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Alkyl- and Arylthiodediazoniations of Dry Arenediazonium *o*-Benzenedisulfonimides. Efficient and Safe Modifications of the Stadler and Ziegler Reactions to Prepare Alkyl Aryl and Diaryl Sulfides

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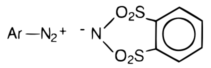
The reaction between dry arenediazonium *o*-benzenedisulfonimides **1** and sodium thiolates in anhydrous methanol represents an efficient and safe procedure, of general validity, for the preparation of unfunctionalized or variously functionalized alkyl aryl and diaryl sulfides. As a rule, the reaction temperature was maintained at 0−5 °C for the alkylthiodediazoniations and at room temperature (20−25 °C) for the arylthiodediazoniations. The sulfide yields are generally high; of the 63 considered examples, 43 gave yields greater than 80% and 13 were between 70% and 80%. Lower yields were obtained only when sterically hindered diazonium salts or thiols were used. A good amount of the *o*-benzenedisulfonimide (**8**) was always recovered from the reactions and could be reused to prepare salts **1**. The copious experimental data collected in homogeneous conditions have offered several starting points for the study of the mechanism of these reactions.

In recent work[1] we reported the preparation and some synthetic applications of a new and quite large family of dry diazonium salts, the arenediazonium *o*-benzenedisulfonimides **1**. In our opinion, the ease of preparation of salts **1** and their exceptional stability, storage safety and ease of handling stand them in competing stead for laboratory synthetic use, compared with the almost 100-year-old family of the arenediazonium tetrafluoroborates.[2] The interesting results achieved till now in synthetic applications of salts **1**[1] have encouraged us to revisit some classical reactions of the diazonium salts. The present work reports the results of a wide study on alkyl- and arylthiodediazoniations of dry arenediazonium *o*-benzenedisulfonimides **1**.



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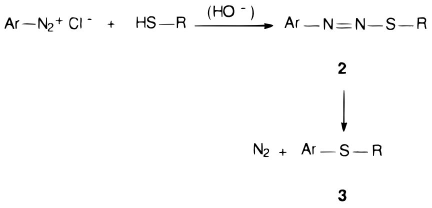
In 1884[3] Stadler described the first alkylthiodediazoniation, forming an alkyl aryl sulfide (**3**; Ar = Ph , R = Et), and 6 years later an analogous reaction resulting in a diaryl sulfide (**3**; Ar = R = Ph) was reported by Ziegler[4] (Scheme 1). It was highlighted that both reactions are dangerous to carry out as a result of the intermediate formation and accumulation in the mixtures of the highly explosive diazosulfides **2**. Starting from this early work, thus for more than a century, alkyl- and arylthiodediazoniations have been subjected to numerous studies concerning both synthetic[5,6] and mechanistic[6] aspects.

Scheme 1



It is to be noted that the preparation of alkyl aryl sulfides through alkylthiodediazoniation has been used extensively for the industrial production of arylthioglycolic acids, which are intermediates in the manufacture of many thioindigoid dyes.[7] However, alkylthiodediazoniation has been used only occasionally in the laboratory, the number of cases being quite limited.[8] In fact, this approach has received little consideration, preference being given to valid alternative routes based on the alkylation of arenethiols that are easily accessible with no-risk procedures. Obviously such routes are safe, but they are certainly more laborious in that there is the need

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[1] (a) Barbero, M.; Degani, I.; Fochi, R.; Perracino, P. (National Research Council of Italy) PCT/EP98/01145, 1998; *Chem. Abstr.* **1998**, *129*, 244942. (b) Barbero, M.; Crisma, M.; Degani, I.; Fochi, R.; Perracino, P. *Synthesis* **1998**, 1171. (c) Barbero, M.; Degani, I.; Dughera, S.; Fochi, R.; Perracino, P. *Synthesis* **1998**, 1235. (d) Barbero, M.; Degani, I.; Dughera, S.; Fochi, R.; Perracino, P. *Synthesis* **1999**, 90. (e) Barbero, M.; Degani, I.; Dughera, S.; Fochi, R. *J. Org. Chem.* **1999**, *64*, 3448.

[2] Bart, H. M. German Patent 281,055, 1913; *Chem. Abstr.* **1915**, *9*, 1830.

[3] Stadler, O. *Chem. Ber.* **1884**, *17*, 2075.

[4] Ziegler, J. H. *Chem. Ber* **1890**, *23*, 2469.

[5] Saunders, K. H.; Allen, R. L. M. *Aromatic Diazo Compounds*, 3rd ed.; Edward Arnold: London, 1985; and references therein.

[6] Zollinger, H. *Diazo chemistry I*; WCH: Weinheim, 1994; and references therein.

[7] (a) Saunders, K. H.; Allen, R. L. M. *Aromatic Diazo Compounds*, 3rd ed.; Edward Arnold: London, 1985; p 722. (b) Yildirir, Y.; Okay, G. *Org. Prep. Proced. Int.* **1991**, *23*, 198 and references therein.

[8] For example, see: (a) Elbel, E. Henkel & Cie. G.m.b.H., German Patent 614,311, 1935; *Chem. Abstr.* **1935**, *29*, 5862. (b) Baleja, J. D. *Synth. Commun.* **1984**, *14*, 215. (c) Schaefer, T.; Baleja, J. D. *Can. J. Chem.* **1986**, *64*, 1376.

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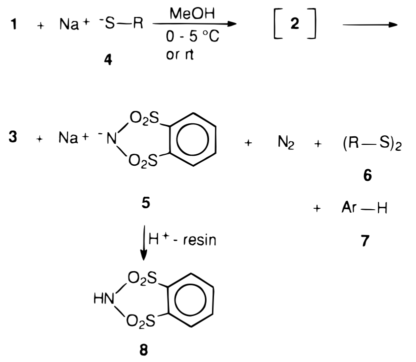
Scheme 2



for the intermediate preparation of the arenethiols. On the contrary, one of the most used approaches for the preparation of symmetrical and unsymmetrical diaryl sulfides is still based on the reaction of Ziegler.[9] Various synthetic devices have been adopted to achieve the gradual decomposition of diazosulfides **2** and avoid explosive courses, but caution is still obligatory.[10] Quite recently there was the description of a mild and efficient approach to diaryl sulfides, which was based on the reaction of arenediazonium tetrafluoroborates and arenethiolates in $\mathrm{Me_2SO}$ at 25 °C.[9a]

The modifications that the present research has made to the reactions of Stadler and Ziegler have led to an efficient and safe procedure, of general validity, for the preparation of unfunctionalized or variously functionalized alkyl aryl and diaryl sulfides.

Results and Discussion

All of the reactions were carried out by adding the dry arenediazonium *o*-benzenedisulfonimides **1** to vigorously stirred solutions of the sodium thiolates **4** in anhydrous methanol (Scheme 2). The reagents were used in a molar ratio of **1** to **4** = 1:1.1, but different molar ratios (1:1.5, 1:2, and 1:3) led to no modifications, neither in reaction time nor in yield. As a rule the reaction temperature was maintained at 0−5 °C for the alkylthiodediazoniations and room temperature (room temperature, 20−25 °C) for the arylthiodediazoniations. However, the methylthiodediazoniations of 2-, 3-, and 4-nitro- and 2,4-dinitrobenzenediazonium *o*-benzenedisulfonimides (Table 1, entries 13−15 and 23) were carried out very cautiously at −15 °C as they were far too lively if done at 0−5 °C. The methylthiodediazoniation of the 4-carboxybenzenediazonium cation (Table 1, entry 17) was done at −78 °C to minimize the formation of benzoic acid that came from the competing hydrodediazoniation. The main reaction products were the sulfides **3** and the sodium salt of *o*-benzenedisulfonimide (**5**). Chromatography of the latter on a cation-exchange resin (Dowex 50X8) led to the recovery of high yields of *o*-benzenedisulfonimide (**8**), which could then be reused to prepare the diazonium salts **1**. Identified among the byproducts and isolated in the case of the arylthiodediazoniations and several alkylthiodediazoniations were the disulfides **6,** in percentage yields almost complementary to those of the sulfides **3**; furthermore, the arenes **7** were identified, a few particular cases also being isolated. Tables 1 and 2 show the examples and results.

