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Synthesis of *S*-Aryl Arenethiosulfonates from *N*,*N*-Di(arenesulfonyl)hydrazines: Reduction of Sulfonyl Chlorides with an Organic Reagent

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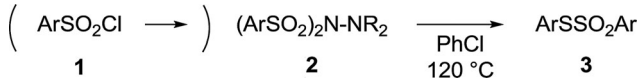
ABSTRACT: *N,N-Di(arenesulfonyl)-N′,N′-dimethylhydrazines, readily prepared from arenesulfonyl chlorides and N,N-dimethylhydrazine, were heated at 120°C in chlorobenzene to give S-aryl arenethiosulfonates, $ArSSO_2Ar$, in good yields.* © 2013 Wiley Periodicals, Inc. Heteroatom Chem 24:336–344, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21088

INTRODUCTION

S-Aryl arenethiosulfonates, $ArSSO_2Ar$, are interesting organosulfur compounds [1] and have found use as a sulfenylating agent in organic synthesis [2]. They are prepared by a variety of methods [1b,c], typically including (i) substitution of sulfonyl halides with thiolates or vice versa [3], (ii) oxidation of thiols or disulfides [4], and (iii) reduction of sulfonyl chlorides [5]. As arenesulfonyl chlorides are primary organosulfur products readily prepared from parent arenes and chlorosulfonic acid [6], their reduction (i.e., the method (iii) above) should be one of the most straightforward methods to prepare thiosulfonates. However, as sulfonic acid derivatives belong to the most stable class of organosulfur compounds, strong reducing agents such as metallic Sm or $Fe(CO)_5$ are usually necessary for this type of transformation [5]. To our best knowledge, other methods replacing these transition metal–based reductions have not been reported. During our study on sulfonamides [7], we found that a sulfonyl derivative of hydrazine **2** afforded *S*-aryl arenethiosulfonates **3** in good yields upon simple heating in chlorobenzene, formally achieving a transition metal–free reduction of sulfonyl chlorides **1** with an organic reagent as shown in Eq. (1).



(1)

RESULTS AND DISCUSSION

N,*N*-Di-*p*-toluenesulfonyl-*N′*,*N′*-dimethylhydrazine (**5**) was readily prepared by standard methods (Eq. (2)) [8], involving (i) monosulfonylation of *N*,*N*-dimethylhydrazine with *p*-$TolSO_2Cl$ (Tol = $CH_3C_6H_4$–) in the presence of Et_3N and DMAP and (ii) the second sulfonylation with NaH as a base. This procedure was conveniently carried out in one pot. The resultant disulfonylhydrazine **5** was then heated in various solvents, the results of which are summarized in Table 1. While higher reaction temperature than 100°C appears essential (entries 1–3), the kind of solvents also influenced the smooth reaction (entries 4–6). Among the conditions examined, heating in chlorobenzene at 120°C for 4 h was found optimal to give a desired product **6** in the highest yield (entry 8). Careful analysis of the crude reaction

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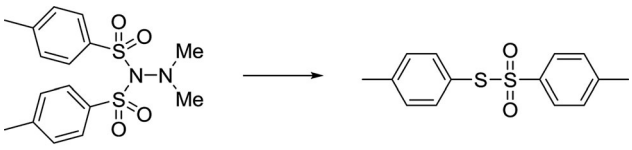
TABLE 1 Optimization of the Thermal Decomposition of **5**

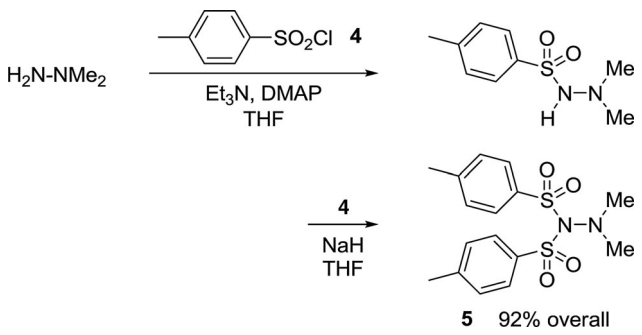


5 **6**

Entry	*Solvent*	*Temperature (°C)*	*Period (h)*	**6** *(%)*[a]	**5** *(%)*[a]
1	THF	Reflux	6	(0)	(Quant.)
2	$(ClCH_2)_2$	80	6	(0)	(Quant.)
3	Toluene	Reflux	6	(21)	(79)
4	DMSO	120	6	30	(Trace)
5	Xylenes	120	6	(46)	(17)
6	PhCl	120	6	60	(Trace)
7	PhCl	120	5	67	(6)
8	PhCl	120	4	71	(Trace)

[a]Isolated yields. Values in parentheses were determined by ^{1}H NMR analysis.

