

## Halodediazoniations of Dry Arenediazonium *o*-Benzenedisulfonimides in the Presence or Absence of an Electron Transfer Catalyst. Easy General Procedures To Prepare Aryl Chlorides, Bromides, and Iodides<sup>†</sup>

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The paper reports the results of a wide study aimed at preparing aryl chlorides **3** (19 examples), bromides **4** (19 examples), and iodides **5** (9 examples) by halodediazotiation of dry arenediazonium *o*-benzenedisulfonimides **1** with tetraalkylammonium halides **2**. The reactions were carried out in anhydrous acetonitrile at room temperature (~20 °C) in the presence of copper powder and at 60 °C or room temperature without the catalyst. In optimal conditions the yields were from good to excellent (60 reactions, 61–94% yield), with only a few exceptions (8 reactions, 51–55% yield). A good amount of the *o*-benzenedisulfonimide (**7**) was always recovered from the reactions and could then be reused to prepare salts **1**. An interesting aspect of this research is the surprising role of the anion of *o*-benzenedisulfonimide (**9**) as an electron transfer agent.

We recently<sup>1</sup> showed that dry arenediazonium *o*-benzenedisulfonimides **1** are easily prepared in excellent yield by diazotization of primary aromatic amines with isopentyl nitrite in the presence of *o*-benzenedisulfonimide (**7**) in acetic or formic acid. Salts **1** are exceptionally stable, able to be kept indefinitely, and ready for use with no ascertained risk,<sup>1</sup> hence their proposal as good synthesis intermediates, especially usable when reactions require anhydrous conditions. Of all the known dry-state arenediazonium salts,<sup>2</sup> only the tetrafluoroborates have several properties and performance comparable to those of salts **1**, and there are numerous examples regarding their preparation and synthetic uses. However, when compared with salts **1**, the arenediazonium tetrafluoroborates have some drawbacks. They are often obtained in good yield but there can be some difficulty in isolating them; most are sensitive to air, though there are exceptions, and therefore cannot be stored for long periods of time, and it is recommended they be used immediately

after preparation. Most tetrafluoroborates are thermally stable, but some can decompose violently on heating. The commercial availability of tetrafluoroboric acid is obviously an important point in favor of tetrafluoroborates. One very favorable feature of dry arenediazonium salts **1** is that *o*-benzenedisulfonimide (**7**), from which the anion of salts **1** derives, though not currently commercially available, is easily prepared starting from *o*-benzenedisulfonyl chloride,<sup>3–5</sup> and at the end of reactions carried out with salts **1** it can be recovered in good amount and reused.

Of all the reactions with diazonium salts, halodediazoniations are among the most studied with regard to both synthetic applications<sup>9,10</sup> and an understanding of the many mechanistic aspects.<sup>2a,10–12</sup>

This work reports the results of a wide study aimed at preparing aryl chlorides **3**, bromides **4**, and iodides **5** by halodediazotiation of salts **1** with tetraalkylammonium halides **2a–c** (Scheme 1). The possible role of the anion of *o*-benzenedisulfonimide (**9**) as an electron transfer agent is suggested.

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(5) The key intermediate *o*-benzenedisulfonyl chloride can be prepared starting from (a) commercially available (Aldrich) *o*-benzenedisulfonic acid dipotassium salt,<sup>6</sup> (b) anthranilic acid,<sup>7</sup> and (c) *o*-bis(methylthio)benzene.<sup>8</sup>

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**Table 1. Halodediazoniations of Dry Arenediazonium *o*-Benzenedisulfonimides (1a-s) Carried Out with Tetraalkylammonium Halides (2a-c) in Anhydrous Acetonitrile in the Presence or Absence of an Electron Transfer Catalyst**