All of the studied reactions took place with a marked development of nitrogen and, at the same time, with a temporary, intense coloration likely imputable to the formation of charge-transfer complexes. Most of the reactions reached completion with the end of the addition and the dissolving of salts **1**. In these cases reaction end was confirmed by a negative test with 2-naphthol; the intermediate diazosulfides **2** were never observed. Instead, for slower alkylthiodediazoniations and arylthiodediazoniations, the presence of the diazosulfides **2** was observed by TLC analysis (experimental). All of the alkylthiodediazoniations were immediate (Table 1), with the exception of the reactions between the benzenediazonium *o*-benzenedisulfonimide and sodium butan-2-thiolate or cyclohexanethiolate (entries 26 and 28) and the reaction between 2,6-dibromobenzenediazonium *o*-benzenedisulfonimide and sodium methanethiolate (entry 24). In this last reaction it was possible to isolate and recognize the diazosulfide intermediate (**2**; Ar = 2,6-$\mathrm{Br_2C_6H_3}$, R = Me). However the sulfide yield was low (21%) and the main product was 1,3-dibromobenzene (53%). The only unsuccessful reaction was that carried out with sodium 2-methylpropan-2-thiolate (entry 27), which stopped with the formation of the diazosulfide (**2**; Ar = Ph, R = *t*-Bu). Also essentially immediate were most of the arylthiodediazoniations (Table 2). However, when there were one or two halogen atoms bonded at positions *ortho* to the diazonium cation the reaction time was significantly longer (entries 8, 11, and 21−23). In these cases the hydrodediazoniation competed with the arylthiodediazoniation. The first reaction even prevailed in entry 23 where the (2,6-dibromophenyl)(phenylsulfanyl)diazene intermediate disappeared after 30 h and gave rise not to the 2,6-dibromophenyl phenyl sulfide but to the 1,3-dibromobenzene (77%). Longer times were also required for the reactions of entries 25−27, cases where two methyl groups or two atoms of either chlorine or bromine are bonded at positions *ortho* to the thiolate anion.

The synthetic value of the proposed procedure can be summarized into the following points: (i) the preparation of dry arenediazonium *o*-benzenedisulfonimides **1** is extremely simple and fast, also in cases where traditional procedures present some difficulty;[1] (ii) easily isolated from the reaction products is the sodium salt of *o*-benzenedisulfonimide (**5**), from which there is the recovery, in good yield, of the *o*-benzenedisulfonimide (**8**), reusable for the preparation of diazonium salts **1**; (iii) the sulfide yields are generally high; of the 63 considered examples, 43 gave yields greater than 80% and 13 were between 70% and 80%; lower yields were obtained only when sterically hindered diazonium salts or thiols were used; (iv) the procedure is of general applicability with regard to both the alkylthiodediazoniations and the arylthiodediazoniations, as only two cases (out of over sixty) could be considered unsuccessful; (v) particularly interesting for manifold synthetic developments is the possibility of obtaining unfunctionalized or variously functionalized alkyl aryl and diaryl sulfides; (vi) the reaction times are, as a rule, short; (vii) the byproducts can be easily separated by column chromatography; and

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(9) For example, see: (a) Petrillo, G.; Novi, M.; Garbarino, G.; Dell'Erba, C. *Tetrahedron* **1986**, *42*, 4007 and references therein. (b) Abeywickrema, A. N.; Beckwith, A. L. J. *J. Am. Chem. Soc.* **1986**, *108*, 8227 and references therein. (c) Permual, S.; Chandrasekaran, R.; Vijayabaskar, V.; Wilson, D. A. *Magn. Reson. Chem.* **1995**, *33*, 779 and references therein.

(10) (a) British Chemical Industry Safety Council *Quarterly Safety Summary* **1969**, *40*, 158. (b) Spencer, H. *Chem. Br.* **1977**, *13*, 240 and references therein.

Table 1. Alkyl Aryl Sulfides

						yield[c] (%)			sulfide **3**		
entry	Ar	R	*T*[a] (°C)	time (h)	chromatographic solvent[b]	**3**	**6**	**8**	MS *m/z* (M^+)	mp[b] or bp (°C/mmHg)	lit. mp or bp (°C/mmHg)
1	Ph	Me	0−5	[d]	P	82	[e]	81	124	45/0.3	58−60/0.6[25]
2	2-MeC_6H_4	Me	0−5	[d]	PE	86	[e]	76	138	52/1	96−97/17[25]
3	3-MeC_6H_4	Me	0−5	[d]	PE	82	[e]	79	138	72/3.5	94/14[26]
4	4-MeC_6H_4	Me	0−5	[d]	PE	86	[e]	81	138	60/0.6	104−105/20[25]
5	2-$MeOC_6H_4$	Me	0−5	[d]	PE−EE (9.8:0.2)	88	[e]	76	154	98/1.5	237/760[25]
6	3-$MeOC_6H_4$	Me	0−5	[d]	PE−EE (9.8:0.2)	85	[e]	76	154	95/2	125−127/18[27]
7	4-$MeOC_6H_4$	Me	0−5	[d]	PE−EE (9.8:0.2)	87	[e]	80	154	26 (M−P)	25−26[25]
8	2-ClC_6H_4	Me	0−5	[d]	PE	82	[e]	77	158	80/1.5	116−117/15[25]
9	3-ClC_6H_4	Me	0−5	[d]	PE	84	[e]	74	158	94/0.7	112/16[25]
10	4-ClC_6H_4	Me	0−5	[d]	PE	86	[e]	80	158	82/1.5	104−105/10[25]
11	2-BrC_6H_4	Me	0−5	[d]	PE	76	[e]	73	202	75/1.5	172−179/13.5[25]
12	4-BrC_6H_4	Me	0−5	[d]	PE	85	[e]	78	202	39−40 (M−P)	38−40[25]
13	2-$O_2NC_6H_4$	Me	−15	[d]	PE−EE (9.8:0.2)	91	[e]	78	169	63−64 (M−P)	64−65[25]
14	3-$O_2NC_6H_4$	Me	−15	[d]	PE−EE (9.8:0.2)	89	[e]	78	169	140/3.5	125/32[25]
15	4-$O_2NC_6H_4$	Me	−15	[d]	PE−EE (9.8:0.2)	88	[e]	77	169	72 (M−P)	72−73[25]
16	4-NCC_6H_4	Me	0−5	[d]	PE−EE (9.8:0.2)	84	[e]	83	149	64 (M−P)	64[25]
17	4-$HOOCC_6H_4$	Me	−78	[d]	[f]	76	[e]	81	168	193−194 (W)	192[25]
18	4-$MeOOCC_6H_4$	Me	0−5	[d]	PE−EE (9.8:0.2)	90	[e]	80	182	81 (M−P)	82[25]
19	2-HOC_6H_4	Me	rt	[d]	PE−EE (9.5:0.5)	77	[e]	58	140	81−82/0.5	104−105/22[25]
20	4-HOC_6H_4	Me	rt	[d]	PE−EE (9.5:0.5)	86	[e]	61	140	84−85 (M−P)	84−85[25]
21	2-$MeSC_6H_4$	Me	0−5	[d]	PE−EE (9.8:0.2)	83	[e]	73	170	102/0.4	93−94/0.2[25]
22	2-naphthyl	Me	0−5	[d]	PE	84	[e]	71	174	62−63 (M−P)	63−64[25]
23	2,4-$(O_2N)_2C_6H_3$	Me	−15	[d]	PE−EE (9.5:0.5)	89	[e]	82	214	125 (M−P)	126[25]
24	2,6-$Br_2C_6H_3$	Me	rt	45 min	PE[g]	21	[e]	70	280	52−53 (P)	[h]
25	Ph	Bu	0−5	[d]	PE	86	13[i]	74	166	154−155/14	92−95/4[26]
26	Ph	*s*-Bu	0−5	2.5	PE	66	38[j]	85	166	148−150/12	50−52/0.05[28]
27	Ph	*t*-Bu	rt	[d]	PE[k]						
28	Ph	*c*-C_6H_{11}	0−5	3.0	PE	67	11[l]	73	192	98−99/0.2	150−152/12[25]
29	4-$MeOC_6H_4$	*n*-C_6H_{13}	0−5	[d]	PE−EE (9.8:0.2)	81	19[m]	78	224	100−101/0.5	138−141/5[25]
30	4-HOC_6H_4	*n*-C_6H_{13}	0−5	[d]	PE−EE (9:1)	82	17[m]	80	210	60−61 (PE)	60[29]
31	Ph	*n*-C_8H_{17}	0−5	[d]	PE	83	14[n]	86	222	115−116/0.3	173−175/18[30]
32	Ph	*n*-$C_{16}H_{33}$	0−5	[d]	PE	75	22[o]	89	334	48 (PE)	48−49[31]
33	Ph	CH_2Ph	0−5	[d]	PE−EE (9.8:0.2)	82	tr[p]	81	200	41−42 (P)	43−44[25]
34	Ph	CH_2COOH	rt	[d]	f	83		79	168	65−66 (PE)	63.5[25]
35	Ph	CH_2CH_2OH	rt	[d]	PE−EE (6:4)	86		81	154	79−80/0.5	135/8[25]
36	Ph	CH_2CH_2COOH	rt	[d]	f	88		78	182	60 (PE)	59.5−60[25]