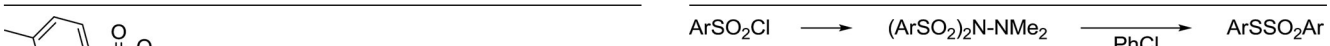
mixture did not show the presence of other isolable organosulfur compounds of a higher or lower oxidation state such as a *vic*-disulfone, thiosulfinate, disulfide, or thiol.



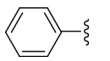
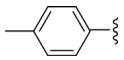
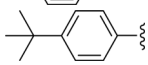
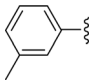
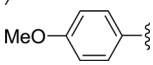
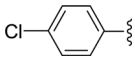
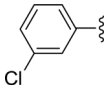
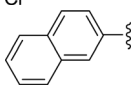
5 92% overall (2)

Table 2 summarizes both results of the preparation of starting disulfonylhydrazines **2** (according to Eq. (2)) and their subsequent conversion to various thiosulfonates **3** (according to entry 8 in Table 1). The preparation of starting materials **5** and **14–20** proceeded in good yields. The thiosulfonates having an electron-rich (entries 2–5 and 8) or -poor (entries 6 and 7) aromatic group could be prepared in good yields. The chloro substituent did not suffer the reduction (entries 6 and 7). Some additional observations are in order (Eqs. (3)–(6)). While commercially available *N,N*-dimethylhydrazine was routinely used as the reductant, its higher homolog, *N,N*-dioctylhydrazine, was also valid for this reaction to give the desired product **6** in good yield via **28** (Eq. (3)). A mixed disulfonylhydrazine, *N*-*p*-toluenesulfonyl-*N*-*p*-anisolesulfonyl-*N′,N′*-dimethylhydrazine (**29**) afforded all possible products **6**, **24**, **30**, and **31** in almost equal amounts (Eq. (4)). This fact clearly suggests that the reductive coupling of two arenesulfonyl groups took place in an intermolecular manner. To the contrary, an aliphatic sulfonyl derivative, *N,N*-dibutanesulfonyl-*N′,N′*-dimethylhydrazine (**32**), did not give the desired product **33**, even though the starting material was consumed (Eq. (5)). Finally, *N,N′*-di-*p*-toluenesulfonylhydrazine (**34**) did not give **6**, either (Eq. (6)), showing that the sulfonimide structure of **2** appears essential.

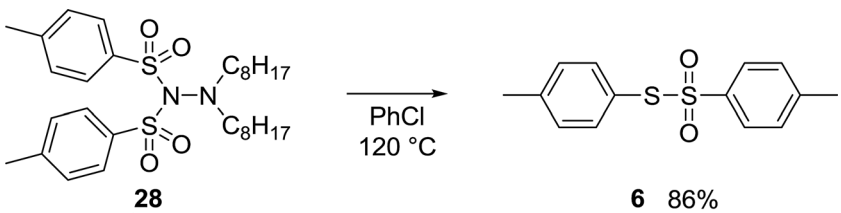
TABLE 2 Preparation of Various *S*-Aryl Arenethiosulfonates



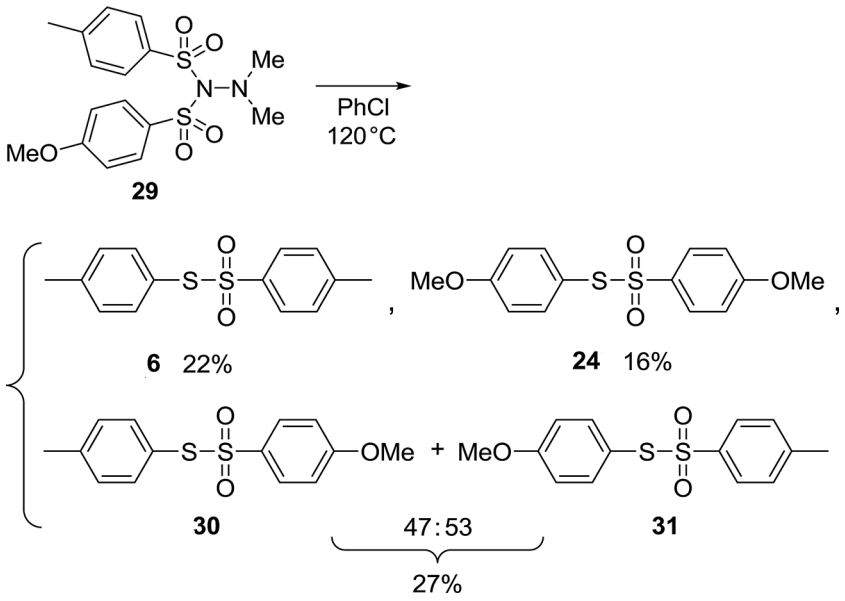
1 **2** **3**

	1		**2**		**3**	
Entry	*Ar*		*Yield (%)*[a]		*Yield (%)*[a]	
1		**7**	**14**	84	**21**	75
2		**4**	**5**	92	**6**	71
3		**8**	**15**	74	**22**	71
4		**9**	**16**	87	**23**	82
5		**10**	**17**	66	**24**	65
6		**11**	**18**	76	**25**	68
7		**12**	**19**	74	**26**	66
8		**13**	**20**	85	**27**	75

