Convenient One-pot Procedure for Converting Aryl Sulfides to Nitroaryl Sulfones

Masatoshi Nose, Hitomi Suzuki*

Department of Chemistry, School of Science, Kwansei Gakuin University, Gakuen 2-1, Sanda 669-1337, Japan Fax +81(795)659077; E-mail: hsuzuki@ksc.kwansei.ac.jp Received 12 February 2002; revised 25 March 2002

Abstract: When treated with nitrogen dioxide and ozone in inert solvent at 0 °C or below, aryl sulfides underwent smooth oxidative nitration to give nitroaryl sulfones in good yield. Using this methodology, a series of mono- and di-nitrated aryl sulfones were prepared from methyl phenyl sulfide and diphenyl sulfide and their physical data are presented.

Key words: nitro compounds, sulfones, sulfides, nitration, nitrogen oxides, ozone

Among various types of functional groups commonly found in organic compounds, the sulfonyl group stands first in the capacity of withdrawing electrons. Due to this uniqueness, the sulfonyl group is widely employed for the activation of C-H bonds as well as the stabilization of carbanionic species arising from the proton removal of activated C-H bonds. In connection with our continued studies on the nonconventional nucleophilic substitution of nitroarenes,¹ where a ring hydrogen atom is replaced by a nucleophile in preference to the nucleofugal substituent group present in the same ring (Scheme 1), we became interested in the behavior of nitroaryl sulfones toward nucleophiles under strongly basic conditions. Unfortunately, these aryl sulfones are not commercially available. Major known methods for the preparation of nitroaryl sulfones involve (a) direct nitration of aryl sulfones,² (b) Friedel-Crafts type reaction between nitroarylsulfonyl chlorides and arenes,³ (c) nucleophilic substitution of halonitroarenes with sulfinates,⁴ and (d) oxidation of nitroaryl sulfides.⁵ However, these methods are not free from some drawbacks. The first method has no choice as to the position occupied by nitro group, while the other methods often suffer from limited scope, difficult access commercial material, side reaction and/or low yield.⁶





The reaction of diphenyl sulfide (4) with nitric acid has long been known to involve partial oxidation of the sulfur atom to afford a mixture of isomeric nitrophenyl sulfides, sulfoxides and sulfones.⁷ However, no detailed information is available on the product composition. Since the sulfanyl, sulfinyl and sulfonyl groups are known to direct the entering electrophiles differently in electrophilic aromatic substitution, the reaction seemed to us to provide a convenient one-step procedure to convert commercially available sulfides 1a and 4 to isomeric nitroaryl sulfones by appropriate choice of experimental conditions. Thus, we have investigated the Kyodai-nitration of aromatic sulfides such as 1a and 4, and of aromatic sulfones such as 3a and 6 under a variety of conditions.⁸ In fact, this method proved to be quite effective for converting aryl sulfides directly to nitroaryl sulfones. Six nitroaryl sulfones and seven dinitro aryl sulfones were isolated from the reaction mixtures and their physical properties including melting points, mass, infrared and ¹H NMR spectral data are presented.

To a stirred solution of methyl phenyl sulfide (1a) in dichloromethane was added an excess of liquid nitrogen dioxide at -10 °C and the resulting mixture was allowed to stand for a while. The substrate was cleanly oxidized to sulfoxide 2a.⁹ When a stream of ozonized oxygen was passed slowly to the resulting solution, sulfoxide 2a was rapidly oxidized to form sulfone 3a (Scheme 2).¹⁰ When this compound was further subjected to the combined action of nitrogen dioxide and ozone (NO₂–O₃), the ring nitration occurred slowly to give a mixture of isomeric nitroaryl sulfones 3b–d (Tables 1 and 2). The addition of methanesulfonic acid as catalyst considerably facilitated the reaction. Sulfone 3a was almost inert toward the action of ordinary nitric acid under similar conditions.