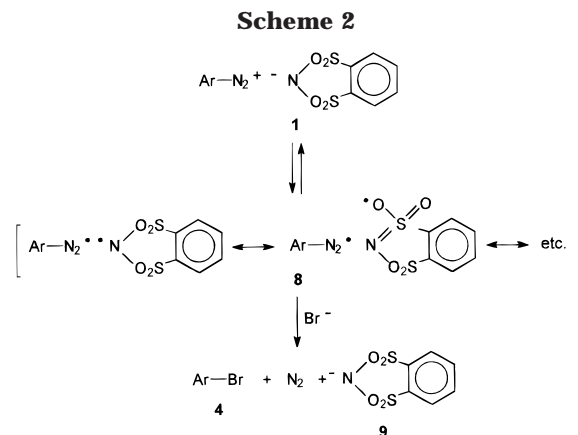
entry no.	Ar	molar ratio 1:2	catalyst	<i>T</i> <sup>b</sup> (°C)	<b>2</b> <sup>d</sup>	yield <sup>a</sup> (%)			yield <sup>c</sup> (%) lit.
						Ar-Cl	Ar-Br	Ar-I	
1	Ph	1:1		60	<b>2a</b>	3			
2		1:2.5		60	<b>2a</b>	7			
3		1:1	Cu	rt	<b>2a</b>	71			
4		1:2.5	Cu	rt	<b>2a</b>	79			95 <sup>e,f</sup>
5		1:1		60	<b>2b</b>		34		
6		1:1.75		60	<b>2b</b>		64		
7		1:2.5		60	<b>2b</b>		83		
8		1:3.5		60	<b>2b</b>		80		
9		1:1	Cu	rt	<b>2b</b>		74		
10		1:1.75	Cu	rt	<b>2b</b>		78		
11		1:2.5	Cu	0-5	<b>2b</b>		81		
12		1:2.5	Cu	rt	<b>2b</b>		86		
13		1:3.5	Cu	rt	<b>2b</b>		85		
14		1:1		rt	<b>2c</b>			88	90 <sup>g,h</sup>
15		1:2.5		rt	<b>2c</b>			90	
16	2-MeC <sub>6</sub> H <sub>4</sub>	1:2.5	Cu	rt	<b>2a</b>	51			
17		1:2.5		60	<b>2b</b>		51		
18		1:2.5	Cu	rt	<b>2b</b>		63		
19		1:1		rt	<b>2c</b>			75	91 <sup>g,h</sup>
20	3-MeC <sub>6</sub> H <sub>4</sub>	1:2.5	Cu	rt	<b>2a</b>	69			
21		1:2.5		60	<b>2b</b>		70		82 <sup>e,i</sup>
22		1:2.5	Cu	rt	<b>2b</b>		74		
23		1:1		rt	<b>2c</b>			81	82, <sup>e,j</sup> 93, <sup>e,k</sup> 96 <sup>g,h</sup>
24	4-MeC <sub>6</sub> H <sub>4</sub>	1:2.5		60	<b>2a</b>	8			
25		1:2.5	Cu	rt	<b>2a</b>	68			
26		1:2.5		60	<b>2b</b>		74		47, <sup>e,i</sup> 60 <sup>e,i,l</sup>
27		1:2.5	Cu	rt	<b>2b</b>		81		
28		1:1		rt	<b>2c</b>			82	49, <sup>e,j</sup> 57, <sup>e,k</sup> 88, <sup>e,j,l</sup> 90-94 <sup>g,h</sup>
29		1:2.5		rt	<b>2c</b>			82	
30	2-MeOC <sub>6</sub> H <sub>4</sub>	1:2.5	Cu	rt	<b>2a</b>	62			
31		1:2.5		60	<b>2b</b>		53		
32		1:2.5	Cu	rt	<b>2b</b>		55		
33	3-MeOC <sub>6</sub> H <sub>4</sub>	1:2.5	Cu	rt	<b>2a</b>	72			
34		1:2.5		60	<b>2b</b>		72		
35		1:2.5	Cu	rt	<b>2b</b>		78		
36	4-MeOC <sub>6</sub> H <sub>4</sub>	1:2.5	Cu	rt	<b>2a</b>	78			95 <sup>e,f</sup>
37		1:2.5		60	<b>2b</b>		74		76 <sup>i,m</sup>
38		1:2.5	Cu	rt	<b>2b</b>		81		
39	2-ClC <sub>6</sub> H <sub>4</sub>	1:2.5	Cu	rt	<b>2a</b>	51			
40		1:2.5		60	<b>2b</b>		52		43, <sup>e,i</sup> 70 <sup>e,i,l</sup>
41		1:2.5	Cu	rt	<b>2b</b>		61		
42	3-ClC <sub>6</sub> H <sub>4</sub>	1:2.5	Cu	rt	<b>2a</b>	68			
43		1:2.5		60	<b>2b</b>		75		88 <sup>e,i</sup>
44		1:2.5	Cu	rt	<b>2b</b>		71		
45	4-ClC <sub>6</sub> H <sub>4</sub>	1:2.5		60	<b>2a</b>	16			
46		1:2.5	Cu	rt	<b>2a</b>	70			
47		1:1		60	<b>2b</b>		29		
48		1:2.5		60	<b>2b</b>		73		84, <sup>e,i</sup> 90 <sup>e,i,l</sup>
49		1:1	Cu	rt	<b>2b</b>		62		
50		1:2.5	Cu	rt	<b>2b</b>		75		
51	2-BrC <sub>6</sub> H <sub>4</sub>	1:2.5	Cu	rt	<b>2a</b>	63			
52		1:2.5		60	<b>2b</b>		53		43 <sup>e,i</sup>
53		1:2.5	Cu	rt	<b>2b</b>		51		
54	3-BrC <sub>6</sub> H <sub>4</sub>	1:2.5	Cu	rt	<b>2a</b>	74			
55		1:2.5		60	<b>2b</b>		78		
56		1:2.5	Cu	rt	<b>2b</b>		80		
57	4-BrC <sub>6</sub> H <sub>4</sub>	1:2.5	Cu	rt	<b>2a</b>	74			
58		1:2.5		60	<b>2b</b>		83		47-67, <sup>e,n,o</sup> 70, <sup>e,n</sup> 77, <sup>e,i,l</sup> 80 <sup>e,i</sup>
59		1:2.5	Cu	rt	<b>2b</b>		87		
60	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	1:1		rt	<b>2a</b>	77			
61		1:1	Cu	rt	<b>2a</b>	74			
62		1:1		rt	<b>2b</b>		83		
63		1:1	Cu	rt	<b>2b</b>		89		
64		1:2.5	Cu	rt	<b>2b</b>		85		
65		1:1		rt	<b>2c</b>			94	88 <sup>g,h</sup>
66	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	1:2.5		60	<b>2a</b>	19			
67		1:1	Cu	rt	<b>2a</b>	67			
68		1:2.5	Cu	rt	<b>2a</b>	72			
69		1:2.5		60	<b>2b</b>		73		
70		1:1	Cu	rt	<b>2b</b>		69		
71		1:2.5	Cu	rt	<b>2b</b>		76		
72		1:1		rt	<b>2c</b>			87	96 <sup>p,q</sup>