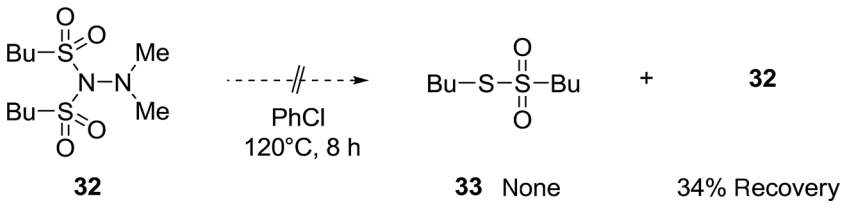
[a]Isolated yields.



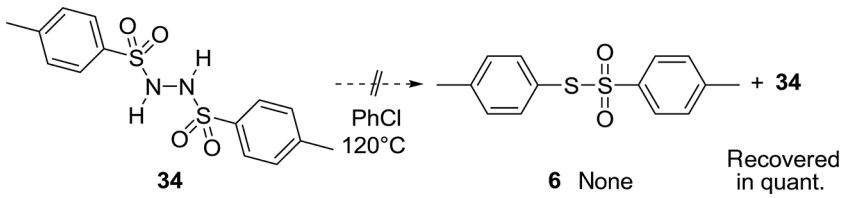
28 **6** 86% (3)



(4)



(5)



(6)

Although arenesulfonylhydrazine-based reductions are well known, their reactions result in the formation of a sulfinic acid, accompanied by another reduced organic fragment and nitrogen gas, as represented by Scheme 1 [9]. Thus, the present reaction forming thiosulfonates is a new entry, which is in stark contrast to the existing protocol shown in Scheme 1.

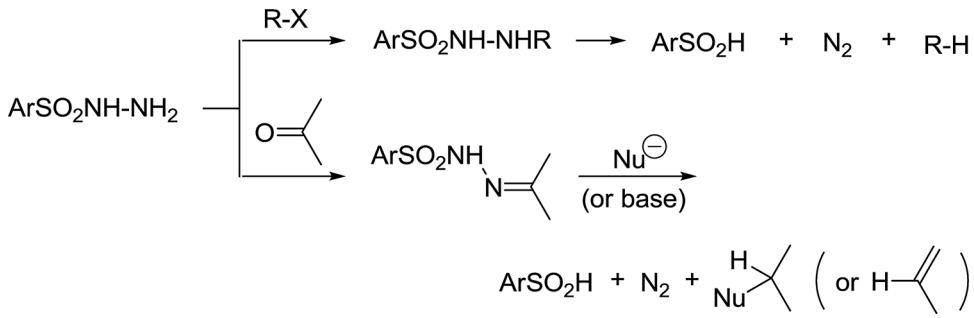
To gain mechanistic insight, we attempted to identify products resulting from the hydrazine residue rather than the arenesulfonyl group. However, even in the reaction of dioctyl derivative **28** (Eq. (3)), only intractable mixtures, except for desired **6**, were always recovered, in which we could not find any useful compounds for the elucidation of a mechanism.

Alternatively, as shown in Eq. (7), the presence of galvinoxyl, a radical scavenger, did not block the reaction, indicating that a radical chain mechanism is not involved.

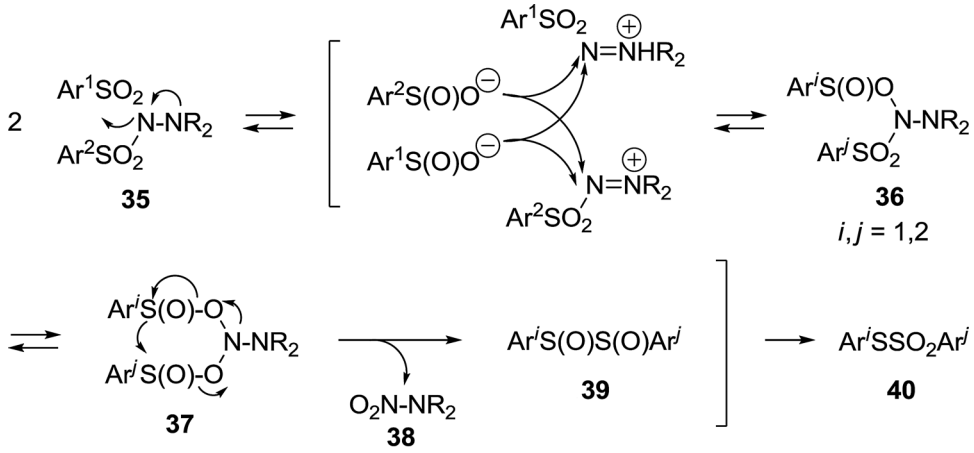
$$(p\text{-TolSO}_2)_2\text{N-NMe}_2 \underset{\text{PhCl, 120°C}}{\xrightarrow{\text{galvinoxyl (5 mol\%)}}} p\text{-TolSSO}_2\text{-}p\text{-Tol}$$
(**5**) (**6**) 63%