Irrespective of the substrate employed, **1a** or **3a**, 3-nitrophenyl sulfone (**3c**) was the predominant product from the Kyodai-nitration. In contrast, the nitration of **1a** by the traditional method gave a product considerably rich in the 4-nitro derivative **3d**. Particularly, when sulfide **1a** was treated with fuming nitric acid using 97% sulfuric acid as the reaction medium, 4-nitrophenyl sulfone **3d** increased up to 38% in the isomer proportion. Such a marked difference in the isomer distribution suggests the involvement of different reaction pathways in the nitration with the NO₂–O₃ and the mixed acid systems. In the former type of nitration where sulfone **3c** is the major product, the oxidation of sulfide **1a** to sulfoxide **2a** to sulfone **3a** would pre-

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Table 1 Nitration of Aryl Sulfides 1a,4,10,14 and Sulfoxide 2a with NO₂–O₃ and Other Nitrating Systems^a

Substrate	Reagent	Solvent	Reaction time (h)/ Temp (°C)	Products	Yield ^b /% (Isomer ratio) ^c
1a	NO2 ^d	CH ₂ Cl ₂	0.5/-10	2a	98
	NO ₂ /O ₃ ^e	CH_2Cl_2	1.0/-10	3a	97
	NO ₂ /O ₃ ^e	CH_2Cl_2	3.0/-10	3b+3c+3d	81 (14:83:3)
	NO ₂ /O ₃ ^e	MeNO ₂	2.5/-10	3b+3c+3d	83 (11:87:2)
	<i>Fum</i> -HNO ₃ ^f	CH_2Cl_2	24/r.t.	2a	94
	<i>Fum</i> -HNO ₃ ^f	CH_2Cl_2	24/80	3a	92
	<i>Fum</i> -HNO ₃ /97%-H ₂ SO4 ^g	CH_2Cl_2	12/80	3b+3c+3d	88 (7:76:17)
	<i>Fum</i> -HNO ₃ /97%-H ₂ SO4 ^g	MeNO ₂	12/80	3b+3c+3d	87 (10:75:15)
	<i>Fum</i> -HNO ₃ ^f	97%-H ₂ SO ₄	12/r.t.	3b+3c+3d	72 (8:54:38)
	<i>Fum</i> -HNO ₃ ^f	Ac ₂ O	6.0/0	3a	98
2a	NO ₂ –O ₃ ^e	CH_2Cl_2	2.5/-10	3b+3c+3d	82 (12:86:2)
	<i>Fum</i> -HNO ₃ ^f	97%-H ₂ SO ₄	6/100	3b+3c+3d	86 (1:81:18)
4	NO_2^{d}	CH_2Cl_2	2.0/-10	5	89
	NO ₂ /O ₃ ^e	CH_2Cl_2	2.0/-10	6	81
	NO ₂ /O ₃ ^e	CH_2Cl_2	4.5/-10	8a+8b+8c	76 (11:84:5)
	<i>Fum</i> -HNO ₃ ^f	CH_2Cl_2	12/80	6	90
	<i>Fum</i> -HNO ₃ /97%-H ₂ SO4 ^g	CH_2Cl_2	12/80	8a+8b+8c+9	91 (8:54:17:21)
	<i>Fum</i> -HNO ₃ ^f	Ac ₂ O	6.0/0	6	90
10	NO_2^{d}	CH_2Cl_2	2.0/-10	12	26 ^{h,i}
	NO ₂ /O ₃ ^e	CH_2Cl_2	4.5/-10	8a+13a+13b	72 (48:23:29)
14	NO ₂ /O ₃ ^e	CH_2Cl_2	3.0/-10	17 + 18	43 (15:28) ^{j, k}

^a Except compound **14**, all reactions were carried out under the conditions indicated in the table, using a substrate (3 mmol) and a given solvent (30 mL). For **14**, see the experimental section.

^b Sum of all products.

^c Isomer ratio was estimated by ¹H NMR.

^d Liquid NO₂ (1.5 mL) was used.

e Ozonized oxygen was introduced at a rate of 10 mmol/h.

^f Fum-HNO₃ (3 mL, d = 1.50) was used.

^g A mixture of *fum*-HNO₃ (2 mL, d = 1.50) and 97%-H₂SO₄ (2 mL, d = 2.0) was used.

^h Isolated yield.

ⁱ Major product was sulfoxide 11, isolated in 70% yield.

^j Ring nitration preceded the oxidation of sulfur atom.

^k Accompanied by minor amounts of isomeric nitro sulfones.

cede the ring nitration. However, in the latter type of nitration where sulfone **3d** becomes important, the ring nitration is supposed to proceed in parallel with the oxidation of sulfur atom, probably due to the partial protonation of the sulfur atom in a strong acid medium such as sulfuric acid. In accordance with the respective *meta-para* and *meta*-orientating nature of the sulfinyl and sulfonyl groups, the reversal of the *ortho/para* isomer ratio was ob-

served in the nitration of sulfoxide 2a with the NO₂–O₃ and the mixed acid systems. Although the carbonyl group is known to favor the *ortho*-substitution in the Kyodai-ni-tration,¹¹ the sulfonyl group showed little *ortho* specificity in site selection. Changing the solvent from dichlor-omethane to nitromethane gave little or no effect on the site selectivity, but interestingly this change was found to halt the reaction at mononitration stage.