[a] rt = room temperature (20−25 °C). [b] P = pentane, PE = petroleum ether, EE = diethyl ether, M = methylene chloride, W = water. [c] Yields of pure products obtained by column chromatography. Yields unchanged when the reactions were carried out under an atmosphere of N_2. [d] The reaction was immediate. [e] The byproduct dimethyl disulfide was isolated in variable amounts, because no particular device was adopted to avoid its loss during the solvent evaporation. [f] The crude residue, obtained after the usual workup of the reaction mixture, was virtually pure (TLC, NMR) sulfide. [g] Hydrodediazoniation product, i.e.,1,3-dibromobenzene, was isolated in 53% yield. [h] The compound is known,[8c] but physical and spectral data are not reported (experimental). [i] Dibutyl disulfide (experimental). [j] Di(*s*-butyl) disulfide (experimental). [k] The reaction product was (*Z*)-(*tert*-butylsulfanyl)(phenyl)diazene (experimental). [l] Dicyclohexyl disulfide: MS *m/z* 230 (M^+), bp 99 °C/0.15 mmHg (lit.[25] bp 195 °C/20 mmHg). [m] Dihexyl disulfide: MS *m/z* 234 (M^+), bp 85−86 °C/0.5 mmHg (lit.[25] bp 98−100 °C/0.1 mmHg). [n] Dioctyl disulfide: MS *m/z* 290 (M^+), bp 162−163 °C/0.3 mmHg (lit.[25] bp 198−203/13 mmHg). [o] Dihexadecyl disulfide: mp 51−52 °C (PE) (lit.[25] mp 55 °C). [p] tr = traces. Dibenzyl disulfide: MS *m/z* 246 (M^+).

(viii) the reactions are safe as a result of the exceptional stability of the arenediazonium *o*-benzenedisulfonimides **1**[1] and the absence of accumulation of the diazosulfides **2** in a separate phase, even when sterically hindered substrates are used (Table 1, entries 24, 26, and 28; Table 2, entries 21−23, 26, and 27). Such accumulation, which occurs for reactions carried out in aqueous media, is the attributed danger of alkylthiodediazoniations and arylthiodediazoniations.

The copious results collected in homogeneous conditions have offered several useful starting points for a study of the mechanism of the alkylthiodediazoniations and arylthiodediazoniations achieved by reacting salts **1** with thiolates **4** in anhydrous methanol. In the first place, there is no reasonable doubt that the studied reactions take place through a homolytic pathway induced by electron transfer. In fact, the electronic (not steric!) effects of the substituents on the reaction times and product yields are negligible. We confirmed the homolytic course induced by electron transfer with a known diagnostic test. Such a test consisted of carrying out the reaction between benzenediazonium *o*-benzenedisulfonimide and sodium benzenethiolate in MeOH in the presence of *m*-dinitrobenzene, an excellent electron acceptor.[9a,11] This reaction, compared with the one without *m*-dinitrobenzene, was definitely very much slower (2.5 h) and the yield of diphenyl sulfide much lower (26%). For arylthiodediazoniations, carried out by reacting various dry arenediazonium tetrafluoroborates with excess sodium arenethiolates in DMSO, an $S_{RN}1$ mechanism was postulated[9a] and this refers to the $S_{RN}1$ mechanism proposed by Bunnett for various aromatic nucleophilic substitutions.[11,12] Such a mechanism, shown with some formal modifications in Scheme 3 (steps 1−5), can explain only a few, not all, of the results from the alkylthiodediazoniations and arylthiodediazoniations considered in the present work.

Let us look at the arylthiodediazoniations carried out

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(11) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413 and references therein.

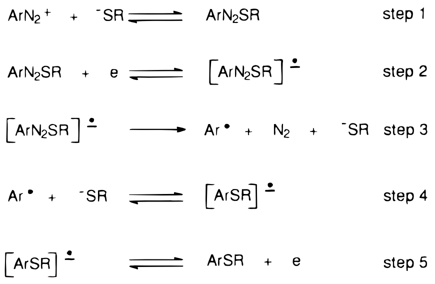
(12) (a) Bunnett, J. F.; Kim, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 7463. (b) Bunnett, J. F.; Kim, J. K.; *J. Am. Chem. Soc.* **1970**, *92*, 7464.

Table 2. Diaryl Sulfides

						yield[c] (%)			sulfide **3**		
entry	Ar	R	*T*[a] (°C)	time (h)	chromatographic solvent[b]	**3**	**6**[d]	**8**	MS *m*/*z* (M^+)	mp[b] or bp (°C/mmHg)	lit. mp or bp (°C/mmHg)
1	Ph	Ph	rt	*e*	PE	73	22	78	186	97−98/3	162−163/18[25]
2	2-MeC_6H_4	Ph	rt	*e*	PE−EE (9.8:0.2)	74	20	78	200	108−110/3	222.5/100[25]
3	3-MeC_6H_4	Ph	rt	*e*	PE−EE (9.8:0.2)	84	14	78	200	111−112/3	164.5/11[25]
4	4-MeC_6H_4	Ph	rt	*e*	PE−EE (9.8:0.2)	91	8	83	200	112−113/3	167.5/11[25]
5	2-$MeOC_6H_4$	Ph	rt	*e*	PE−EE (9.8:0.2)	78	17	78	216	130/0.3	154/3[25]
6	3-$MeOC_6H_4$	Ph	rt	*e*	PE−EE (9.8:0.2)	79	15	78	216	122/0.3	162−164/5.5[9c]
7	4-$MeOC_6H_4$	Ph	rt	*e*	PE−EE (9.8:0.2)	79	14	78	216	140/5	120/2[32]
8	2-ClC_6H_4	Ph	rt	15 min	PE	77	16	77	220	164−165/5	153−155/3.5[25]
9	3-ClC_6H_4	Ph	rt	*e*	PE	81	16	78	220	166−167/5	148−150/0.2[9c]
10	4-ClC_6H_4	Ph	rt	*e*	PE	82	14	77	220	170−171/5	139−140/1.5[33]
11	2-BrC_6H_4	Ph	rt	25 min	PE	81	15	77	264	146−147/5	174−176/12[9c]
12	3-BrC_6H_4	Ph	rt	*e*	PE	87	13	78	264	149−150/5	151−153/3[9c]
13	4-BrC_6H_4	Ph	rt	*e*	PE	89	10	82	264	25−26 (P)	24−25[34]
14	2-$O_2NC_6H_4$	Ph	rt	*e*	PE−EE (9.8:0.2)	82	13	78	231	80−81 (M−P)	80.2[25]
15	3-$O_2NC_6H_4$	Ph	rt	*e*	PE−EE (9.5:0.5)	81	9	80	231	41−42 (M−P)	42.5[25]
16	4-$O_2NC_6H_4$	Ph	rt	*e*	PE−EE (9.8:0.2)	84	14	91	231	55 (M−P)	55[25]
17	4-NCC_6H_4	Ph	rt	*e*	PE−EE (9.8:0.2)	83	15	76	211	40 (M−P)	39−40[25]
18	4-$MeOOCC_6H_4$	Ph	rt	*e*	PE−EE (9.8:0.2)	82	15	74	244	73−74 (M−P)	69−70[25]
19	2-naphthyl	Ph	rt	*e*	PE	84	12	71	236	51−52 (E)	51−52[25]
20	2,6-$Me_2C_6H_3$	Ph	rt	*e*	PE	81	13	82	214	118/0.3	112−122/1[35]
21	2,6-$F_2C_6H_3$	Ph	rt	2	PE[f]	71	23	73	222	114−116/0.3[g]	
22	2,6-$Cl_2C_6H_3$	Ph	rt	8	PE[h]	47	40	73	255	51−52 (PE)[i]	
23	2,6-$Br_2C_6H_3$	Ph	rt	30	PE[j]	tr[k]	56	77	342		
24	2,4-$(O_2N)_2C_6H_3$	Ph	rt	*e*	PE−EE(9.5:0.5)	83	8	80	277	121−122 (M−P)	121[25]
25	Ph	2,6-$Me_2C_6H_3$	rt	0.5	PE	82	tr[k,l]	73	214	118/0.3	
26	Ph	2,6-$Cl_2C_6H_3$	rt	1.5	PE	86	tr[k,m]	76	255	51−52 (PE)[i]	
27	Ph	2,6-$Br_2C_6H_3$	rt	2	PE	60	tr[k,n]	72	342	77−78 (E)[o]	