(7)

Thus, Scheme 2 shows a proposed mechanism, in which the sterically congested sulfonimide moiety of **35** thermally isomerizes to less bulky hydroxylamine *O*-sulfinate derivatives **36** or **37** [10a]. During this process, the scrambling of the sulfur groups via the intermolecular addition may take place, which is consistent with the observation of Eq. (4). The resultant **37** should then collapse to the putative *vic*-disulfoxide **39**, whose well-known, spontaneous disproportionation [4i,5a,10b,11] finally gives the thiosulfonate **40**. However, as mentioned above, the



SCHEME 1 Known arenesulfonylhydrazine-based reductions.



SCHEME 2 A proposed mechanism.

isolation of the key by-product **38** [10c] is not so far successful.

At any event, the hydrazine moiety should accept two oxygen atoms from two sulfonyl groups to effect their reduction to the thiosulfonate stage, and the mechanistic rationale must await further research.

CONCLUSIONS

In conclusion, we reported herein a new preparation of *S*-aryl arenethiosulfonates from *N,N*-di(arenesulfonyl)hydrazines. This reduction of the sulfonyl group does not need a metallic reductant, but instead it utilizes an organic reducing agent in the same molecule.

EXPERIMENTAL

General Information

^{1}H and ^{13}C NMR spectra were taken on an Agilent 400-MR spectrometer at 400 and 100 MHz, respectively. For NMR spectra, $CDCl_3$ was used as the solvent and chemical shifts are reported in parts per million shift (δ value) from Me_4Si (δ 0 ppm for ^{1}H) or based on the middle peak of the solvent ($CDCl_3$) (δ 77.00 ppm for ^{13}C NMR) as an internal standard. Signal patterns are indicated as br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (J) are given in hertz. Infrared (IR) spectra were recorded on a JASCO A-100 spectrometer (Tokyo, Japan) and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II by the electron ionization (EI) or positive electrospray ionization (ESI) method calibrated with sodium formate at the Suzukake-dai Material Analysis Center, Technical Department, Tokyo Institute of Technology. Dry solvents (THF, diethyl ether, and CH_2Cl_2) were purchased from Kanto Chemicals (Tokyo, Japan). Chemicals were purified or dried in a standard manner, if necessary. All reactions were carried out under argon.

*N,N-Bis(4-methylbenzenesulfonyl)-N′, N′-dimethylhydrazine (**5**)*

This was prepared according to the literature [8a].

To a mixture of *p*-toluenesulfonyl chloride (**4**) (0.687 g, 3.60 mmol) and DMAP (37.2 mg, 0.304 mmol) in THF (12.0 mL),

N,N-dimethylhydrazine (0.228 mL, 3.00 mmol) and NEt_3 (0.499 mL, 3.60 mmol) were added in this order at 0°C. After stirring at room temperature for 30 min, the mixture was cooled to 0°C and NaH (0.265 g of a 60% dispersion in oil, 6.63 mmol) was added. After the mixture was stirred at room temperature for 20 min and cooled to 0°C, an additional *p*-toluenesulfonyl chloride (**4**) (0.685 g, 3.59 mmol) was added. After the mixture was stirred at room temperature for 15 h, it was cooled to 0°C and was quenched with water. To the resultant mixture, ethyl acetate was added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed successively with brine, dried over Na_2SO_4, and concentrated in vacuo to give a crude oil, which was chromatographed on silica gel (hexane–ethyl acetate) to afford the title compound (1.02 g, 92%) as a white solid.

^{1}H NMR (400 MHz) δ 2.42 (s, 6H), 2.75 (s, 6H), 7.30 (d, J = 8.4 Hz, 4H), 7.81 (d, J = 8.4 Hz, 4H). ^{13}C NMR (100 MHz) δ 21.63 (two carbons), 45.07 (two carbons), 128.61 (four carbons), 129.43 (four carbons), 136.58 (two carbons), 144.81 (two carbons). IR (KBr) 3067, 3051, 2992, 2961, 2931, 2897, 1595, 1365, 1162, 911 cm^{-1}. Anal. Calcd for $C_{16}H_{20}N_2O_4S_2$: C, 52.15; H, 5.47. Found: C, 51.94; H, 5.54. mp 156–157 °C.