Scheme 2

The Kyodai and traditional methods observed a significant contrast in the nitration of diphenyl sulfide (4). The former type of nitration of sulfide 4 and sulfone 6 gave the dinitration products of similar isomeric composition (Table 1 and Table 2). This means that the oxidation of sulfide 4 to sulfone 6 preceded the ring nitration. Thus, the action of NO_2-O_3 on sulfide 4 at low temperature readily gave nitrosulfone 7, which underwent the second nitration at the opposite ring to afford a mixture of isomeric dinitroaryl sulfones 8a-c (Scheme 3). Rather unexpectedly, the second nitration was found to be facile and ran parallel with the initial nitration. Hence, it was difficult to obtain the mononitro derivative 7 as the sole initial product. The initial nitration occurred almost exclusively at 3-position of 6 and other isomers were detected only in a slight amount. In contrast, the second nitration took place at all positions of the unsubstituted ring of 7, giving three possible dinitroaryl sulfones 8a-c in a good combined yield. On the other hand, the traditional nitration of sulfide 4 using an excess of mixed acid at elevated temperature produced a considerable amount of 3,4'-dinitrophenyl and 4,4'-dinitrodiphenyl sulfones 8c and 9. The latter isomer could not be detected in the double Kyodai-nitration of **4** (Table 1), and neither in the single Kyodai-nitration of **6** (Table 2). The sulfanyl function is *para*-directing, therefore, a noticeable difference in the product composition suggests a significant competition between the ring carbon and the sulfur atoms for the nitronium ion at initial stage of the traditional nitration of **4**.

When 2-nitrodiphenyl sulfide (10) was subjected to the action of the NO_2-O_3 system, 2,3'-dinitrodiphenyl sulfone (8a) was obtained as the main product, together with appreciable amounts of 2,2'-dinitro- and 2,4'-dinitrodiphenyl sulfones (13a) and (13b) (Scheme 4). When sulfide 10 was allowed to stand in contact with nitrogen dioxide alone, a slow ring nitration took place in parallel with the oxidation of sulfur atom, giving a mixture of sulfoxide 11 and sulfide 12 in good combined yield (Table 1). Formation of 12 is consistent with the *para*-directing nature of the sulfanyl function and two nitro groups in 12 were enough to prevent this sulfide from being oxidized to sulfoxide.

A previous paper reported that phenyl trifluoromethyl sulfide (14) reacted with nitric and sulfuric acids to form 4nitro and 2,4-dinitro derivatives with the sulfur atom intact.¹² In our case, treatment of sulfide 14 with excess of mixed acid gave an oily product, in which 2,4-dinitrophenyl trifluoromethyl sulfide and sulfoxide were found to be major components. Unfortunately, the product was poorly crystallized from common organic solvents and so it was oxidized to sulfone 18 before isolation. The Kyodai-nitration of 14 gave nitroaryl sulfoxides 15 and 16 as an inseparable mixture. Hence, after the oxidation to sulfones, the product was subjected to chromatographic separation to obtain 4-nitrophenyl and 2,4-dinitrophenyl trifluoromethyl sulfones 17 and 18. In contrast, the Kyodai nitration of phenyl trifluoromethyl sulfone (19) afforded two isomeric

Table 2 Nitration of Phenyl Sulfones 3a,6,19 with NO₂–O₃ and Mixed Acid Systems^a