[a] rt = room temperature (20−25 °C). [b] PE = petroleum ether, EE = diethyl ether, P = pentane, M = methylene chloride, E = EtOH. [c] Yields of pure products obtained by column chromatography. Yields unchanged when the reactions were carried out under an atmosphere of N_2. [d] Diphenyl disulfide, unless otherwise noted. [e] The reaction was immediate. [f] GC-MS analysis of the reaction mixture showed also the presence of the product of hydrodediazoniation, i.e., 1,3-difluorobenzene (experimental). [g] ^{1}H NMR ($CDCl_3$) δ 6.72−7.60 ppm (m). Anal. Calcd for $C_{12}H_8F_2S$: C, 64.85; H, 3.63; F, 17.10; S, 14.43. Found: C, 64.76; H, 3.63; F, 17.07; S, 14.42. [h] The product of hydrodediazoniation, i.e., 1,3-dichlorobenzene, was also isolated in 35% yield (experimental). [i] ^{1}H NMR ($CDCl_3$) δ 7.10−7.70 ppm (m). Anal. Calcd for $C_{12}H_8Cl_2S$: C, 56.49; H, 3.16; Cl, 27.79; S, 12.56. Found: C, 56.44; H, 3.19; Cl, 27.76; S, 12.60. [j] The product of hydrodediazoniation, i.e. 1,3-dibromobenzene, was isolated in 77% yield (experimental). [k] tr = traces. [l] Bis(2,6-dimethylphenyl) disulfide: MS *m*/*z* 274 (M^+). [m] Bis(2,6-dichlorophenyl) disulfide: MS *m*/*z* 354 (M^+). [n] Bis(2,6-dibromophenyl) disulfide: MS *m*/*z* 530 (M^+). [o] ^{1}H NMR ($CDCl_3$) δ 6.70−7.40 and 7.42−7.90 ppm (2 m, 1:1). Anal. Calcd for $C_{12}H_8Br_2S$: C, 41.89; H, 2.34; Br, 46.45; S, 9.32. Found: C, 41.80; H, 2.44; Br, 46.35; S, 9.40.

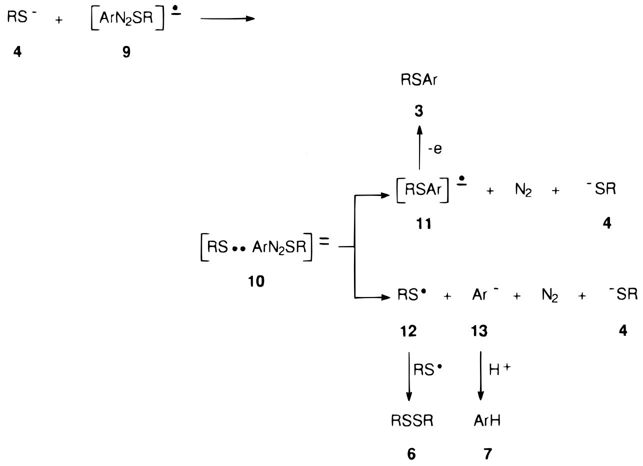
Scheme 3



with arenediazonium *o*-benzenedisulfonimides **1** in MeOH and with arenediazonium tetrafluoroborates in DMSO.[9a] The results suggest the following observations: (i) by using a protic solvent, MeOH, instead of a polar aprotic solvent, DMSO, the reactions are very much faster; (ii) there is no need to use a big excess of arenethiolate compared to the diazonium salt; in fact, the reactions reported here use a molar ratio of arenediazonium salt to arenethiolate = 1:1.1, instead of 1:3; (iii) the main products of the reactions are sulfides **3**, but along with these there is the formation of consistent amounts of disulfides **6** and arenes **7**; instead, in DMSO these last are present in negligible amounts; and (iv) there was never any halogen substitution when haloarenediazonium salts were used; this is quite different from the reactions carried out in DMSO.

Assuming that the dissociation (step 3) is the slow step of the chain process (steps 2−5), such dissociation would be favored by the greater solvation of the leaving group RS^-, performed by MeOH versus DMSO. In fact, a collateral reaction carried out by reacting benzenediazonium *o*-benzenedisulfonimide with sodium benzenethiolate in DMSO (molar ratio 1:1.1) was not immediate. On adding MeOH to the reaction mixture, the reaction went to completion very rapidly and afforded diphenyl sulfide in high yield (experimental). Furthermore, always assuming that step 3 determines the reaction rate, the concentration of the nucleophile RS^- would have no influence. The increase in the dissociation rate, due to the greater solvation of the leaving group, could also lead to the dissociation reaction prevailing to such a degree as to make the substitution of halogens on the diazonium cation comparatively negligible. However the hypothesis that arylthiodediazoniation performed in MeOH takes place by a mechanism identical to that postulated for the arylthiodediazoniation carried out in DMSO (Scheme 3) does not justify the formation of considerable amounts of disulfides **6** and arenes **7** (Table 1, entry 24; Table 2, entries 22 and 23). Furthermore it does not explain the marked steric effects exercised on the reactions by bulky substituents in the *ortho* positions on the diazonium cation (Table 1, entries 24; Table 2, entries 21−23) and thiolate anion (Table 2, entries 25−27). In fact, such effects would find no adequate justification if there were

Scheme 4



a simple coupling between an aryl radical and a thiolate anion (step 4).

Recently, many experimental data relative to the most important reactions within the framework of the currently accepted $S_{RN}1$ mechanism[13] have been reconsidered and reinterpreted by an alternative bimolecular $S_{RN}2$ mechanism.[14] This therefore, as the $S_{RN}1$, is a homolytic chain process but differs from the last one in that the nucleophile reacts directly with the radical anion derived from the starting substrate, instead of with the aryl radical that originates from the dissociation step.[15]

Scheme 4 shows an adaptation of the $S_{RN}2$ mechanism to the alkyl- and arylthiodediazoniations we studied. Reacting the thiolate anion **4** with the diazosulfide radical anion **9** would lead to the intermediate dianion **10**. From this, through competitive dissociation reactions, there would be formed (a) the radical anion **11**, which by loss of an electron would give rise to the sulfide **3**, and (b) the aryl anion **13**, which by protonation would give the arene **7**, and the thiyl radical **12**, which by dimerization would give the disulfide **6**. According to this mechanism, assuming the formation of the dianion **10** to be faster than the two following dissociation reactions, the overall process would be independent of the concentration of the thiolate anions **4**, and the ratios of the reaction products, the sulfides **3** and arenes **7**, would depend on the relative rate of the two dissociation processes. Furthermore, both processes could be accelerated by MeOH, able to solvate, to a greater degree than DMSO, the species where the charge is less dispersed, specifically, the leaving group RS^- **4** and the aryl anion Ar^- **13**. We confirmed the formation of arenes via aryl anions, rather than via aryl radicals,[17] by a collateral reaction. In fact, reacting the 2,6-dibromobenzenediazonium *o*-benzenedisulfonimide with sodium methanethiolate in MeOD leads to the product derived by a deuteriodediazoniation (experimental). Finally, the bimolecular mechanism would justify, on the basis of steric effects, the course of the reactions where the arenediazonium cations or the arenethiols are substituted at the *ortho* positions. The results in entries 21−23, 26, and 27 of Table 2 are good examples of the drastic effect of the growing bulkiness of the three halogen couples. Steric effects can also explain the difficulties met in the reactions of entries 24, 26, and 28 of Table 1 and the lack of success of entry 27. Obviously attractive or repulsive electrostatic interactions between the *ortho* substituents on the arenediazonium cations and the attacking nucleophiles cannot be ignored (Table 2, entries 20 and 21).

In conclusion, the present work has completely fulfilled the synthetic objective; the synthesis of alkyl aryl and diaryl sulfides has been rendered efficient and safe through adequate modifications to the reactions of Stadler and Ziegler. Furthermore, the copious experimental data collected have prompted several mechanistic considerations that, to be confirmed, need further targeted research.