*S-(4-Methylphenyl) (4-methylbenzene) thiosulfonate (**6**) [5a,11–13]*

A solution of *N,N*-bis(4-methylbenzenesulfonyl)-*N′,N′*-dimethylhydrazine (**5**) (59.4 mg, 0.160 mmol) in chlorobenzene (0.8 mL) was stirred in an oil bath maintained at 120°C for 4 h. After being cooled to room temperature, the mixture was concentrated in vacuo to give a crude oil, which was chromatographed on silica gel (hexane–ethyl acetate) to afford the title compound (31.6 mg, 71%) as a white solid.

^{1}H NMR (400 MHz) δ 2.38 (s, 3H), 2.42 (s, 3H), 7.14 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz) δ 21.46, 21.64, 124.57, 127.58 (two carbons), 129.34 (two carbons), 130.17 (two carbons), 136.48 (two carbons), 140.45, 142.01, 144.54. IR (KBr) 3082, 3066, 3034, 2917, 2862, 1590, 1488, 1323, 1138, 806 cm^{-1}. MS (EI, 70 eV) *m/z* (rel. intensity): 278 ([M]$^+$, 85), 155 (28), 139 (100), 123 (31), 91 (38). HRMS (EI, 70 eV) Calcd for $C_{14}H_{14}O_2S_2$ [M]$^+$: 278.0435. Found: 278.0429. Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07. Found: C, 60.47; H, 5.15. mp 77–78°C (lit. 71°C [4i], 74–75°C [11, 14], 75.5–77.0°C [5b], 76–78°C [15]).

*N,N-Di(benzenesulfonyl)-N′, N′-dimethylhydrazine (**14**)*

^{1}H NMR (400 MHz) δ 2.77 (s, 6H), 7.54 (t, J = 7.6 Hz, 4H), 7.65 (t, J = 7.6 Hz, 2H), 7.95 (d, J = 7.6 Hz, 4H). ^{13}C NMR (100 MHz) δ 45.10 (two carbons), 128.58 (four carbons), 128.87 (four carbons), 133.82 (two carbons), 139.34 (two carbons). IR (KBr) 3075, 3064, 2993, 2960, 2931, 2896, 1583, 1447, 1363, 1165, 1080, 908 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_2O_4S_2$: C, 49.40; H, 4.74. Found: C, 49.49; H, 4.70. mp 115–116°C.

*N,N-Bis(4-tert-butylbenzenesulfonyl)-N′, N′-dimethylhydrazine (**15**)*

^{1}H NMR (400 MHz) δ 1.35 (s, 18H), 2.78 (s, 6H), 7.53 (d, J = 8.8 Hz, 4H), 7.87 (d, J = 8.8 Hz, 4H). ^{13}C NMR (100 MHz) δ 31.01 (six carbons), 35.23 (two carbons), 45.13 (two carbons), 125.79 (four carbons), 128.43 (four carbons), 136.39 (two carbons), 157.71 (two carbons). IR (KBr) 3073, 2961, 2903, 2869, 1593, 1477, 1370, 1181, 908 cm^{-1}. HRMS (ESI) Calcd for $C_{22}H_{32}N_2O_4S_2Na$ [M + Na]$^+$: 475.1696. Found: 475.1695. mp 145–146°C.

*N,N-Bis(3-methylbenzenesulfonyl)-N′, N′-dimethylhydrazine (**16**)*

^{1}H NMR (400 MHz) δ 2.43 (s, 6H), 2.78 (s, 6H), 7.42 (t, J = 7.2 Hz, 2H), 7.45 (d, J = 7.2 Hz, 2H), 7.72 (s, 2H), 7.75 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz) δ 21.29 (two carbons), 45.09 (two carbons), 125.74 (two carbons), 128.67 (two carbons), 128.76 (two carbons), 134.55 (two carbons), 139.06 (two carbons), 139.18 (two carbons). IR (KBr) 3093, 3065, 3004, 2962, 2926, 2891, 1477, 1366, 1180, 1084, 902 cm^{-1}. Anal. Calcd for $C_{16}H_{20}N_2O_4S_2$: C, 52.15; H, 5.47. Found: C, 52.19; H, 5.58. mp 91–92°C.

*N,N-Bis(4-methoxybenzenesulfonyl)-N′, N′-dimethylhydrazine (**17**)*

^{1}H NMR (400 MHz) δ 2.77 (s, 6H), 3.89 (s, 6H), 6.99 (d, J = 8.8 Hz, 4H), 7.88 (d, J = 8.8 Hz, 4H). ^{13}C NMR (100 MHz) δ 45.06 (two carbons), 55.68 (two carbons), 113.94 (four carbons), 130.87 (four carbons), 130.95 (two carbons), 163.69 (two carbons). IR (KBr) 3075, 3000, 2965, 2898, 1593, 1498, 1355, 1257, 1150, 1018, 911 cm^{-1}. Anal. Calcd for $C_{16}H_{20}N_2O_6S_2$: C, 47.99; H, 5.03. Found: C, 47.97; H, 4.97. mp 144–145°C.

