane (10 ml) and methanol (1 ml) and the mixture was stirred at room temperature for 1 h. CH_2Cl_2 (30 ml) was added to the reaction mixture, and the whole was washed with 30% aqueous Na_3CO_3 solution twice, and then once with water (30 ml). After being dried over $MgSO_4$, the organic layer was concentrated to dryness, and the residue was purified with LiChroprep Si 60 size C (Merck) using benzene as an eluent to give **1b** (720.0 mg).

The following compounds were obtained by essentially the same procedure and recrystallized from ethanol if necessary.

4′-Bromo-*N*-methyl-2-nitrobenzenesulfenanilide (**2b**): mp 118—119 °C. (from EtOH). IR ν_{max}^{KBr} cm^{-1}: 1490 (NO_2), 1310 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 3.47 (3H, s, NCH_3), 7.02 (2H, d, J=9.22 Hz, aromatic protons), 7.18 (1H, dd, J=1.42, 8.32 Hz, aromatic proton), 7.31 (1H, dt, J=1.36, 7.23 Hz, aromatic proton), 7.36 (2H, d, J=9.13 Hz, aromatic protons), 7.54 (1H, dt, J=1.33, 7.15 Hz, aromatic proton), 8.36 (1H, dd, J=1.32, 8.30 Hz, aromatic proton). MS *m/z*: 338, 340 (M^+), 184, 186 ($M^+ - O_2NC_6H_4S$), 154 ($O_2NC_6H_4S^+$). *Anal.* Calcd for $C_{13}H_{11}BrN_2O_2S$: C, 46.03; H, 3.26; N, 8.25. Found: C, 46.20; H, 3.23; N, 8.07.

4′-Bromo-*N*-ethyl-2-nitrobenzenesulfenanilide (**3b**): mp 105—107 °C. (from EtOH). IR ν_{max}^{KBr} cm^{-1}: 1510 (NO_2), 1350 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 1.38 (3H, t, J=7.08 Hz, CH_3), 3.53—3.63 (1H, m, CH_2), 3.90—3.99 (1H, m, CH_2), 7.01 (2H, d, J=9.23 Hz, aromatic protons), 7.27—7.36 (4H, m, aromatic protons), 7.54 (1H, dt, J=1.38, 7.64 Hz, aromatic proton), 8.35 (1H, md, J=8.05 Hz, aromatic proton). MS *m/z*: 352, 354 (M^+), 198, 200 ($M^+ - O_2NC_6H_4S$), 154 ($O_2NC_6H_4S^+$). *Anal.* Calcd for $C_{14}H_{13}BrN_2O_2S$: C, 47.60; H, 3.70; N, 7.93. Found: C, 47.90; H, 3.73; N, 7.89.

6-Bromo-1,2,3,4-tetrahydro-*N*-(2-nitrophenylthio)quinoline (**4b**): mp 146—148 °C. IR ν_{max}^{KBr} cm^{-1}: 1510 (NO_2), 1335 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 1.90—2.17 (2H, m, CH_2), 2.86 (2H, t, J=6.25 Hz, CH_2), 3.67—3.78 (2H, m, CH_2), 7.05 (1H, d, J=8.79 Hz, aromatic proton), 7.11 (1H, dd, J=2.44, 8.81 Hz, aromatic proton), 7.17 (1H, ds, J=2.22 Hz, aromatic proton), 7.28—7.34 (3H, m, aromatic protons), 8.35 (1H, d, J=8.10 Hz, aromatic proton). MS *m/z*: 364, 366 (M^+), 210, 212 ($M^+ - O_2NC_6H_4S$), 154 ($O_2NC_6H_4S^+$). *Anal.* Calcd for $C_{15}H_{13}BrN_2O_2S$: C, 49.32; H, 3.58; N, 7.66. Found: C, 49.32; H, 3.58; N, 7.59.

