An Efficient Synthesis of Naphthyl Alkyl and Aryl Sulfides by the Reaction of Naphthols with Alkane- and Arenethiols

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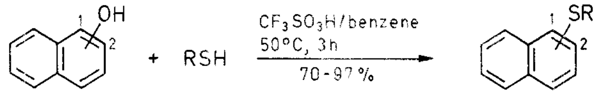
The reaction of 1- and 2-naphthols **1** and **2** with a variety of thiols **3** in the presence of trifluoromethanesulfonic acid afforded naphthyl alkyl and aryl sulfides **4** and **5**, respectively, in good yields. Similarly naphthyl bis(alkyl) or bis(aryl) sulfides **10–13** were prepared from the corresponding dihydroxynaphthalenes **6–9**.

Organic sulfides are starting materials for the synthesis of sulfur compounds such as sulfoxides, sulfones, and sulfonium salts; alkyl aryl sulfides are especially important as intermediates for sulfur containing heterocyclic compounds. Alkyl aryl sulfides are generally prepared by the condensation of aromatic thiols with alkyl halides,[1] but the types of aromatic thiols available are limited. Futhermore, aryl sulfides are synthesized[2-6] by the reaction of aryl halides with thiols, which necessitates high temperature and long reaction times. In addition, there are methods of substituting phenolic hydroxy groups with thiols, which require severe reaction conditions[7] with simple phenols. Furman and co-workers[8] have reported the formation of naphthyl phenyl sulfide in approximately 43 % yield by the reaction of 2-naphthol with benzenethiol in the presence of *p*-toluenesulfonic acid. This method has not been investigated for the synthesis of naphthyl alkyl and aryl sulfides. Herein, we report on the synthesis of naphthyl alkyl and aryl sulfides by the reaction of naphthols with alkyl and aryl thiols.

When 2-naphthol (**2**) and thiols **3a,d** were dissolved in benzene and reacted in the presence of trifluoromethanesulfonic acid at 50 °C for 3 h, the substitution of the hydroxy group of 2-naphthol with thiols readily takes place to give 2-naphthyl alkyl and aryl sulfides **5a,d** quantitatively. This reaction was applicable for a variety of thiols, such as octanethiol (**3b**), ethyl mercaptoethanoate (**3c**), and methyl- or chloro substituted benzenethiols **3e–g**, giving the corresponding naphthyl sulfides **5** in a good yield (Table 1). In a similar reaction with 1-naphthol (**1**), roughly the same result was obtained although with a somewhat lower yield.



1 1-OH
2 2-OH

3

4 1-SR
5 2-SR

3–5	R
a	n-C_4H_9
b	n-C_8H_{17}
c	CH_2CO_2Et
d	Ph
e	4-$CH_3C_6H_4$
f	2-$CH_3C_6H_4$
g	4-ClC_6H_4

Furthermore, with the purpose of obtaining bis-sulfides, reaction between dihydroxynaphthalene and thiols were tried. Dihydroxynaphthalenes **6–9** are less soluble in aromatic solvents,