Table 1 (Continued)

entry no.	Ar	molar ratio 1:2	catalyst	$T^b$ (°C)	<b>2<sup>d</sup></b>	yield <sup>a</sup> (%)			yield <sup>c</sup> (%) lit.
						Ar-Cl	Ar-Br	Ar-I	
73	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	1:1		60	<b>2a</b>	76		24 <sup>r</sup>	
74		1:1	Cu	rt	<b>2a</b>	77			
75		1:1		rt	<b>2b</b>		77		63, <sup>e,n</sup> 70, <sup>q,s</sup> 72, <sup>i,m</sup> 84, <sup>e,n,o</sup>
76		1:1	Cu	rt	<b>2b</b>		83		
77		1:2.5	Cu	rt	<b>2b</b>		83		
78		1:1		rt	<b>2c</b>			92	68, <sup>e,n</sup> 72, <sup>i,m</sup> 74, <sup>e,n,o</sup> 80, <sup>e,k</sup> 80, <sup>q,t</sup> 90, <sup>g,h</sup> 91 <sup>p,q</sup>
79	2-PhSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	1:1		60	<b>2a</b>	73 <sup>u,v</sup>			
80		1:1	Cu	rt	<b>2a</b>	75 <sup>u,v</sup>			
81		1:1		rt	<b>2b</b>		88 <sup>u,w</sup>		
82		1:1	Cu	rt	<b>2b</b>		85 <sup>u,w</sup>		
83	2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1:1		rt	<b>2a</b>	90 <sup>x</sup>			
84		1:1		rt	<b>2b</b>		92 <sup>x</sup>		
85		1:1		rt	<b>2c</b>			88 <sup>x</sup>	
86	1-naphthyl	1:1		60	<b>2a</b>	22			
87		1:2.5		60	<b>2a</b>	32			
88		1:1	Cu	rt	<b>2a</b>	78			
89		1:2.5	Cu	rt	<b>2a</b>	78			
90		1:1		60	<b>2b</b>		87		
91		1:1	Cu	rt	<b>2b</b>		81		
92		1:1		rt	<b>2c</b>			87	