Substrate	Reagent	Solvent	Reaction time (h) / Temp (°C)	Products	Yield ^b /% (Isomer ratio) ^c
3a	NO ₂ /O ₃ ^e , MeSO ₂ H ¹	CH ₂ Cl ₂	2.5/-10	3b+3c+3d	87 (9:90:1)
	NO ₂ /O ₃ ^e , MeSO ₂ H ¹	MeNO ₂	2.0/-10	3b+3c+3d	89 (10:89:1)
	Fum-HNO ₂ /97% H ₂ SO4 ^g	CH ₂ Cl ₂	12/80	3b+3c+3d	89 (8:91:1)
	Fum-HNO ₂ /97% H ₂ SO4 ^g	MeNO ₂	12/80	3b+3c+3d	94 (14:84:2)
6	NO ₂ /O ₃ ^e	CH ₂ Cl ₂	2.5/-10	7	59 ^{h, k}
	NO ₂ /O ₃ ^e , MeSO ₂ H ¹	CH ₂ Cl ₂	4.0/-10	8a+8b+8c	74 (10:87:3)
	NO ₂ /O ₃ ^e , MeSO ₂ H ¹	MeNO ₂	3.0/-10	8a+8b+8c	78 (13:81:6)
	Fum-HNO ₂ /97% H ₂ SO4 ^g	CH ₂ Cl ₂	12/r.t.	8a+8b+8c	90 (15:78:7)
19	NO ₂ /O ₃ ^e , MeSO ₂ H ¹	CH_2Cl_2	2.5/-10	20+21	94 (6:93)

 $^{a-c,\ e,\ g,\ h,\ k}$ See footnotes of Table 1.

¹ Methanesulfonic acid (2 mmol) was added as catalyst.



Scheme 3



Scheme 4

mononitro derivatives again as an inseparable mixture, where the major component was 3-nitrophenyl trifluoromethyl sulfone (21), accompanied by small amounts of 2-nitro isomer 20 (Scheme 5). Compound 21 could be isolated in pure form only after repeated chromatography on silica gel. Compound 20 was quite low in yield and identified by GC-MS, NMR and IR. The formation of 2,4dinitro sulfoxide (16) as the main product from the Kyodai-nitration of sulfide 14 implies that the double ring nitration became more favored over the oxidation of sulfur(IV) to sulfur(VI) atom in the presence of a powerful electron-withdrawing trifluoromethyl group. This group is not stable in strong acid media and tends to be hydrolyzed to the carboxylic acid function.

In conclusion, a convenient and effective one-pot procedure has been developed for the conversion of aryl sulfides into nitroaryl sulfones, in which aryl sulfides were simply treated with the NO₂–O₃ system at low temperature. Yields were generally good and in many cases a noticeable difference of the isomer proportion was observed between the products from the nitration with the NO₂–O₃ and the mixed acid systems. The Kyodai-nitration followed by chromium trioxide oxidation of deactivated sulfide **14** gave 2,4-dinitrophenyl sulfone **18** as the major product, which would be laborious to obtain by other methods.



Scheme 5

Table 3 Physical Data of Nitration Products 2b–d, 3b–d, 7, 8a–c, 9, 12, 13a–b, 17, 18 and 21