Experimental Section

All of the reactions were performed in oven-dried glassware and anhydrous methanol was used as solvent. No particular device was, however, adopted to exclude moisture or oxygen. Besides, the representative reactions described below were also performed under an atmosphere of nitrogen. Column chromatography and TLC were performed on Merck silica gel 60 (70−230 mesh ASTM) and GF 254, respectively. Petroleum ether refers to the fraction boiling in the range 40−70 °C and is abbreviated as PE. Room temperature (ca. 20−25 °C) is abbreviated as rt. Details for the reactions, chromatographic solvents, and yields of the pure (GC, GC-MS, TLC, NMR) isolated alkyl aryl sulfides and diaryl sulfides **3** are reported in Tables 1 and 2, respectively. Structures of all the products obtained in this research were confirmed by comparison of their physical (mp or bp) and spectral data (^1H NMR) with those reported in the literature or with those of the corresponding commercially available samples of analytical purity.

All of the amines and thiols, with the only exception of 2,6-dibromobenzenethiol,[18] sodium methanethiolate and benzenethiolate, anhydrous MeOH and DMSO, MeOD (isotopic purity 99.5%), sodium methoxide (30% solution in MeOH), and all of the reference compounds were purchased from the Aldrich Chemical Co. Dowex 50X8 ion-exchange resin was purchased from Fluka. Benzenediazonium tetrafluoroborate was prepared as reported.[19]

o-Benzenedisulfonimide (**8**) was prepared according to the literature procedure,[20] starting from *o*-benzenedisulfonyl chloride[21] and NH_3 gas, via ammonium *o*-benzenedisulfonimide and its conversion using Dowex 50X8 resin (H^+).[22] Dry

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[13] For recent reviews on aromatic substitution by the $S_{RN}1$ mechanism, see: (a) Rossi, R. A.; Pierini, A. B.; Santiago, A. N. In *Organic Reactions*; Paquette, L. A., Ed.; Wiley & Sons: New York, 1999; Vol. 54, Chapter 1. (b) Rossi, R. A.; Pierini, A. B.; Penenory, A. B. In *The Chemistry of Functional Groups: The Chemistry of Halides, Pseudo-Halides and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley & Sons: New York, 1995; Supplement D2, Part 2, Chapter 24. (c) Norris, R. K. In *Comprehensive Organic Synthesis*; Trost B. M., Ed.; Pergamon Press: New York, 1991; Vol. 4, pp 451−482. (d) Savéant, J.-M. *Adv. Phys. Org. Chem.* **1990**, *26*, pp 1−130.

[14] (a) Denney, D. B.; Denney, D. Z. *Tetrahedron* **1991**, *47*, 6577. (b) Denney, D. B.; Denney, D. Z.; Perez, A. J. *Tetrahedron* **1993**, *49*, 4463. (c) Denney, D. B.; Denney, D. Z.; Fenelli, S. P. *Tetrahedron* **1997**, *53*, 9835.

[15] The Denneys' mechanistic proposal was strongly contested.[16] However, "absolute rejection of the Denney hypotheses for all cases seems not possible."[16a]

[16] (a) Bunnett, J. F. *Tetrahedron* **1993**, *49*, 4477. (b) Rossi, R. A.; Palacios, S. M. *Tetrahedron* **1993**, *49*, 4485. (c) Savéant, J.-M. *Tetrahedron* **1994**, *50*, 10117.

[17] Zollinger, H. In *The Chemistry of Functional Groups: The Chemistry of Triple-Bonded Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley & Sons: New York, 1983; Supplement C, Part 1, Chapter 15, p 619 and references therein.

[18] Stoyanovich, F. M.; Marakatkin, M. A.; Gol'dfarb, Ya. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, *11*, 2537.

[19] Flood, D. T. *Org. Synth. Collect. Vol. II* **1943**, 295.

[20] Blaschette, A.; Jones, P. G.; Hamann, T.; Naveke, M.; Schomburg, D.; Cammenga, H. K.; Steppuhn, I. *Z. Anorg. Allg. Chem.* **1993**, *619*, 912.

[21] Barbero, M.; Degani, I.; Fochi, R.; Regondi, V. *Gazz. Chim. Ital.* **1986**, *116*, 165.

[22] Hendrickson, J. B.; Okano, S.; Bloom, R. K. *J. Org. Chem.* **1969**, *34*, 3434.

arenediazonium *o*-benzenedisulfonimides (**1**; Ar = Ph; 2-, 3-, and 4-MeC_6H_4; 2-, 3-, and 4-$MeOC_6H_4$; 2-, 3-, and 4-ClC_6H_4; 2-, 3-, and 4-BrC_6H_4; 2-, 3- and 4-$O_2NC_6H_4$; 2-$MeSC_6H_4$; 2-naphthyl; 2,4-$(O_2N)_2C_6H_3$; 2,6-$Me_2C_6H_3$; 2,6-$F_2C_6H_3$; 2,6-$Cl_2C_6H_3$; 2,6-$Br_2C_6H_3$) were prepared as described previously by us.[1] The crude salts were virtually pure and could be used in the next alkyl- and arylthiodediazoniations, without further crystallization.

Dry Arenediazonium *o*-Benzenedisulfonimides (1). Representative Procedure. Dry 4-Cyanobenzenediazonium *o*-Benzenedisulfonimide (1; Ar = 4-NCC_6H_4). According to the procedure previously reported,[1] diazotization of 4-cyanoaniline (1.18 g, 10 mmol) was carried out with isopentyl nitrite (1.29 g, 11 mmol) in the presence of *o*-benzenedisulfonimide (**8**; 2.63 g, 12 mmol) in glacial AcOH (60 mL) at 0−5 °C. The virtually pure (NMR, dp) title compound was obtained in 92% yield (3.20 g). For analytical purposes, a sample was purified by dissolution in hot anhydrous acetonitrile and precipitation with anhydrous Et_2O after cooling: dp (dec point) 126−128 °C; ^1H NMR (CF_3COOD) δ 7.40−7.75 (m, 4 H), 7.88 and 8.42 ppm (2 d, 1:1, $J = 8.5$ Hz, 4 H). Anal. Calcd for $C_{13}H_8N_4O_4S_2$: C, 44.82; H, 2.31; N, 16.08; S, 18.41. Found: C, 44.93; H, 2.40; N, 16.17; S, 18.34. Yields and physical and specral data of the new diazonium salts are given below.

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.

Dry 4-Carboxybenzenediazonium *o*-Benzenedisulfonimide (1; Ar = 4-$HOOCC_6H_4$). 94% (3.44 g); dp 136 °C; ^1H NMR (CF_3COOD) δ 7.55−7.95 and 8.25−8.70 ppm (2 m, 1:1). Anal. Calcd for $C_{13}H_9N_3O_6S_2$: C, 42.51; H, 2.47; N, 11.44; S, 17.45. Found: C, 42.41; H, 2.48; N, 11.34; S, 17.53.

Dry 4-Methoxycarbonylbenzenediazonium *o*-Benzenedisulfonimide (1; Ar = 4-$MeOOCC_6H_4$). 97% (3.69 g); dp 103−105 °C; ^1H NMR (CF_3COOD) δ 3.93 (s, 3 H), 7.60−7.90 and 8.12−8.52 ppm (2 m, 1:1, 8 H). Anal. Calcd for $C_{14}H_{11}N_3O_6S_2$: C, 44.09; H, 2.91; N, 11.02; S, 16.81. Found: C, 44.20; H, 3.00; N, 11.04; S, 16.70.

Dry 2-Hydroxybenzenediazonium *o*-Benzenedisulfonimide (1; Ar = 2-HOC_6H_4). 83% (2.81 g); dp 162 °C; ^1H NMR (CF_3COOD) δ 6.60−7.10 and 7.30−7.80 ppm (2 m, 1:3). Anal. Calcd for $C_{12}H_9N_3O_5S_2$: C, 42.47; H, 2.67; N, 12.38; S, 18.90. Found: C, 42.56; H, 2.76; N, 12.33; S, 18.82.

Dry 4-Hydroxybenzenediazonium *o*-Benzenedisulfonimide (1; Ar = 4-HOC_6H_4). 87% (2.94 g); dp 138−139 °C; ^1H NMR (CF_3COOD) δ 6.75 (d, $J = 8.5$ Hz, 2 H), 7.25−7.62 (m, 4 H), 7.82 ppm (d, $J = 8.5$ Hz, 2 H). Anal. Calcd for $C_{12}H_9N_3O_5S_2$: C, 42.47; H, 2.67; N, 12.38; S, 18.90. Found: C, 42.40; H, 2.74; N, 12.31; S, 18.80.