<sup>a</sup> Yields refer to the pure (GC, GC-MS, TLC, NMR) products isolated by column chromatography, eluting with PE-CH<sub>2</sub>Cl<sub>2</sub> (9:1, v/v). Standard reaction time was 45 min. Yields were not influenced by longer reaction times. Identical physical and spectral data and retention times, by co-injection, for the resultant halides **3–5** and the corresponding commercially available samples of analytical purity were observed. <sup>b</sup> rt = room temperature (~20 °C). <sup>c</sup> Yields reported in the literature for the corresponding halides obtained by reaction of dry arenediazonium tetrafluoroborates with the reagents reported in the footnotes. <sup>d</sup> In the chlorodediazoniations, use of tetrabutylammonium chloride instead of benzyltriethylammonium chloride (**2a**) gave the corresponding aryl chlorides **3** in comparable yields. Choice of **2a** is only due to its inexpensiveness. <sup>e</sup> Yields determined by GC or GLC analyses. <sup>f</sup> Ar-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>:FeCl<sub>2</sub>:FeCl<sub>3</sub> = 1:3.04:1.18; CCl<sub>4</sub>-MeCN, 3:1; rt.<sup>19</sup> <sup>g</sup> Yield of isolated product with > 98% purity. <sup>h</sup> Ar-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>:KI:I<sub>2</sub> = 1:1.06:0.54; DMSO; 40 °C.<sup>20</sup> <sup>i</sup> Ar-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>:AcOK:18-crown-6:BrCCl<sub>3</sub> = 1:2:0.05:16.8; CHCl<sub>3</sub>; rt.<sup>13d</sup> <sup>j</sup> Ar-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>:AcOK:18-crown-6:MeI = 1:2:0.05:41.7; CHCl<sub>3</sub>; rt.<sup>13d</sup> <sup>k</sup> Ar-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>:AcOK:18-crown-6:I<sub>2</sub> = 1:2:0.05:16.8; CHCl<sub>3</sub>; rt.<sup>13d</sup> <sup>l</sup> Ar-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>:AcOK:18-crown-6:BrCCl<sub>3</sub> = 1:2:0.05:16.8; THF; rt.<sup>13d</sup> <sup>m</sup> Yield of isolated product of > 99% purity. <sup>n</sup> Ar-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>:AcOK:18-crown-6:BrCCl<sub>3</sub> = 1:2:0.05:16.8; CHCl<sub>3</sub>; rt.<sup>21</sup> <sup>o</sup> Ar-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>:AcOK:PEG:BrCCl<sub>3</sub> = 1:2:0.5-3.3:16.8; CHCl<sub>3</sub>; rt.<sup>21</sup> <sup>p</sup> Ar-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>:Me<sub>3</sub>SiI:MeI = 1:1.2:33.5; DMF; rt.<sup>13g</sup> <sup>q</sup> Yield of isolated product. <sup>r</sup> Obtained in mixture with 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-OH and coupled products, by reaction of 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> and LiCl (reagent ratio is not reported) in DMSO.<sup>13c</sup> <sup>s</sup> 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> and LiBr (reagent ratio is not reported) in DMSO.<sup>13c</sup> <sup>t</sup> 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-N<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> and LiI (reagent ratio is not reported) in DMSO.<sup>13c</sup> <sup>u</sup> The chromatographic eluent was PE-Et<sub>2</sub>O (7:3, v/v). <sup>v</sup> Mp 104–105 °C (CH<sub>2</sub>Cl<sub>2</sub>-PE) (lit.<sup>22</sup> mp 105–107 °C). <sup>w</sup> Mp 117–118 °C (CH<sub>2</sub>Cl<sub>2</sub>-PE) (lit.<sup>22</sup> mp 116–117.5 °C). <sup>x</sup> The reaction was immediate.