2′-Bromo-4′-methyl-2-nitrobenzenesulfenanilide (**5b**): mp 152—154 °C.

IR ν_{max}^{KBr} cm^{-1}: 3395 (NH), 1485 (NO_2), 1330 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 1.56 (3H, s, CH_3), 5.73 (1H, s, NH), 6.97 (1H, d, J=8.28 Hz, aromatic proton), 7.03 (1H, d, J=8.28 Hz, aromatic proton), 7.30 (1H, dt, J=1.45, 7.00 Hz, aromatic proton), 7.34 (1H, s, aromatic proton), 7.50 (1H, dd, J=1.43, 8.35 Hz, aromatic proton), 7.56 (1H, dt, J=1.42, 8.29 Hz, aromatic proton), 8.33 (1H, dd, J=1.48, 8.29 Hz, aromatic proton). MS m/z: 337, 339 (M^+), 183, 185 ($M^+ - O_2NC_6H_4S$), 154 ($O_2NC_6H_4S^+$). *Anal.* Calcd for $C_{13}H_{11}BrN_2O_2S$: C, 46.03; H, 3.26; N, 8.25. Found: C, 45.95; H, 3.05; N, 8.07.

2′-Bromo-4′-ethoxycarbonyl-2-nitrobenzenesulfenanilide (**6b**): mp 131—133 °C. IR ν_{max}^{KBr} cm^{-1}: 3475 (NH), 1710 (C=O), 1505 (NO_2), 1297 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 1.37 (3H, t, J=7.12 Hz, CH_3), 4.34 (2H, q, J=7.12 Hz, CH_2), 6.13 (1H, s, NH), 7.17 (1H, d, J=8.89 Hz, aromatic proton), 7.34 (1H, dt, J=1.26, 7.14 Hz, aromatic proton), 7.40 (1H, dd, J=1.15, 8.08 Hz, aromatic proton), 7.58 (1H, dt, J=1.34, 7.14 Hz, aromatic proton), 7.85 (1H, dd, J=1.88, 8.63 Hz, aromatic proton), 8.22 (1H, d, J=1.87 Hz, aromatic proton), 8.36 (1H, dd, J=1.39, 8.38 Hz, aromatic proton). MS m/z: 396, 398 (M^+), 242, 244 ($M^+ - O_2NC_6H_4S$), 154 ($O_2NC_6H_4S^+$). *Anal.* Calcd for $C_{15}H_{13}BrN_2O_4S$: C, 45.35; H, 3.29; N, 7.05. Found: C, 45.14; H, 3.26; N, 6.98.

2′,4′-Dibromo-2-nitrobenzenesulfenanilide (**7b**): mp 198—199 °C (recrystallized from CH_3COOEt). IR ν_{max}^{KBr} cm^{-1}: 3395 (NH), 1495 (NO_2), 1330 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 5.83 (1H, s, NH), 7.02 (1H, d, J=8.78 Hz, aromatic proton), 7.26—7.36 (2H, m, aromatic protons), 7.42 (1H, d, J=1.19, 8.30 Hz, aromatic proton), 7.58 (1H, dt, J=1.41, 7.14 Hz, aromatic proton), 7.65 (1H, d, J=2.19 Hz, aromatic proton), 8.34 (1H, dd, J=1.39, 8.30 Hz, aromatic proton). MS m/z 402, 404, 406 (M^+), 248, 250, 252 ($HN^+C_6H_3Br_2$), 154 ($O_2NC_6H_4S^+$). *Anal.* Calcd for $C_{12}H_8Br_2N_2O_2S$: C, 35.66; H, 1.99; N, 6.91. Found: C, 36.11; H, 2.06; N, 6.90.