Dry 2,6-Difluorobenzenediazonium *o*-Benzenedisulfonimide (1; Ar = 2,6-$F_2C_6H_3$). 93% (3.36 g); dp 170 °C; ^1H NMR (CF_3COOD) δ 7.10−7.50, 7.50−7.90 and 8.00−8.40 ppm (3 m, 2:4:1). Anal. Calcd for $C_{12}H_7F_2N_3O_4S_2$: C, 40.11; H, 1.96; F, 10.57; N, 11.69; S, 17.84. Found: C, 40.21; H, 2.01; F, 10.66; N, 11.80; S, 17.75.

Dry 2,6-Dibromobenzenediazonium *o*-Benzenedisulfonimide (1; Ar = 2,6-$Br_2C_6H_3$). 99% (4.76 g); dp 126−128 °C; ^1H NMR (CF_3COOD) δ 7.45−7.80 ppm (m). Anal. Calcd for $C_{12}H_7Br_2N_3O_4S_2$: C, 29.96; H, 1.47; Br, 33.21; N, 8.73; S, 13.33. Found: C, 29.87; H, 1.51; Br, 33.26; N, 8.65; S, 13.23.

Caution! Diazosulfides can decompose violently when not in solution. In the reactions described in this work most of the diazosulfides formed as intermediates reacted immediately. However in all cases, also when the conversion of the diazosulfides in the final products was slow, they were fully dissolved in MeOH. Although no accident took place during our work, caution is needed during the handling of the reaction mixtures till the intermediate diazosulfides are present.

Methylthiodediazoniations of Dry Arenediazonium *o*-Benzenedisulfonimides (1). Representative Procedures. Methyl Phenyl Sulfide (3; Ar = Ph, R = Me). In entry 1 of Table 1 benzenediazonium *o*-benzenedisulfonimide (**1**, Ar = Ph; 1.62 g, 5 mmol) was added in one portion with vigorous stirring to a solution of sodium methanethiolate (**4**, R = Me; 0.39 g, 5.5 mmol) in anhydrous MeOH (10 mL), previously cooled at 0−5 °C with an ice bath. The salt dissolved at once, and the resultant solution became temporary deep orange and then cleared quickly to yellow. Simultaneously a plentiful evolution of nitrogen took place and a fine solid substance constituted of sodium *o*-benzenedisulfonimide (**5**) began to precipitate. A test of azo coupling with 2-naphthol, carried out immediately after the addition of the salt, was negative. This confirmed a sudden reaction of the diazonium salt. TLC (PE), GC, and GC-MS analyses of the reaction mixture showed the presence of dimethyl disulfide (**6**; R = Me), MS m/z 94 (M^+), and the title compound, MS m/z 124 (M^+), as major product. GC-MS analysis showed also the presence of benzene (**7**; Ar = Ph), MS m/z 78 (M^+). The intermediate (methylsulfanyl)(phenyl)diazene (**2**; Ar = Ph, R = Me) was not observed on TLC. The products were isolated according to the following procedures.

Procedure A: the reaction mixture was poured into Et_2O−water (100 mL, 1:1). The aqueous layer was separated and extracted with Et_2O (2 × 50 mL). The combined organic extracts were washed with water (2 × 50 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The crude residue was chromatographed on a short column, using pentane as eluent. The first eluted product was dimethyl disulfide (it was isolated in variable amounts, because no particular device was adopted to avoid its loss during the solvent evaporation). The second eluted product was the pure (GC, GC-MS, TLC, NMR) title compound (0.51 g, 82% yield). Identical physical and spectral data and retention time, by co-injection, for the product and a commercially available sample of analytical purity were observed. The aqueous layer and the aqueous washings containing the salt **5** were collected and evaporated under reduced pressure. The residue was passed through a column of Dowex 50X8 ion-exchange resin (1.6 g for 1 g of product), eluting with water (about 35 mL). After removal of the water under reduced pressure, virtually pure (NMR) *o*-benzenedisulfonimide (**8**) was recovered in 81% yield (0.89 g); mp 192−194 °C (toluene) (lit.[1] mp 192−194 °C).

Procedure B: the reaction mixture was stirred at 0−5 °C for a further 30 min, to complete the precipitation of **5**, which was gathered by filtration on a Buchner, washed with cold MeOH (3−4 mL), and then passed through a Dowex column. *o*-Benzenedisulfonimide (**8**) was recovered in yield comparable to that obtained in procedure A. The methanolic filtrate and washings were collected and diluted with Et_2O (150 mL). The organic solution was washed several times with water (4 × 50 mL) and dried over Na_2SO_4. By a workup identical to that described in Procedure A, the pure (GC, GC-MS, TLC, NMR) title compound was obtained in comparable yield.

The reaction was also carried out under an atmosphere of nitrogen. Neither the reaction rate nor yields of the products changed.

All the aryl methyl sulfides (**3**, R = Me) reported in entries 2−23 of Table 1 were prepared according to the above procedure. In particular, entries 13−15 and 23 were carried out at −15 °C to avoid too fast reactions.

Entry 17 was carried out at −78 °C to minimize the competitive hydrodediazoniation. Under these conditions the crude residue was virtually pure (TLC, NMR) 4-(methylsulfanyl)benzoic acid. When the same reaction was carried out at 0 °C, two products were instead obtained, i.e., 4-(methylsulfanyl)benzoic acid and benzoic acid, in a 5:1 GC ratio.

Entries 19 and 20 were carried out at room temperature. In these cases the workup was slightly modified, i.e., the reaction mixture was directly concentrated under reduced pressure and the crude residue was column chromatographed, using at first PE/Et_2O (9.5:0.5, v/v) and then water, to elute 2- or 4-(methylsulfanyl)phenol and, respectively, sodium *o*-benzenedisulfonimide (**5**). The aqueous solution was concentrated and passed through Dowex to recover *o*-benzenedisulfonimide (**8**).

In all of these reactions the intermediates (methylsulfanyl)(aryl)diazenes **2** were never observed on TLC.

2,6-Dibromophenyl Methyl Sulfide (3; Ar = 2,6-$Br_2C_6H_3$, R = Me). (1) According to the above procedure, in entry 24 of Table 1 2,6-dibromobenzenediazonium *o*-benzenedisulfonimide (**1**, Ar = 2,6-$Br_2C_6H_3$; 2.40 g, 5 mmol) was added to a solution of sodium methanethiolate (**4**, R = Me; 0.39 g, 5.5 mmol) in anhydrous MeOH (10 mL), maintained at rt. The salt dissolved at once. At the same time a slow evolution of nitrogen was observed and sodium *o*-benzenedisulfonimide (**5**) began slowly to precipitate. The sudden reaction of the diazonium salt was confirmed by absence of azo coupling with 2-naphthol. TLC (PE) analysis of the reaction mixture showed the presence of four products, i.e., dimethyl disulfide, 1,3-dibromobenzene, the title compound, and (methylsulfanyl)(2,6-dibromophenyl)diazene (**2**; Ar = 2,6-$Br_2C_6H_3$, R = Me). The last product was fully dissolved in MeOH. It was identified by a test on TLC, i.e., a small drop of $HBF_4 \cdot Et_2O$ was put on the corresponding spot to free the diazonium salt that gave positive azo coupling with a small drop of an alkaline solution of 2-naphthol. The reaction mixture was stirred for a further 45 min, until complete disappearance of the intermediate diazosulfide, and then worked up according to Procedure A described previously for entry 1. In this case, during evaporation of the extraction solvent under reduced pressure, the mixture was heated to 70−80 °C, to remove all the dimethyl disulfide. The crude residue was column chromatographed, eluting with PE. The first eluted product was 1,3-dibromobenzene (0.63 g, 53% yield), MS *m*/*z* 234 (M^+). Identical physical and spectral data and retention time, by co-injection, for the product and a commercially available sample of analytical purity were observed. The second eluted product was 2,6-dibromophenyl methyl sulfide (0.30 g, 21% yield), MS *m*/*z* 280 (M^+); mp 52−53 °C (after crystallization from pentane); ^1H NMR ($CDCl_3$) δ 2.48 (s, 3 H), 6.65−7.20 and 7.32−7.80 ppm (2 m, 1:2). Anal. Calcd for $C_7H_6Br_2S$: C, 29.82; H, 2.14; Br, 56.67; S, 11.37. Found: C, 29.81; H, 2.14; Br, 56.64; S, 11.32. Virtually pure (NMR) *o*-benzenedisulfonimide (**8**) was recovered in 70% yield (0.76 g).