in the electrophilicity of the diazonium cation (**1o**), compared to that of the previously considered cations (**1n,p,q,r**). The very need to operate at 60 °C already shows that some difficulties arise in both these reactions. Furthermore the very poor yield of the chlorodediazonation, compared to bromodediazonation, demonstrates that the electron transfer from Cl<sup>-</sup> occurs with greater difficulty than that from Br<sup>-</sup>, in accordance with the redox potentials of the two halide anions. It is evident that the chlorodediazonation of the 3-nitrobenzenediazonium cation, which can no longer be exploited from the synthetic point of view (entry 66), takes place in critical conditions. On the contrary, it is worth noting that the reactions of entries 83 and 84 are immediate as the two nitro groups *ortho* and *para* positioned on the aromatic ring strongly enhance the electrophilicity of the diazonium cation. Apart from these particular cases, today's knowledge of the halodediazonation mechanisms is inadequate for a valid interpretation of bromodediazoniations that involve arenediazonium cations of limited electrophilicity and that have been successful in the absence of copper (Table 1). For these reactions a heterolytic mechanism must be excluded. In fact, if bromodediazonation had taken place through a heterolytic mechanism, via aryl cations, a similar mechanism would have acted not only in the presence of Br<sup>-</sup> ions but also in the presence of Cl<sup>-</sup> ions. Hence, given the poor selectivity of the aryl cations, the chloroarenes should have formed in an amount comparable to that of the bromoarenes (see Table 1: entries 2, 7; 24, 26; 45, 48 and 86, 90). To explain the success of these reactions there



is an attractive hypothesis based on the possibility that the anion of salts **1** could act by a primary electron donor reagent toward the arenediazonium cations, most likely giving rise to the outer-sphere (or not bonded) electron transfer complex **8** (Scheme 2). Such charge transfer would be actively favored by the formation of a complex where the partner of the aryldiazanyl radical is a species that is highly stabilized by resonance. Then the complex **8** would react with Br<sup>-</sup> to give **4**. So, the complex **8** could be productive in the bromodediazoniations and unproductive in the chlorodediazoniations, in accordance with the redox potentials of the two halide anions.

In conclusion, the present work presents a useful approach of general validity for the preparation of aryl chlorides **3**, bromides **4**, and iodides **5** by reaction of

arene-diazonium *o*-benzenedisulfonimides **1** with tetraalkylammonium halides **2a–c** in anhydrous acetonitrile and in the presence or absence of copper. The notable collection of homogeneous data has given the possibility of arriving at a reasonable interpretation of the mechanisms of the halodediazoniations carried out in acetonitrile, with and without copper. Further investigations are in progress concerning the hypothesized role of the anion of *o*-benzenedisulfonimide (**9**) as an electron transfer agent.

### Experimental Section

All of the reactions were performed in oven-dried glassware. Column chromatography and TLC were performed on Merck silica gel 60 (70–230 mesh ASTM) and GF 254, respectively, eluting with petroleum ether–methylene chloride (9:1, v/v), unless otherwise noted. Petroleum ether refers to the fraction boiling in the range 40–70 °C and is abbreviated as PE. Details for reactions 1–92 and yields of the pure (GC, GC-MS, TLC, NMR) isolated halides are listed in Table 1. With two only exceptions, identical physical and spectral data and retention times, by co-injection, for the resultant pure halides **3–5** and the corresponding commercially available samples of analytical purity were observed. Only 2-phenylsulfonylchlorobenzene (**3q**) and 2-phenylsulfonylbromobenzene (**4q**) are not commercially available. Structures of the two products obtained in this research were confirmed by comparison of their physical and spectroscopic data with those reported in the literature.