Table 1. 1- and 2-Naphthyl Alkyl and Aryl Sulfides **4** and **5** Prepared

Product	Yield[a] (%)	mp (°C) or bp (°C)/5 mbar	Molecular Formula[b]	HRMS m/z (M^+)	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)
4a	81	bp 133–136	$C_{14}H_{16}S$ (216.3)	216.0993	0.92 (t, 3H, J = 7.1, CH_3); 1.47 (qt, 2H, J = 7.1, 7.1, CH_2); 1.66 (tt, 2H, J = 7.1, 7.1, CH_2); 2.98 (t, 2H, J = 7.1, CH_2); 7.40–8.40 (m, 7H_{arom})
4b	95	bp 148–150	$C_{18}H_{24}S$ (272.5)	272.1585	0.88 (t, 3H, J = 6.9, CH_3); 1.26–1.28 (m, 8H, CH_2); 1.43 (tt, 2H, J = 7.4, 7.4, CH_2); 1.66 (tt, 2H, J = 7.4, 7.4, CH_2); 2.97 (t, 2H, J = 7.4, CH_2); 7.37–8.41 (m, 7H_{arom})
4c	88	bp 162–163	$C_{14}H_{14}O_2S$ (246.3)	246.0701	1.12 (t, 3H, J = 7.1, CH_3); 3.65 (s, 2H, CH_2); 4.08 (q, 2H, J = 7.1, CH_2); 7.39–8.44 (m, 7H_{arom})
4d	81	bp 167–168	$C_{16}H_{12}S$ (236.3)	236.0683	7.09–8.46 (m, 12H_{arom})
4e	72	bp 181–182	$C_{17}H_{14}S$ (250.4)	250.0831	2.30 (s, 3H, CH_3); 7.05–8.40 (m, 11H_{arom})
4f	79	bp 167–169	$C_{17}H_{14}S$ (250.4)	250.0792	2.45 (s, 3H, CH_3); 6.99–8.33 (m, 11H_{arom})
4g	70	bp 183–184	$C_{16}H_{11}ClS$ (270.8)	270.0299	6.99–8.40 (m, 11H_{arom})
5a	95	bp 143–144	$C_{14}H_{16}S$ (216.3)	216.0965	0.93 (t, 3H, J = 7.3, CH_3); 1.48 (qt, 2H, J = 7.3, 7.3, CH_2); 1.68 (tt, 2H, J = 7.3, 7.3, CH_2); 3.02 (t, 2H, J = 7.3, CH_2); 7.38–7.78 (m, 7H_{arom})
5b	97	bp 184–185	$C_{18}H_{24}S$ (272.5)	272.1586	0.87 (t, 3H, J = 7.3, CH_3); 1.26–1.35 (m, 8H, CH_2); 1.45 (tt, 2H, J = 7.3, 7.3, CH_2); 1.69 (tt, 2H, J = 7.3, 7.3, CH_2); 3.01 (t, 2H, J = 7.3, CH_2); 7.38–7.78 (m, 7H_{arom})
5c	85	bp 167–169	$C_{14}H_{14}O_2S$ (246.3)	246.0696	1.20 (t, 3H, J = 7.1, CH_3); 3.73 (s, 2H, CH_2); 4.16 (q, 2H, J = 7.1, CH_2); 7.44–7.85 (m, 7H_{arom})
5d	95	mp 42–43	$C_{16}H_{12}S$ (236.3)	236.0635	7.23–7.84 (m, 12H_{arom})
5e	95	mp 66–67	$C_{17}H_{14}S$ (250.4)	250.0787	2.35 (s, 3H, CH_3); 7.10–7.82 (m, 11H_{arom})
5f	78	bp 173–174	$C_{17}H_{14}S$ (250.4)	250.0789	2.40 (s, 3H, CH_3); 7.12–7.79 (m, 11H_{arom})
5g	87	mp 106–107	$C_{16}H_{11}ClS$ (270.8)	270.0257	7.24–7.85 (m, 11H_{arom})

[a] Yield based on starting 1- or 2-naphthol.

[b] Satisfactory microanalyses obtained: C ±0.30, H ±0.25, S ±0.30.