Prod- uct	Mp (°C)	Lit. mp (°C)	MS (70 eV) <i>m</i> / <i>z</i> (%)	IR (KBr, cm ⁻¹)	¹ H NMR (CDCl ₃ /TMS), δ , <i>J</i> (Hz)
2b	100–102	101-102 ¹⁴	185 (M ⁺ , 48), 135 (8), 109 (100)	1518 (NO ₂), 1346 (NO ₂), 1065, 1034, 972	8.37–8.39 (dd, J = 8.0, 1.6, 1 H), 8.33– 8.35 (dd, J = 8.0, 1.6, 1 H), 7.98–8.02 (m, 1 H), 7.73–7.77 (m, 1 H), 2.97 (s, 3 H, Me)
2c	114–116	115–116 ¹⁶	185 (M ⁺ , 100), 170 (97), 139 (23), 124 (54)	1524 (NO ₂), 1348 (NO ₂), 1073, 1044	8.51 (t, <i>J</i> = 2.0, 1 H), 8.36–8.39 (m, 1 H), 8.01–8.04 (m, 1 H), 7.76–7.80 (t, <i>J</i> = 8.0, 1 H), 2.82 (s, 3 H, Me)
2d	152–153	152-15314	185 (M ⁺ , 100), 170 (41), 140 (23), 124 (17)	1520 (NO ₂), 1345 (NO ₂), 1088, 1047, 853	8.39–8.41 (d, <i>J</i> = 8.4, 2 H), 7.83–7.86 (d, <i>J</i> = 8.4, 2 H), 2.80 (s, 3 H, Me)
3b	105–106	104–105 ¹⁷	201 (M ⁺ , 46), 186 (74), 139 (100), 122 (25), 109 (26)	1547 (NO ₂), 1360 (NO ₂), 1306, 1154, 1121	8.21–8.23 (m, 1 H), 7.80–7.86 (m, 3 H), 3.44 (s, 3 H, Me)
3c	144–146	148.5 ^{2a}	201 (M ⁺ , 40), 186 (27), 139 (100), 122 (51), 109 (8)	1530 (NO ₂), 1356 (NO ₂), 1319, 1302, 1161	8.81 (t, J = 1.6, 1 H), 8.52–8.55 (m, 1 H), 8.30–8.32 (m, 1 H), 7.82–7.86 (t, J = 8.0, 1 H), 3.15 (s, 3 H, Me)
3d	142–144	142.5 ¹⁸	201 (M ⁺ , 32), 186 (23), 139 (100), 122 (56)	1530 (NO ₂), 1350 (NO ₂), 1323, 1304, 1154	8.43–8.45 (d, <i>J</i> = 9.2, 2 H), 8.16–8.18 (d, <i>J</i> = 9.2, 2 H), 3.13 (s, 3 H, Me)
7	79–81	84–85 ¹⁹	263 (M ⁺ , 64), 170 (100), 152 (14), 141 (26), 125 (94)	1524 (NO ₂), 1354 (NO ₂), 1327, 1308, 1159, 1132	8.77 (t, <i>J</i> = 2.0, 1.6, 1 H), 8.41–8.43 (m, 1 H), 8.27–8.29 (m, 1 H), 7.98–8.01 (m, 2 H), 7.72–7.76 (t, <i>J</i> = 8.0, 1 H), 7.62–7.64 (m, 1 H), 7.55–7.59 (m, 2 H)
8a	177–179	173–175 ^{4a}	308 (M ⁺ , 1), 170 (100), 151 (6), 139 (6), 122 (12)	1535 (NO ₂), 1372, 1356 (NO ₂), 1327, 1163, 590	8.73 (t, <i>J</i> = 2.0, 1 H), 8.48–8.50 (m, 2 H), 8.35–8.37 (m, 1 H), 7.80–7.92 (m, 4 H),
8b	199–201	202-20315	308 (M ⁺ , 13), 170 (100), 139 (6), 122 (12)	1609, 1535 (NO ₂), 1352 (NO ₂), 1335, 1167, 1109, 671	8.81 (t, <i>J</i> = 2.0, 2 H), 8.48–8.50 (m, 2 H), 8.33–8.35 (m, 2 H), 7.80–7.84 (t, <i>J</i> = 8.4, 2 H)
8c	181–184	182–184 ^{4a}	308 (M ⁺ , 13), 170 (100), 139 (5), 122 (8)	1532 (NO ₂), 1354 (NO ₂), 1312, 1163	8.81 (t, $J = 2.0, 1$ H), 8.48–8.50 (m, 1 H), 8.39–8.41 (d, $J = 9.2, 2$ H), 8.30–8.32 (m, 1 H), 8.18–8.21 (d, $J = 9.2, 2$ H), 7.78– 7.82 (t, $J = 8.0, 1$ H)
9	281–282	280-281 ²⁰	308 (M ⁺ , 14), 278 (4), 170 (100), 140 (10), 122 (19)	1547 (NO ₂), 1352 (NO ₂), 1308, 1161, 1105	8.39–8.41 (d, <i>J</i> = 9.2, 4 H), 8.16–8.19 (d, <i>J</i> = 9.2, 4 H)
12	158–161	162 ²¹	276 (M ⁺ , 17), 195 (12), 183 (11), 171 (19), 166 (100), 139 (47)	1593, 1566, 1518 (NO ₂), 1337 (NO ₂), 1306, 1256, 855, 743	8.26–8.28 (d, $J = 9.2, 2$ H), 8.20–8.22 (dd, J = 8.0, 1.6, 1 H), 7.66–7.68 (d, $J = 9.2, 2H), 7.43–7.48 (m, 1 H), 7.35–7.39 (m, 1H), 7.05–7.08 (dd, J = 8.0, 1.6, 1 H)$
13a	180–182	183 ^{5a}	170 (100), 139 (5), 122 (6)	1539 (NO ₂), 1358 (NO ₂), 1321, 1155, 1121	8.47–8.49 (dd, <i>J</i> = 8.0, 1.6, 2 H), 7.97– 7.99 (dd, <i>J</i> = 8.0, 1.6, 2 H), 7.88–7.93 (m, 2 H), 7.80–7.85 (m, 2 H)
13b ^a	204–208	-	308 (M ⁺ , 2), 170 (100), 152 (6), 139 (7), 122 (13)	1535 (NO ₂), 1364 (NO ₂), 1327, 1161, 1125	8.45–8.48 (m, 1 H), 8.39–8.41 (d, <i>J</i> = 8.8, 2 H), 8.14–8.16 (d, <i>J</i> = 8.8, 2 H), 7.85– 7.91 (m, 3 H)
17 ^b	78–80	-	255 (M ⁺ , 3), 186(100), 131 (4), 122 (73),	1547 (NO ₂), 1375 (NO ₂), 1318, 1213, 1132, 1071, 627	8.27–8.29 (d, <i>J</i> = 8.8, 2 H), 8.51–8.54 (d, <i>J</i> = 8.8, 2 H)
18°	92–93	_	300 (M ⁺ , 3), 231 (100), 186 (4)	1564 (NO ₂), 1379 (NO ₂), 1352, 1213, 1123, 1094, 625	8.50–8.52 (d, <i>J</i> = 8.8, 1 H), 8.68–8.71 (dd, <i>J</i> = 8.8, 2.0, 1 H), 8.74 (d, J = 2.0, 1 H)