All the reagents and the reference compounds, i.e., chlorides **3**, bromides **4**, and iodides **5**, were purchased from the Aldrich Chemical Co.

*o*-Benzenedisulfonimide (**7**) was prepared according to the literature procedure,<sup>4</sup> starting from *o*-benzenedisulfonyl chloride<sup>7</sup> and NH<sub>3</sub> gas, via ammonium *o*-benzenedisulfonimide and its conversion using Dowex 50X8 resin (H<sup>+</sup>).<sup>16</sup> Dry arene-diazonium *o*-benzenedisulfonimides **1a–p,s** were prepared as described previously by us.<sup>1,17,18</sup> The crude salts were virtually pure and could be used in the next halodediazoniations, without further crystallization.

**Dry 2-Phenylsulfonylbenzenediazonium *o*-Benzenedisulfonimide (1q).** According to the procedure previously reported,<sup>1</sup> diazotization of 2-phenylsulfonylaniline (2.33 g, 10 mmol) was carried out with isopentyl nitrite (1.29 g, 11 mmol) in the presence of *o*-benzenedisulfonimide (**7**; 2.63 g, 12 mmol) in glacial AcOH (60 mL) at 0–5 °C. The virtually pure (NMR, dp) title compound **1q** was obtained in 92% yield (4.26 g). For analytical purposes, a sample was purified by dissolution in hot anhydrous acetonitrile and precipitation with anhydrous Et<sub>2</sub>O, after cooling: dp (decomposition point) 131–132 °C; <sup>1</sup>H NMR (CF<sub>3</sub>COOD) δ 7.10–8.18 and 8.28–8.65 ppm (2 m, 12:1). Anal. Calcd for C<sub>18</sub>H<sub>13</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>: C, 46.64; H, 2.83; N, 9.07; S, 20.75. Found: C, 46.53; H, 2.89; N, 8.97; S, 20.76.

**Dry 2,4-Dinitrobenzenediazonium *o*-Benzenedisulfonimide (1r).** Diazotization of 2,4-dinitroaniline (1.84 g, 10 mmol) was carried out as above with isopentyl nitrite (1.29 g, 11 mmol) in the presence of *o*-benzenedisulfonimide (**7**; 2.63 g, 12 mmol) in glacial AcOH (60 mL) at 0–5 °C. The virtually pure (NMR, dp) title compound **1r** was obtained in 85% yield

(3.53 g). For analytical purposes, a sample was crystallized as described for **1q**: dp 142–143 °C; <sup>1</sup>H NMR (CF<sub>3</sub>COOD) δ 7.60–7.80 and 8.60–9.25 ppm (2 m, 4:3). Anal. Calcd for C<sub>12</sub>H<sub>7</sub>N<sub>3</sub>O<sub>8</sub>S<sub>2</sub>: C, 34.87; H, 1.71; N, 16.95; S, 15.48. Found: C, 34.79; H, 1.73; N, 16.89; S, 15.44.