Neither the reaction rate nor yields of the products changed, when the reaction was carried out under an atmosphere of nitrogen.

(2) The same reaction, carried out in MeOD (isotopic purity 99.5%; 10 mL) instead of MeOH, and under an atmosphere of nitrogen, afforded 2,6-dibromophenyl methyl sulfide (21% yield, 0.30 g) and 1,3-dibromo-2-deuteriobenzene (53% yield, 0.63 g), MS *m*/*z* 235 (isotopic purity 96%); ^1H NMR δ 6.90−7.20, 7.30−7.40 and 7.42−7.55 ppm (3 m, 1:1:1).

(3) The reaction described in (1) was carried out at 0−5 °C. Also in this condition the diazonium salt dissolved and reacted at once with sodium methanethiolate, as confirmed by a negative test of azo coupling with 2-naphthol. No evolution of nitrogen was observed. TLC (PE) analysis of the resultant solution showed the presence of the intermediate (methylsulfanyl)(2,6-dibromophenyl)diazene as only product. GC and GC-MS analyses showed the thermal decomposition of the diazosulfide into dimethyl disulfide and 2,6-dibromophenyl methyl sulfide. The reaction mixture was poured into cold water and extracted speedily with cold pentane, which was washed with cold water and dried. The solvent was removed under reduced pressure, maintaining always cooling with an ice bath. The residue was the diazosulfide accompanied by small amounts of 1,3-dibromobenzene and 2,6-dibromophenyl methyl sulfide; ^1H NMR (CD_3SOCD_3) δ 3.40 (s, 3 H), 7.20−7.28 and 7.75−7.78 ppm (2 m, 1:2). This product could be stored in freezer but decomposed speedily at rt.

Alkylthiodediazoniations of Dry Arenediazonium *o*-Benzenedisulfonimides (1). Representative Procedures. Butyl Phenyl Sulfide (3; Ar = Ph, R = Bu). In entry 25 of Table 1, benzenediazonium *o*-benzenedisulfonimide (**1**, Ar = Ph; 1.62 g, 5 mmol) was added in one portion with vigorous stirring, to a solution of sodium butan-1-thiolate (**4**; R = Bu), prepared from butan-1-thiol (0.50 g, 5.5 mmol) and sodium methoxide (30% solution in MeOH; 1.00 g, 5.5 mmol) in anhydrous MeOH (10 mL), previously cooled at 0−5 °C with an ice bath. The behavior of the reaction was identical to that described above for entry 1. TLC (PE), GC and GC-MS analyses of the reaction mixture showed the presence of dibutyl disulfide (**6**; R = Bu), MS *m*/*z* 178 (M^+), and the title compound, MS *m*/*z* 166 (M^+). GC-MS analysis showed also the presence of benzene (**7**; Ar = Ph), MS *m*/*z* 78 (M^+). After the above workup, the crude mixture was column chromatographed, eluting with PE. The first eluted product was dibutyl disulfide (0.06 g, 13%). Identical physical and spectral data and retention time, by co-injection, for the product and the corresponding commercially available sample of analytical purity was observed. The second eluted product was butyl phenyl sulfide (0.72 g, 86%). *o*-Benzenedisulfonimide (**8**) was recovered in 74% yield (0.82 g). The intermediate diazosulfide (**2**; Ar = Ph, R = Bu) was not observed on TLC.

The reaction rate and yields of the products remained unchanged when the reaction was carried out under an atmosphere of nitrogen.

According to the same procedure, also the reactions of entries 29−36 of Table 1 were immediate. In particular, entries 34−36 were carried out at room temperature. In entries 34 and 36, the crude residues obtained after the usual workup of the reaction mixtures were the virtually pure (TLC, NMR) sulfides.

***s*-Butyl Phenyl Sulfide (3; Ar = Ph, R = *s*-Bu).** As above, in entry 26 of Table 1 benzenediazonium *o*-benzenedisulfonimide (**1**, Ar = Ph; 1.62 g, 5 mmol) was added to a solution of sodium butan-2-thiolate (**4**; R = *s*-Bu), prepared from butan-2-thiol (0.50 g, 5.5 mmol) and sodium methoxide (30% solution in MeOH; 1.00 g, 5.5 mmol) in anhydrous MeOH (10 mL), previously cooled at 0−5 °C under an atmosphere of N_2. The salt dissolved at once. Tests of azo coupling with 2-naphthol were positive for 30 min. A slow evolution of nitrogen was observed and sodium *o*-benzenedisulfonimide (**5**) began slowly to precipitate. TLC analysis (PE) showed the presence of three products, di(*s*-butyl) disulfide (**6**; R = *s*-Bu), the title compound, and (*s*-butylsulfanyl)(phenyl)diazene (**2**; Ar = Ph, R = *s*-Bu). The last was the major product and was fully dissolved in MeOH. It was identified, as described for entry 24, by a positive test of azo coupling with 2-naphthol, carried out on TLC, after treatment with $HBF_4 \cdot Et_2O$. Stirring was maintained for a further 2.5 h, until complete disappearance of the intermediate diazosulfide. GC-MS analysis of the reaction mixture showed also the presence of benzene (**7**; Ar = Ph), MS *m*/*z* 78 (M^+). After the usual workup, the two reaction products were separated by column chromatography, eluting with PE. The first eluted product was di(*s*-butyl) disulfide (20%, 0.09 g), MS *m*/*z* 178 (M^+). Identical physical and spectral data and retention time, by co-injection, for the product and the corresponding commercially available sample of analytical purity was observed. The second eluted product was *s*-butyl phenyl sulfide (66%, 0.33 g), MS *m*/*z* 166. *o*-Benzenedisulfonimide (**8**) was recovered in 85% yield (0.93 g).

The reaction rate and yields of the products remained unchanged when the reaction was carried out under an atmosphere of nitrogen. Also entry 28 had the same behavior and the reaction time was 3 h. Details for all the alkylthiodediazoniations are reported in Table 1.

(*Z*)-(*tert*-Butylsulfanyl)(phenyl)diazene (2; Ar = Ph, R = *t*-Bu). In entry 27 of Table 1 benzenediazonium *o*-benzenedisulfonimide (**1**, Ar = Ph; 1.62 g, 5 mmol) was added to a solution of sodium 2-methylpropan-2-thiolate (**4**; R = *t*-Bu), prepared from 2-methylpropan-2-thiol (0.50 g, 5.5 mmol) and sodium methoxide (30% solution in MeOH; 1.00 g, 5.5 mmol) in anhydrous MeOH (10 mL), at rt. The salt dissolved at once and an orange solution was obtained. No evolution of nitrogen was observed and the test of azo coupling with 2-naphthol was negative. TLC analysis showed the presence of one only product, i.e., the title diazosulfide, that remained unchanged also after 24 h. The residue obtained after the usual workup, was column chromatographed, eluting with PE/Et_2O (9.5:0.5, v/v). A yellow substance was obtained in 74% yield (0.72 g): mp 48−50 °C (after crystallization from pentane) (lit.[23] mp 48−49 °C); ^1H NMR ($CDCl_3$) δ 1.52 (s, 9 H), 6.90−7.52 ppm (m, 5 H); identical to that reported in the literature.[23] The same product was obtained when the reaction was carried out under an atmosphere of nitrogen. The title diazosulfide gave a positive azo coupling test when it was treated with $HBF_4{\cdot}Et_2O$ and then with an alkaline solution of 2-naphthol. Attempts at thermal decomposition of the diazosulfide gave only tars.[24]

Arylthiodediazoniations of Dry Arenediazonium *o*-Benzenedisulfonimides (1). Representative Procedures. Diphenyl Sulfide (3; Ar = R = Ph). (1) In entry 1 of Table 2, benzenediazonium *o*-benzenedisulfonimide (**1**, Ar = Ph; 1.62 g, 5 mmol) was added in one portion with vigorous stirring, to a solution of sodium benzenethiolate (**4**; R = Ph), prepared from benzenethiol (0.61 g, 5.5 mmol) and sodium methoxide (30% solution in MeOH; 1.00 g, 5.5 mmol) in anhydrous MeOH (10 mL), maintained at room temperature. The salt dissolved at once and, as described for entry 1 of Table 1, the resultant solution became temporary deep orange and then cleared quickly to yellow. Simultaneously a plentiful evolution of nitrogen took place and sodium *o*-benzenedisulfonimide (**5**) began to precipitate. A test of azo coupling with 2-naphthol, carried out immediately after the addition of the salt, was negative. This confirmed a sudden reaction of the diazonium salt. TLC (PE), GC and GC-MS analyses of the reaction mixture showed the presence of only two products, i.e., diphenyl disulfide (**6**; Ar = R = Ph), MS m/z 218 (M^+) and the title compound, MS m/z 186 (M^+), as major product. GC-MS analysis showed also the presence of benzene (**7**; Ar = Ph), MS m/z 78 (M^+). The reaction mixture was worked up according to Procedure A, described for entry 1 of Table 1. By column chromatography, eluting with PE, diphenyl disulfide and diphenyl sulfide were obtained in 22% (0.13 g) and 73% yield (0.68 g), respectively. Identical physical and spectral data and retention time, by co-injection, for the products and the corresponding commercially available samples of analitycal purity were observed. *o*-Benzenedisulfonimide (**8**) was recovered in 78% yield (0.85 g). Procedure B afforded the two products and **8** in comparable yields. Identical results were obtained when the reaction was carried out under an atmosphere of nitrogen or when the reaction solvent, i.e. anhydrous MeOH, was previously placed under an atmosphere of argon and deaerated under vacuum.