2′,4′-Dibromo-3′-methoxy-2-nitrobenzenesulfenanilide (**8b**): mp 177—179 °C. IR ν_{max}^{KBr} cm^{-1}: 3400 (NH), 1510 (NO_2), 1340 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 3.73 (3H, s, OCH_3), 5.80 (1H, s, NH), 6.77 (1H, s, aromatic proton), 7.34 (1H, dt, J=1.34, 7.15 Hz, aromatic proton), 7.42 (1H, dd, J=1.16, 8.11 Hz, aromatic proton), 7.60 (1H, dt, J=1.42, 7.16 Hz, aromatic proton), 7.63 (1H, s, aromatic proton), 8.34 (1H, dd, J=1.16, 8.18 Hz, aromatic proton). MS m/z: 432, 434, 436 (M^+), 278, 280, 282 (H_3CO– $C_6H_3Br_2$–N^+–H), 154 (O_2N–$C_6H_4S^+$). *Anal.* Calcd for $C_{13}H_{10}Br_2N_2O_3S$: C, 35.96; H, 2.32; N, 6.45. Found: C, 36.18; H, 2.16; O, 6.44.

2′,4′-Dibromo-3′-methyl-2-nitrobenzenesulfenanilide (**9b**): mp 143—149 °C. IR ν_{max}^{KBr} cm^{-1}: 3400 (NH), 1510 (NO_2), 1335 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 1.55 (3H, s, CH_3), 5.74 (1H, s, NH), 7.03 (1H, s, aromatic proton), 7.33 (1H, dt, J=1.29, 8.24 Hz, aromatic proton), 7.44 (1H, dd, J=1.20, 8.22 Hz, aromatic proton), 7.59 (1H, dt, J=1.33, 8.34 Hz, aromatic proton), 7.65 (1H, s, aromatic proton), 8.35 (1H, dd, J=1.37, 8.35 Hz, aromatic proton). MS m/z: 415, 417, 419 (M^+), 261, 263, 265 ($M^+ - O_2NC_6H_4S$), 154 ($O_2NC_6H_4S^+$). *Anal.* Calcd for $C_{13}H_{10}Br_2N_2O_2S$: C, 37.34; H, 2.41; N, 6.70. Found: C, 37.79; H, 2.54; N, 6.76.

4′-Bromo-2′-ethoxycarbonyl-2-nitrobenzenesulfenanilide (**10b**): mp 122 °C. IR ν_{max}^{KBr} cm^{-1}: 3310 (NH), 1692 (C=O), 1510 (NO_2), 1310 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 1.45 (3H, t, J=7.12 Hz, CH_3), 4.41 (2H, q, J=7.13 Hz, CH_2), 7.17 (1H, d, J=8.96 Hz, aromatic proton), 7.30 (1H, t, J=2.19, 8.36 Hz, aromatic proton), 7.42—7.45 (2H, m, aromatic protons), 7.53 (1H, t, J=1.36, 7.05 Hz, aromatic proton), 8.11 (1H, d, J=2.41 Hz, aromatic proton), 8.33 (1H, dd, J=1.30, 8.33 Hz, aromatic proton), 9.04 (1H, s, NH). MS m/z: 396, 398 (M^+), 242, 244 ($HN^+C_6H_3BrCOOEt$), 154 ($O_2NC_6H_4S^+$).

Anal. Calcd for $C_{15}H_{13}BrN_2O_4S$: C, 45.35; H, 3.29; N, 7.05. Found: C, 45.26; H, 3.07; N, 7.02.

Determination of Products A typical example is described. An aliquot (0.2 ml) of the reaction mixture was filtered on a Columngard (Nihon Millipore Ltd.). One μl of filtrate was diluted to 20 μl with the mobile phase, MeOH–H_2O (3 : 1), and the rest of the filtrate was added to the reaction vessel. Five μl of the diluted solution was injected into a Nova-pak cartridge column. The detector was operated at 254 nm. After 1 h, NBS (365 mg, 2 mM) and K_2CO_3 (138 mg, 2 mM) were added to the solution again, and it was stirred at room temperature for 1 h. One-fifth ml of the resulting solution was treated as mentioned above.

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