**Halodediazoniations Carried Out in the Absence of an Electron Transfer Catalyst. Representative Procedures. Bromobenzene (4a).** In entry 7 (Table 1) tetrabutylammonium bromide (**2b**; 8.06 g, 25 mmol) was added in one portion, under vigorous stirring, to a suspension of dry benzenediazonium *o*-benzenedisulfonimide (**1a**; 3.23 g, 10 mmol) in anhydrous MeCN (20 mL), maintained at room temperature (~20 °C). The reaction mixture was put into an oil bath previously warmed at 60 °C. During the first 20–30 min a slow evolution of nitrogen was observed and at the same time the salt dissolved. The resultant red-brown solution was warmed for a further 15 min. Completion of the reaction was confirmed by absence of azo coupling with 2-naphthol. GC and GC-MS analyses of the reaction mixture showed bromobenzene (**4a**) as major product and small amounts of three byproducts, i.e., acetanilide, MS *m/z* 135 (M<sup>+</sup>), *O*-phenyl-*o*-benzenedisulfonimide, and *N*-phenyl-*o*-benzenedisulfonimide, each with MS *m/z* 295 (M<sup>+</sup>). The solution was cooled and poured into Et<sub>2</sub>O–water (200 mL, 1:1). The aqueous layer, containing MeCN and a suspension of a fine white solid substance, was separated and extracted again with Et<sub>2</sub>O (80 mL). The combined organic extracts were washed several times with water (4 × 50 mL) to eliminate all the MeCN, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The crude residue was column chromatographed, eluting with PE–CH<sub>2</sub>Cl<sub>2</sub> (9:1, v/v), to afford the pure (GC, GC-MS, TLC, NMR) title compound **4a** as a colorless oil (1.30 g, 83% yield); MS *m/z* 156, 158 (M<sup>+</sup>). Identical physical and spectral data and retention time, by co-injection, for the product and an authentic sample of analytical purity were observed. The aqueous layer and the aqueous washings containing MeCN were collected and evaporated under reduced pressure. The residue was dissolved in CHCl<sub>3</sub> (6 mL). By addition of Et<sub>2</sub>O (24 mL) to the solution, a white precipitate of tetrabutylammonium *o*-benzenedisulfonimide (**6b**) was formed. It was gathered by filtration: mp 108.5–109.5 °C (CHCl<sub>3</sub>–PE); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.65–1.05, 1.05–1.85, 2.85–3.35, and 7.30–7.75 ppm (4 m, 12:16:8:4). Anal. Calcd for C<sub>22</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C, 57.36; H, 8.76; N, 6.09; S, 13.89. Found: C, 57.46; H, 8.67; N, 6.03; S, 13.99. Compound **6b** was then passed through a 30 g column of Dowex 50X8 ion exchange resin (Fluka), eluting with water (about 50 mL). After removal of the water under reduced pressure, virtually pure (NMR) *o*-benzenedisulfonimide (**7**) was recovered in 68% yield (1.49 g); mp 192–194 °C (toluene) (lit.<sup>1</sup> mp 192–194 °C). The filtrate was evaporated under reduced pressure. The resultant residue was virtually pure (NMR) tetrabutylammonium bromide (**2b**; 3.30 g, 41%, calculated on the amount of **2b** put in the reaction).

To separate the three byproducts, in a parallel test the aqueous layer and the aqueous washings containing MeCN were evaporated and the residue was column chromatographed. Elution with CHCl<sub>3</sub> afforded 0.02 g (~1%) of acetanilide (identical to an authentic sample of commercial origin) and 0.04 g (~1%) of *O*-phenyl-*o*-benzenedisulfonimide. The following elution with MeCOMe afforded 0.06 g (~2%) of *N*-phenyl-*o*-benzenedisulfonimide. Structures of the last two byproducts were confirmed by comparison with the authentic samples previously prepared.<sup>1</sup>

Comparable yields of **4a** and **7** were obtained when 35 mmol (11.27 g) of **2b** was used (entry 8). Entries 17, 21, 26, 31, 34, 37, 40, 43, 48, 52, 55, 58, and 69 were performed according to the above procedure. In entries 62, 75, 81, 84, and 90 the molar ratio **1:2b** was 1:1. While the last entry was carried out at 60 °C, the first four entries occurred at room temperature.

**2-Chloronitrobenzene (3n).** In entry 60 (Table 1) benzyltriethylammonium chloride (TEBA, **2a**; 2.27 g, 10 mmol) was added in one portion, under vigorous stirring, to a suspension of dry 2-nitrobenzenediazonium *o*-benzenedisulfonimide (**1n**; 3.68 g, 10 mmol) in anhydrous MeCN (20 mL), maintained at room temperature (~20 °C). A rapid evolution of nitrogen took

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(18) *Caution!* In our laboratory was no case of sudden decomposition during the preparation, purification, and handling of salts **1**. Nevertheless it must be born in mind that all diazonium salts in the dry state are potentially explosive. Therefore they must be carefully stored and handled.