Prod- uct	Mp (°C)	Lit. mp (°C)	MS (70 eV) <i>m</i> / <i>z</i> (%)	IR (KBr, cm ⁻¹)	¹ H NMR (CDCl ₃ /TMS), δ , <i>J</i> (Hz)
21	54–56	56–57 ²²	255 (M ⁺ , 2), 187 (8), 186(100), 122 (60)	1607, 1543 (NO ₂), 1372, 1356 (NO ₂), 1209, 1152, 1109, 1065, 880, 606	7.96–8.00 (t, <i>J</i> = 8.1 8.3, 1 H), 8.39–8.41 (d, <i>J</i> = 7.80, 1 H), 8.70–8.73 (m, 1 H), 8.89 (s, 1 H)

^a Anal. Calcd for C₁₂H₈N₂O₆S (308.26): C, 46.75; H, 2.62; N, 9.09. Found: C, 46.60; H, 2.71; N, 9.01.

^b Anal. Calcd for C₇H₄F₃NO₄S (255.18): C, 32.95; H, 1.58; N, 5.50. Found: C, 32.61; H, 1.54; N, 6.10.

^c Anal. Calcd for C₇H₃F₃N₂O₆S (300.18): C, 28.01; H, 1.01; N, 9.33. Found: C, 28.01; H, 1.11; N, 9.72.

All melting points were measured on a YANACO MP-S3 apparatus and are uncorrected. ¹H NMR spectra were obtained with a JEOL JNM-A400 spectrometer at 400 MHz for CDCl₃ solutions with TMS as an internal standard. *J* values are given in Hz. IR measurements were made on a JEOL FTIR-5300 spectrophotometer for KBr pellets and only prominent peaks below 2000 cm⁻¹ were recorded. Electron ionization (EI) mass spectra were obtained on a Shimadzu GCMS QP-5000 instrument at ionization potential of 70 eV. Merck precoated silica gel sheets 60F-254 were used for TLC monitoring. Chromatographic separation and purification were performed with Wakogel 200 (100–200 mesh) using hexane–EtOAc, 1→5:1 as the eluent. Products were identified by NMR, IR, MS and elemental analyses or by direct comparison with the authentic samples.

Reagents and solvents were all reagent-grade commercial products. Dichloromethane and 1,2-dichloroethane were distilled from CaH_2 prior to use. Nitrogen dioxide (99% purity, impurities involving nitrogen monoxide and small amounts of nitrogen) was purchased from Sumitomo Seika Co. Ltd. and used after transfer distillation. An apparatus (Nippon Ozone Co. Ltd., type ON-1–2) was used for the generation of ozone. The machine produced ozone at a rate of 10 mmol h⁻¹ under the conditions of oxygen flow rate 10 dm³ h⁻¹ and applied voltage 80 V. Aryl sulfides **1a**, **4** and **14** were purchased from Aldrich and aryl sulfoxides **2b–d** prepared by the oxidation of sulfides **1b–d** with nitrogen dioxide. Sulfone **19** was obtained by the oxidation of **14** with chromium trioxide in sulfuric acid.