(2) The reaction was carried out also at 0−5 and −78 °C. In both cases the reaction was immediate and the products were obtained in yields comparable to those reported in (1). The intermediate (phenylsulfanyl)(phenyl)diazene (**2**; Ar = R = Ph) was never observed on TLC.

(3) The reaction was carried out with an 1:2 reagent molar ratio, i.e., benzenediazonium *o*-benzenedisulfonimide (**1**, Ar = Ph; 1.62 g, 5 mmol), benzenethiol (1.10 g, 10 mmol) and sodium methoxide (30% solution in MeOH; 1.82 g, 10 mmol) in anhydrous MeOH (10 mL). Yield of diphenyl sulfide remained unchanged (0.68 g, 73%) and diphenyl disulfide was obtained in 37% yield (0.40 g).

(4) The reaction (3) was carried out with an 1:3 reagent molar ratio, i.e., benzenediazonium *o*-benzenedisulfonimide (1.62 g, 5 mmol), benzenethiol (1.65 g, 15 mmol) and sodium methoxide (30% solution in MeOH; 2.73 g, 15 mmol) in anhydrous MeOH (15 mL). Yield of diphenyl sulfide remained unchanged (0.68 g, 73%) and diphenyl disulfide was obtained in 55% yield (0.59 g).

(5) The reaction (1) was carried out in the presence of 1,3-dinitrobenzene (0.25 g, 1.5 mmol). In this case the test of azo coupling with 2-naphthol was positive for 15 min and TLC (PE) analysis showed the presence of the intermediate (phenylsulfanyl)(phenyl)diazene, as major product. Its decomposition into diphenyl disulfide and diphenyl sulfide was slowed (2.5 h). Usual workup afforded the two products in 28% (0.15 g) and 26% yield (0.24 g), respectively. When 1,3-dinitrobenzene was used in equimolar amount (0.92 g, 5.5 mmol) with respect to benzenethiol, the reaction was further slowed (4 h).

All the entries reported in Table 2 (2−27) were carried out according to the above procedure (1). The intermediate diazosulfides **2**, that always were fully dissolved in MeOH, were observed only when the reaction was slower, i.e., when one or two halide atoms were present in the *ortho* positions of the diazonium salt or of the benzenethiolate (entries 8, 11, 21−23, and 25−27). In entries 21−23, the products of hydrodediazoniation were also highlighted or isolated. Entry 21: 1,3-difluorobenzene, MS m/z 114 (M^+). As a result of its volatility, it was not isolated. Entry 22: 1,3-dichlorobenzene (35% yield, 0.26 g), MS m/z 146 (M^+). Entry 23: 1,3-dibromobenzene (77% yield, 0.91 g), MS m/z 234 (M^+). Identical physical and spectral data and retention time, by co-injection, for the products and the corresponding commercially available samples of analytical purity were observed.

Collateral Proofs. Reaction of Benzenediazonium *o*-Benzenedisulfonimide with Sodium Benzenethiolate in DMSO. (1) Sodium benzenethiolate (**4**, R = Ph; 1.98 g, 15 mmol) was added with vigorous stirring to a solution of benzenediazonium *o*-benzenedisulfonimide (**1**, Ar = Ph; 1.62 g, 5 mmol) in anhydrous DMSO (10 mL), maintained under an atmosphere of N_2. The solution became dark and no evolution of N_2 was observed. Tests of azo coupling with 2-naphthol were positive for 30 min. TLC analysis (PE) of the reaction mixture showed the presence of the intermediate (phenylsulfanyl)(phenyl)diazene (**2**; Ar = R = Ph) as major product. It disappeared after 2.5 h. After the usual workup, the residue was column chromatographed, eluting with PE. Two products were obtained, diphenyl disulfide (0.08 g, 5%), MS m/z 218 (M^+) and diphenyl sulfide (0.68 g, 73%), MS m/z 186 (M^+).

(2) The above reaction was carried out with a reagent molar ratio of 1:1. Tests of azo coupling with 2-naphthol were positive for 30 min and the intermediate diazosulfide was still present after 24 h. It disappeared during the usual workup. Diphenyl disulfide was isolated in traces (0.01 g) and diphenyl sulfide in 12% yield (0.11 g).

(3) The reaction mixture prepared as described in (2) was stirred at rt for 30 min. When the test of azo coupling with 2-naphthol was negative, anhydrous MeOH (10 mL) was added. A plentiful evolution of N_2 occurred and the intermediate diazosulfide disappeared after 5−10 min (TLC: PE). Yields of diphenyl disulfide and diphenyl sulfide were comparable to those obtained in (1).

Reaction of Benzenediazonium Tetrafluoroborate with Sodium Benzenethiolate in DMSO. (1) According to the literature[9a] sodium benzenethiolate (**4**, R = Ph; 1.98 g, 15 mmol) was added to a solution of benzenediazonium tetrafluoroborate[19] (0.96 g, 5 mmol) in anhydrous DMSO (10 mL), under stirring and under an atmosphere of Argon. The behavior of the reaction was identical to that described above for benzenediazonium *o*-benzenedisulfonimide and the intermediate diazosulfide disappeared after 3.5 h. The above workup afforded diphenyl disulfide (0.08 g, 5%) and diphenyl sulfide (0.69 g, 75%).

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[23] van Zvet, H.; Kooyman, E. C. *Rec. Trav. Chim. Pays Bas* **1967**, *86*, 993.

[24] According to the procedure reported in the literature,[23] (*E*)-(*tert*-butylsulfanyl)(phenyl) diazene was obtained by refluxing (*Z*)-(*tert*-butylsulfanyl)(phenyl)diazene for 8 h in benzene. The E isomer was then dissolved in anhydrous MeOH and equimolar amounts of sodium 2-methylpropan-2-thiolate (prepared from 2-methylpropan-2-thiol and sodium methoxide in MeOH) were added. The reaction mixture was stirred for 24 h, at room temperature and under an atmosphere of N_2. No change was observed.

[25] *Dictionary of Organic Compounds on Cd-ROM*, version 7.1; Chapman & Hall Electronic Publishing Division: London, 1999.

[26] Vowinkel, E. *Synthesis* **1974**, 430.

[27] Chianelli, D.; Testaferri, L.; Tiecco, M.; Tingoli, M. *Synthesis* **1982**, 475.

[28] Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1979**, *44*, 713.

[29] Miller, E.; Read, R. R. *J. Am. Chem. Soc.* **1933**, *55*, 1224.

[30] Landini, D.; Maia, A.; Rampoldi, A. *Gazz. Chim. Ital.* **1989**, *119*, 513.

[31] King, J. F.; Skonieczny, S.; Poole, G. A. *Can. J. Chem.* **1983**, *61*, 235.

[32] Cristau, H. J.; Chabaud, B.; Chene, A.; Christol, H. *Synthesis* **1981**, 892.

[33] Kunieda, N.; Suzuki, A.; Kinoshita, M.; Imoto, M. *Makromol. Chem.* **1972**, *152*, 35.

[34] Boeseken, M. J. *Rec. Trav. Chim. Pays Bas* **1910**, 315.

[35] Truce, W. E.; Ray, W. J. *J. Org. Chem.* **1959**, *24*, 481.

(2) When the reagent molar ratio was 1:1, the reaction of the diazonium salt with the benzenethiolate was complete after 30 min and the intermediate diazosulfide was still present after 24 h. It disappeared during the usual workup. Diphenyl disulfide was isolated in traces (0.01 g) and diphenyl sulfide in 13% yield (0.12 g).

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