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place at once and a pale-orange solution was obtained. Stirring at room temperature was maintained for 45 min. After this time, a test of azo coupling with 2-naphthol was negative. The crude residue obtained after a workup identical to that described above was column chromatographed using PE-CH<sub>2</sub>-Cl<sub>2</sub> (9:1, v/v) as eluent, to afford the pure (GC, GC-MS, TLC, NMR) title compound **3n** in 77% yield (1.21 g): mp 33–34 °C (PE); MS *m/z* 157 (M<sup>+</sup>). It was identical to an authentic sample of analytical purity. Virtually pure (NMR) *o*-benzenedisulfonimide (**7**) was recovered in 73% yield (1.60 g).

Entry 83 was performed according to the above procedure; entries 73 and 79 were carried out at 60 °C. Entries 2, 24, 45, 66, and 87 were carried out at 60 °C with a molar ratio **1:2a** = 1:2.5; the corresponding chlorides were obtained in very small yields (7–32%).

**Iodobenzene (5a).** In entry 14 (Table 1) tetrabutylammonium iodide (**2c**; 3.69 g, 10 mmol) was added in one portion, under vigorous stirring, to a suspension of dry **1a** (3.23 g, 10 mmol) in anhydrous MeCN (20 mL), maintained at room temperature (~20 °C). A rapid evolution of nitrogen took place at once, and a violet-brown solution was obtained. Stirring at room temperature was maintained for 45 min. After this time, a test of azo coupling with 2-naphthol was negative. The above workup afforded the pure (GC, GC-MS, TLC, NMR) title compound **5a** in 88% yield (1.80 g), as a pale-yellow oil; MS *m/z* 204 (M<sup>+</sup>). It was identical to an authentic sample of analytical purity. Virtually pure (NMR) *o*-benzenedisulfonimide (**7**) was recovered in 82% yield (1.80 g).

When 25 mmol (9.23 g) of **2c** was used (entry 15), **5a** and **7** were obtained in comparable yields. Entries 19, 23, 28, 65, 72, 78, 85, and 92 were performed according to the same procedure.

**Halodediazoniations Carried Out in the Presence of Copper. Representative Procedures. Bromobenzene (4a).** In entry 12 (Table 1), copper powder (0.02 g) was added, under vigorous stirring, to the reaction mixture prepared as described above in entry 7. A rapid evolution of nitrogen took place at once. The salt dissolved and the solution became red and then

cleared to pale orange. Stirring at room temperature (~20 °C) was maintained for 45 min. After this time, a test of azo coupling with 2-naphthol was negative. The solution was filtered to remove the copper and then worked up as described above for entry 7. The pure (GC, GC-MS, TLC, NMR) title compound **4a** was obtained in 86% yield (1.35 g) as a colorless oil, MS *m/z* 156, 158 (M<sup>+</sup>). It was identical to an authentic sample of analytical purity. Compounds **7** and **2b** were recovered in yields of 71% (1.55 g) and 40%, calculated on the amount of **2b** put in reaction (3.22 g), respectively.

The same reaction was also carried out at 0–5 °C (entry 11), and with a molar ratio salt **1a:2b** = 1:3.5 (entry 13). In both cases **4a** and **7** were obtained in comparable yields. Entries 18, 22, 27, 32, 35, 38, 41, 44, 50, 53, 56, 59, 64, 71, and 77 were performed according to the same procedure. Entries 49, 63, 70, 76, 82, and 91 were performed with a molar ratio salt **1:2b** = 1:1.

**Chlorobenzene (3a).** In entry 4 (Table 1), the reaction mixture was constituted of dry **1a** (3.23 g, 10 mmol), TEBA (**2a**; 5.68 g, 25 mmol), copper powder (0.02 g), and anhydrous MeCN (20 mL). As above, the reaction was immediate. Stirring at room temperature was continued for 45 min (negative test of azo coupling with 2-naphthol). The usual workup afforded the pure (GC, GC-MS, TLC, NMR) title compound **3a** as a colorless oil (79%, 0.89 g), MS *m/z* 112 (M<sup>+</sup>). It was identical to an authentic sample of analytical purity. *o*-Benzenedisulfonimide (**7**) was recovered in 72% yield (1.58 g).

Entries 16, 20, 25, 30, 33, 36, 39, 42, 46, 51, 54, 57, and 68 were performed according to the same procedure. In entries 61, 74, 80 and 88 the molar ratio salt **1:2a** was 1:1.

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