*N,N-Bis(4-chlorobenzenesulfonyl)-N′, N′-dimethylhydrazine (**18**)*

^{1}H NMR (400 MHz) δ 2.78 (s, 6H), 7.53 (td, J = 2.4, 8.8 Hz, 4H), 7.91 (td, J = 2.4, 8.8 Hz, 4H). ^{13}C NMR (100 MHz) δ 45.22 (two carbons), 129.31 (four carbons), 130.06 (four carbons), 137.68 (two carbons), 140.73 (two carbons). IR (KBr) 3098, 3027, 2988, 2961, 2926, 2896, 1575, 1473, 1370, 1187, 1090, 907, 759 cm^{-1}. Anal. Calcd for $C_{14}H_{14}Cl_2N_2O_4S_2$: C, 41.08; H, 3.45. Found: C, 41.29; H, 3.36. mp 167–168°C.

*N,N-Bis(3-chlorobenzenesulfonyl)-N′, N′-dimethylhydrazine (**19**)*

^{1}H NMR (400 MHz) δ 2.80 (s, 6H), 7.52 (t, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.90 (s, 2H). ^{13}C NMR (100 MHz) δ 45.23 (two carbons), 126.73 (two carbons), 128.55 (two carbons), 130.26 (two carbons), 134.16 (two carbons), 135.17 (two carbons), 140.66 (two carbons). IR (KBr) 3088, 3069, 2999, 2969, 2944, 2897, 1579, 1458, 1421, 1373, 1299, 1170, 899 cm^{-1}. Anal. Calcd for $C_{14}H_{14}Cl_2N_2O_4S_2$: C, 41.08; H, 3.45. Found: C, 41.29; H, 3.36. mp 62–63°C.

*N,N-Di(2-naphthalenesulfonyl)-N′, N′-dimethylhydrazine (**20**)*

^{1}H NMR (400 MHz) δ 2.82 (s, 6H), 7.61 (t, J = 7.6 Hz, 2H), 7.68 (t, J = 7.6 Hz, 2H), 7.88–7.99 (m, 8H), 8.49 (s, 2H). ^{13}C NMR (100 MHz) δ 45.28 (two carbons), 123.03 (two carbons), 127.62 (two carbons), 127.90 (two carbons), 129.09 (two carbons), 129.48 (two carbons), 129.59 (two carbons), 130.67 (two carbons), 131.82 (two carbons), 135.25 (two carbons), 136.08 (two carbons). IR (KBr) 3063, 2996, 2965, 2935, 2899, 1591, 1365, 1156, 1066, 899 cm^{-1}. Anal. Calcd for $C_{22}H_{20}N_2O_4S_2$: C, 59.98; H, 4.58. Found: C, 59.67; H, 4.80. mp 144–145°C.

*S-Phenyl benzenethiosulfonate (**21**) [3e,4h,4i]*

^{1}H NMR (400 MHz) δ 7.30–7.38 (m, 4H), 7.39–7.50 (m, 3H), 7.57 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz) δ 127.56 (two carbons), 127.83, 128.78 (two carbons), 129.42 (two carbons), 131.40, 133.60, 136.58 (two carbons), 142.96. IR (neat) 3062, 1474, 1446, 1327, 1146, 1077 cm^{-1}. MS (EI, 70 eV) *m/z* (rel. intensity): 250 ([M]$^+$, 100), 141 (38), 125 (90), 109 (40), 77 (60). HRMS (EI, 70 eV) Calcd for $C_{12}H_{10}O_2S_2$ [M]$^+$: 250.0122. Found: 250.0129. Anal. Calcd for $C_{12}H_{10}O_2S_2$: C, 57.57; H, 4.03. Found: C, 57.47; H, 4.19. mp 38–39°C (lit. 39–41°C [4i], 40–41°C [3e], 43.0–45.0°C [5b], 44–45°C [15]).

Spectral properties of this compound were same as those of an authentic sample from a commercial source.

*S-(4-tert-Butylphenyl) (4-tert-butylbenzene) thiosulfonate (**22**) [5c,16,17]*

^{1}H NMR (400 MHz) δ 1.31 (s, 9H), 1.33 (s, 9H), 7.28 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz) δ 31.01 (three carbons), 31.11 (three carbons), 34.90, 35.23, 124.60, 125.63 (two carbons), 126.42 (two carbons), 127.41 (two carbons), 136.28 (two carbons), 140.18, 154.99, 157.51. IR (KBr) 3064, 2959, 2869, 1589, 1486, 1399, 1364, 1328, 1147, 1105, 1076, 826 cm^{-1}. HRMS (ESI) Calcd for $C_{20}H_{26}O_2S_2Na$ [M + Na]$^+$: 385.1266. Found: 385.1271. mp 155–156°C (lit. 143–145°C [16], 147.5–149.5°C [17], 150–151°C [5c]).