Phenyl 2-Nitrophenyl Sulfide (10)

To a mixture of thiophenol (0.66 g, 6 mmol) and sodium hydride (0.32 g, 13 mmol) in DMF (40 mL) was added 2-chloronitrobenzene (0.95 g, 6 mmol) and the resulting deep purple soln was stirred at 10 °C for 24 h under argon. The mixture was diluted with ice H₂O and the organic phase was extracted with CH_2Cl_2 (2 × 50 mL). The combined extracts were washed with brine, dried over MgSO₄, and evaporated under reduced pressure to leave a solid residue, which was recrystallized from EtOH to give sulfide **10** (1.14 g, 83%) as yellow needles, mp 79–80 °C (Lit.¹³ mp 80.2 °C).

Methyl Nitrophenyl Sulfoxides 2b-d; Typical Procedure

To a soln of methyl 4-nitrophenyl sulfide [(1d), 0.085 g, 0.5 mmol] in CH₂Cl₂ (15 mL) was added liquid nitrogen dioxide (0.5 mL, 15 mmol) in one portion. The resulting mixture was stirred at -10 °C for 30 min, then diluted with ice H₂O, and washed with sat. aq NaHCO₃. The organic phase was extracted with CH₂Cl₂ (2 × 50 mL) and the combined extracts were washed with brine, dried over MgSO₄, and evaporated under reduced pressure. A solid residue was recrystallized from EtOH to give sulfoxide 2d (89 mg, 96%) as pale yellow needles, mp 152–153 °C (Lit.¹⁴ mp 152–153 °C).

Kyodai-Nitration of Aromatic Sulfides 1a,4 and Sulfones 3a,6,10; Typical Procedure

A soln of diphenyl sulfide [(4), 0.56 g, 3 mmol] in freshly distilled CH₂Cl₂ (30 mL) was stirred at -10 °C and liquid nitrogen dioxide (2.0 mL, 60 mmol) was introduced in one portion. After 15 min, a stream of ozonized oxygen was introduced slowly with vigorous stirring. Ozonized oxygen was continuously fed for 3-4 h at this temperature and the progress of the reaction intermittently monitored by TLC. When the reaction was almost complete, the cooling bath was removed and excess nitrogen dioxide was expelled by blowing air into the solution to collect in a cold trap for reuse. The reaction mixture was washed with sat. aq NaHCO3 and the organic phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with brine, dried over MgSO₄, and evaporated under reduced pressure to leave a solid residue (0.76 g), which was recrystallized from EtOH to obtain 3,3'-dinitrodiphenyl sulfone [(**8b**), 0.46 g] as yellow plates, mp 199–201 °C (Lit.¹⁵ mp 202– 203 °C). The mother liquor was evaporated to dryness and the residue was chromatographed on silica gel using hexane-EtOAc as the solvent to elute 3,4'-dinitrodiphenyl sulfone 8c, 8b and 2,3'-dinitrodiphenyl sulfone (8a) respectively.

Kyodai-Nitration of Phenyl Trifluorometyl Sulfide (14)

Phenyl trifluoromethyl sulfide [(14), 0.35 g, 2 mmol] was dissolved in freshly distilled CH_2Cl_2 (30 mL) and subjected to the Kyodai-nitration in a manner similar to that described above. The resulting mixture was worked up as usual to give nitroaryl sulfoxides 15 and 16 as an oily mixture (0.5 g). The mixture was suspended in a mixture of 97% H_2SO_4 (0.6 mL) and H_2O (1 mL) then heated with CrO_3 (0.6 g) at 100 °C for 8 h. The organic phase was extracted with CH_2Cl_2 (2 × 50 mL) and the combined extracts were washed successively with brine, sat. aq NaHCO₃, dried over MgSO₄, and evaporated under reduced pressure. The solid residue was chromatographed on silica gel using hexane–EtOH, 5:1 as the solvent to afford 4-nitrophenyl trifluoromethyl sulfone 17 (74 mg, 15%) as colorless needles.

Anal. Calcd for C₇H₄F₃NO₄S: C, 32.95; H, 1.58; N, 5.50. Found: C, 32.61; H, 1.54; N, 6.10.

Further elution gave 2,4-dinitrophenyl trifluoromethyl sulfone [(**18**), 165 mg, 28%] as white crystals.

Anal. Calcd for $C_7H_3F_3N_2O_6S$: C, 28.01; H, 1.01; N, 9.33. Found: C, 28.05; H, 1.11; N, 9.72.

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