Table 2. Naphthyl Bis(alkyl) and Bis(aryl) Sulfides **10–13** Prepared

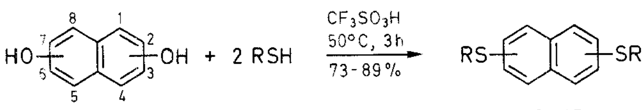
Product	Substituent Positions	Yield[a] (%)	mp (°C)	Molecular Formula[b]	HRMS m/z (M^+)	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)
10a	1,5	85[c]	52–54	$C_{18}H_{24}S_2$ (304.5)	304.1316	0.92 (t, 6H, J = 7.3, CH_3); 1.47 (qt, 4H, J = 7.3, 7.3, CH_2CH_3); 1.66 (tt, 4H, J = 7.3, 7.3, SCH_2CH_2); 2.98 (t, 4H, J = 7.3, SCH_2); 7.44–8.32 (m, 6H_{arom})
10d	1,5	89	148–149	$C_{22}H_{16}S_2$ (344.5)	344.0666	7.15–8.43 (m, 16H_{arom})
11a	1,6	88[c]	oil	$C_{18}H_{24}S_2$ (304.5)	304.1314	0.91 (t, 3H, J = 7.3, CH_3); 0.93 (t, 3H, J = 7.3, CH_3); 1.46 (qt, 3H, J = 7.3, 7.3, $C\underline{H}_2CH_3$); 1.48 (qt, 2H, J = 7.3, 7.3, $C\underline{H}_2CH_3$); 1.64 (tt, 2H, J = 7.3, 7.3, $SCH_2C\underline{H}_2$); 1.68 (tt, 2H, J = 7.3, 7.3, $SCH_2C\underline{H}_2$); 2.97 (t, 2H, J = 7.3, SCH_2); 3.03 (t, 2H, J = 7.3, SCH_2); 7.35–8.30 (m, 6H_{arom})
11d	1,6	74	oil	$C_{22}H_{16}S_2$ (344.5)	344.0693	7.12–8.32 (m, 16H_{arom})
12a	2,6	81[c]	72–74	$C_{18}H_{24}S_2$ (304.5)	304.1303	0.93 (t, 6H, J = 7.1, CH_3); 1.47 (qt, 4H, J = 7.1, 7.1, $C\underline{H}_2CH_3$); 1.67 (tt, 4H, J = 7.1, 7.1, $SCH_2C\underline{H}_2$); 3.01 (t, 4H, J = 7.1, SCH_2); 7.39–7.67 (m, 6H_{arom})
12d	2,6	84	131–133	$C_{22}H_{16}S_2$ (344.5)	344.0688	7.28–7.76 (m, 16H_{arom})
13a	2,7	82[c]	27–29	$C_{18}H_{24}S_2$ (304.5)	304.1321	0.94 (t, 6H, J = 7.1, CH_3); 1.48 (qt, 4H, J = 7.1, 7.1, $C\underline{H}_2CH_3$); 1.68 (tt, 4H, J = 7.1, 7.1, $SCH_2C\underline{H}_2$); 3.02 (t, 4H, J = 7.1, SCH_2); 7.33–7.66 (m, 6H_{arom})
13d	2,7	73	102–105	$C_{22}H_{16}S_2$ (344.5)	344.0717	7.23–7.15 (m, 16H_{arom})

[a] Yield based on starting dihydroxynaphthalenes; **a** R = n-C_4H_9, **d** R = Ph.

[b] Satisfactory microanalyses obtained: C ±0.20, H ±0.15, S ±0.25.

[c] Reaction temperature: 30 °C.

and were therefore dissolved in an excess of trifluoromethanesulfonic acid and reacted with twice the molar amount of thiols **3a,d** in the absence of solvent at 30–50 °C for 3 h to give the corresponding bis-sulfides **10a–13a, d** in good yields (Table 2).



6 1,5-dihydroxy
7 1,6-dihydroxy
8 2,6-dihydroxy
9 2,7-dihydroxy

3

10–13

It seems likely that the ease of formation of naphthylsulfides is dependent on the presence of trifluoromethanesulfonic acid. In the first step, protonation of the aromatic ring of naphthols occurs and an intermediate carbocation is produced. The carbocation then reacts rapidly with thiols followed by dehydration (aromatization).

Thus, the present work provides convenient methods, which are applicable to the preparation of a variety of naphthyl alkyl and aryl sulfides. Analytical and spectroscopic data of all products are in agreement with the described structures (Tables 1 and 2).

Melting points were determined with a Yanaco micromelting point apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer 240C elemental analyzer. Mass spectra were recorded on a Hitachi M-80B spectrometer. ^{1}H-NMR spectra were recorded on a JEOL-JNM-GX-400 spectrometer.

1- and 2-Naphthyl Alkyl and Aryl Sulfides 4, 5; General Procedure:
To a stirred solution of naphthol **1** or **2** (7.2 g, 50 mmol) and thiol **3** (50 mmol) in benzene (100 mL) is added dropwise CF_3SO_3H (15.0 g, 100 mmol). The mixture is stirred at 50 °C for 3 h under N_2, and poured into ice-cold water (200 mL). The organic layer is washed with 2 % aq. NaOH (200 mL), water, and dried (Na_2SO_4). The solvent is removed, the oily residue is distilled under reduced pressure and the solid product is recrystallized from hexane (Table 1).

Naphthyl Bis(alkyl and aryl) Sulfides 10–13; General Procedure:
To a solution of dihydroxy naphthalene **6–9** (3.2 g, 20 mmol) in CF_3SO_3H (6.0 g, 40 mmol) is added thiol **3** (40 mmol) and the mixture is stirred at 50 °C for 3 h under N_2. The mixture is then poured into ice-cold water (250 mL) and extracted with Et_2O (3 × 50 mL). The organic layer is washed with 2% aq. NaOH, water, dried (Na_2SO_4), and evaporated under reduced pressure. The solid residue is recrystallized from petroleum ether (bp 60 °C) and the liquid product is purified by distillation (Table 2).

Received: 28 March 1989; revised: 10 July 1989

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