*S-(3-Methylphenyl) (3-methylbenzene) thiosulfonate (**23**) [15]*

^{1}H NMR (400 MHz) δ 2.30 (s, 3H), 2.34 (s, 3H), 7.15 (d, J = 7.6 Hz, 1H), 7.15 (s, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.33–7.40 (m, 3H). ^{13}C NMR (100 MHz) δ 21.09, 21.11, 124.71, 127.58, 127.98, 128.51, 129.10, 132.13, 133.59, 134.27, 137.16, 138.97, 139.36, 142.73. IR (neat) 3058, 3024, 2953, 2923, 1592, 1474, 1330, 1141, 1079, 783 cm^{-1}. MS (EI, 70 eV) *m/z* (rel. intensity): 278 ([M]$^+$, 80), 153 (100), 139 (81), 89 (58), 77 (82). HRMS (EI, 70 eV) Calcd for $C_{14}H_{14}O_2S_2$ [M]$^+$: 278.0435. Found: 278.0437. Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07. Found: C, 60.47; H, 5.15.

*S-(4-Methoxyphenyl) (4-methoxybenzene) thiosulfonate (**24**) [4i,5b,18]*

^{1}H NMR (400 MHz) δ 3.83 (s, 3H), 3.87 (s, 3H), 6.85 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz) δ 55.45, 55.68, 113.80 (two carbons), 114.89 (two carbons), 118.91, 129.89 (two carbons), 134.92, 138.35 (two carbons), 162.18, 163.49. IR (KBr) 3060, 2941, 2836, 1590, 1494, 1323, 1260, 1139, 1020 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_4S_2$: C, 54.17; H, 4.55. Found: C, 54.18; H, 4.79. mp 83–84°C (lit. 86–88°C [18], 89.0–89.5°C [5b], 89–90°C [4i].

*S-(4-Chlorophenyl) (4-chlorobenzene) thiosulfonate (**25**) [4h,12]*

^{1}H NMR (400 MHz) δ 7.31 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz) δ 126.01, 128.93 (two carbons), 129.27 (two carbons), 129.92 (two carbons), 137.68 (two carbons), 138.56, 140.56, 141.28. IR (KBr) 3086, 2924, 1570, 1473, 1322, 1145, 1092, 1010, 823 cm^{-1}. Anal. Calcd for $C_{12}H_8Cl_2O_2S_2$: C, 45.15; H, 2.53. Found: C, 44.99; H, 2.54. mp 137–138°C (lit. 134–136°C [4i], 135–136°C [15].

*S-(3-Chlorophenyl) (3-chlorobenzene) thiosulfonate (**26**) [19,20]*

^{1}H NMR (400 MHz) δ 7.30 (td, J = 1.6, 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 1.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.46 (td, J = 1.6, 7.6 Hz, 1H), 7.49 (td, J = 1.6, 7.6 Hz, 1H), 7.55 (t, J = 1.6 Hz, 1H), 7.59 (td, J = 1.6, 7.6 Hz, 1H). ^{13}C NMR (100 MHz) δ 125.56, 127.61, 129.00, 130.16, 130.57, 131.90, 134.01, 134.62, 135.14, 135.28, 136.08, 143.96. IR (neat) 3087, 1573, 1460, 1402, 1336, 1150, 1074, 784 cm^{-1}. Anal. Calcd for $C_{12}H_8Cl_2O_2S_2$: C, 45.15; H, 2.53. Found: C, 45.12; H, 2.65.

*S-(2-Naphthyl) 2-naphthalenethiosulfonate (**27**) [4i,5b]*

^{1}H NMR (400 MHz) δ 7.34 (dd, J = 1.6, 8.0 Hz, 1H), 7.44–7.69 (m, 7H), 7.73 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz) δ 122.38, 125.13, 126.87, 127.64, 127.69, 127.85, 128.21, 128.37, 129.09, 129.30 (two carbons), 129.36, 129.43, 131.57, 131.81, 133.22, 134.07, 135.08, 137.68, 139.63. IR (KBr) 3056, 1587, 1500, 1322, 1142, 1063, 860, 811 cm^{-1}. MS (EI, 70 eV) *m/z* (rel. intensity): 350 ([M]$^+$, 87), 175 (100), 159 (51), 127 (57), 115 (59). HRMS (EI, 70 eV) Calcd for $C_{20}H_{14}O_2S_2$ [M]$^+$: 350.0435. Found: 350.0434. Anal. Calcd for $C_{20}H_{14}O_2S_2$: C, 68.54; H, 4.03. Found: C, 68.56; H, 3.93. mp 111–112°C (lit. 104.5–106.5°C [5b], 104–106°C [4i].

N,N-Dioctylhydrazine

This was prepared according to the literature method [21].

^{1}H NMR (400 MHz) δ 0.89 (t, J = 8 Hz, 6H), 1.18–1.40 (m, 22H), 1.54 (br s, 4H), 2.44 (t, J = 8 Hz, 4H).

*N,N-Bis(4-methylbenzenesulfonyl)-N′, N′-dioctylhydrazine (**28**)*

^{1}H NMR (400 MHz) δ 0.89 (t, J = 7.2 Hz, 6H), 1.01–1.35 (m, 24H), 2.45 (s, 6H), 2.98 (t, J = 8.0 Hz, 4H), 7.32 (d, J = 8.4 Hz, 4H), 7.87 (d, J = 8.4 Hz, 4H). ^{13}C NMR (100 MHz) δ 14.10 (two carbons), 21.64 (two carbons), 22.63 (two carbons), 26.98 (two carbons), 28.62 (two carbons), 29.23 (two carbons), 29.34 (two carbons), 31.81 (two carbons), 57.21 (two carbons), 128.98 (four carbons), 129.34 (four carbons), 136.71 (two carbons), 144.75 (two carbons). IR (neat) 3068, 3029, 2955, 2926, 2855, 1597, 1466, 1371, 1165, 1084 cm^{-1}. Anal. Calcd for $C_{30}H_{48}N_2O_4S_2$: C, 63.79; H, 8.57. Found: C, 63.71; H, 8.40.

*N-(4-Methoxybenzenesulfonyl)-N-(4-methylbenzenesulfonyl)-N′,N′-dimethylhydrazine (**29**)*

^{1}H NMR (400 MHz) δ 2.45 (s, 3H), 2.77 (s, 6H), 3.89 (s, 3H), 6.99 (d, J = 9.2 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz) δ 21.64, 45.05 (two carbons), 55.67, 113.94 (two carbons), 128.55 (two carbons), 129.41 (two carbons), 130.87 (three carbons), 136.55, 144.77, 163.72. IR (KBr) 3070, 2965, 2845, 1595, 1498, 1360, 1268, 1160, 1084, 1027, 897 cm^{-1}. HRMS (ESI) Calcd for $C_{16}H_{20}N_2O_5S_2Na$ [M + Na]$^+$: 407.0706. Found: 407.0703. mp 97–98°C.

*Reaction of N-(4-Methoxybenzenesulfonyl)-N-(4-methylbenzenesulfonyl)-N′, N′-dimethylhydrazine (**29**)*

A solution of *N*-(4-methoxybenzenesulfonyl)-*N*-(4-methylbenzenesulfonyl)-*N′*,*N′*-dimethylhydrazine (**29**) (76.9 mg, 0.200 mmol) in chlorobenzene (1.0 mL) was stirred in an oil bath maintained at 120°C for 8 h. After being cooled to room temperature, the mixture was concentrated in vacuo to give a crude oil, which was chromatographed on silica gel (hexane–ethyl acetate) to afford *S*-(4-methylphenyl) (4-methylbenzene)thiosulfonate (**6**) (12.1 mg, 22%) as a white solid, *S*-(4-methoxyphenyl) (4-methoxybenzene)thiosulfonate (**24**) (10.0 mg, 16%) as a white solid, and a 47:53 mixture of *S*-(4-methylphenyl) (4-methoxybenzene)thiosulfonate (**30**), and *S*-(4-methoxyphenyl) (4-methylbenzene)thiosulfonate (**31**) (15.9 mg, 27%) as a solid by ^{1}H NMR analysis.

The spectral data for **6** or **24** have been already shown.

*S-(4-methylphenyl) (4-methoxybenzene) thiosulfonate (**30**).* ^{1}H NMR (400 MHz) (characteristic peaks are shown) : 2.38 ppm (Me) and 3.87 ppm (MeO).

*S-(4-methoxyphenyl) (4-methylbenzene) thiosulfonate (**31**).* ^{1}H NMR (400 MHz) (characteristic peaks are shown) : 2.42 ppm (Me) and 3.83 ppm (MeO).

The characteristic peaks of **30** and **31** were assigned on the basis of the assumption that the Me or MeO group bearing the SO_2Ar group should show low-field shifts.

*N,N′-Bis(4-methylbenzenesulfonyl)hydrazine (**34**) [22]*

^{1}H NMR (400 MHz) δ 2.43 (s, 6H), 6.28 (s, 2H), 7.17 (d, $J = 8.0$ Hz, 4H), 7.59 (d, $J = 8.0$ Hz, 4H). IR (KBr) 3206 (NH), 3065, 2929, 1597, 1331, 1166, 1090, 813, 695 cm^{-1}.

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