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N-Trifluoroacetyl arenesulfenamides, effective precursors for synthesis of unsymmetrical disulfides and sulfenamides

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Abstract—*N*-Trifluoroacetyl arenesulfenamides (**3**) were effective precursors for the synthesis of unsymmetrical disulfides (**4**) and sulfenamides (**5**). Reactions of **3** with a variety of aromatic thiols at room temperature were generally complete within 5 min and gave unsymmetrical diaryl disulfides in high yields. Aralkyl disulfides were isolated in high yields from the reaction of **3** with aliphatic thiols. The nucleophilic substitution reactions of **3** with amines proceeded smoothly and provided N-substituted sulfenamides in good to excellent yields.

1. Introduction

Disulfides and sulfenamides have attracted considerable interest because of their practical applications in biochemistry, pharmacological chemistry, and industrial chemistry as well as their utility as synthetic reagents.[1] The development of an efficient method for the preparation of disulfides and sulfenamides is still a challenge in organic synthesis. Although symmetrical disulfides can be prepared by the direct transformation of thiols, the synthesis of unsymmetrical disulfides usually requires the construction of sulfenyl derivatives in advance, followed by nucleophilic substitution with thiols. Over the past three decades, many sulfenyl derivatives have been prepared for the synthesis of unsymmetrical disulfides: dithioperoxyesters,[2] thiosulfinates and thiosulfonates,[3] *S*-alkylthiosulfates and *S*-arylthiosulfates (Bunte salts),[4] 4′-nitroarenesulfenanilides,[5] thioimides (thiophthalimides, thiosuccinimides, and thiomaleimides),[6] thionitrites,[7] alkylthiodialkylsulfonium salts,[8] sulfenyl thiocarbonates,[9] sulfenyl thiocyanates,[10] and *S*-alkylthioisothioureas.[11] However, using these sulfenyl compounds to synthesize unsymmetrical disulfides often has drawbacks. For example, because rapid thiol–disulfide exchange occurs under the typical reaction conditions (high temperature, acidic conditions), pure unsymmetrical diaryl disulfides are not always obtained.

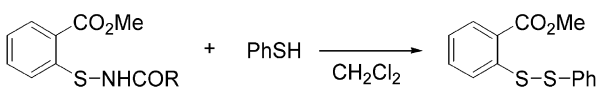
N-Sulfenylphthalimides[12] and 3-sulfenylhydantoins,[13] derived from the reaction of phthalimides or hydantoins with sulfenyl chlorides, can be used as sulfenyl-transfer reagents to prepare other sulfenamides. However, generation of sulfenyl chlorides requires chlorination of disulfides or thiols with hazardous, poisonous, and corrosive chlorine gas, the use of which does not reflect the modern trend toward using safer reagents.

We have recently reported the efficient preparation of *N*-trifluoroacetyl arenesulfenamides by a chlorine-free procedure.[14] Herein, we report the use of *N*-trifluoroacetyl arenesulfenamides as effective precursors for the synthesis of unsymmetrical disulfides and sulfenamides.

2. Results and discussion

2.1. Synthesis of unsymmetrical disulfides

In our initial studies, we investigated nucleophilic substitution reactions of *N*-acetyl-2-(methoxycarbonyl)-benzenesulfenamide (**1**), *N*-benzoyl-2-(methoxycarbonyl)-benzenesulfenamide (**2**), and *N*-(trifluoroacetyl)-2-(methoxycarbonyl)benzenesulfenamide (**3a**) with benzenethiol in dichloromethane at room temperature (Scheme 1). After the reaction mixture of **1** or **2** with



1: R = Me; **2**: R = Ph
3a: R = CF_3

4a

Scheme 1.

Keywords: synthesis; unsymmetrical disulfides; sulfenamides; *N*-trifluoroacetyl arenesulfenamides.
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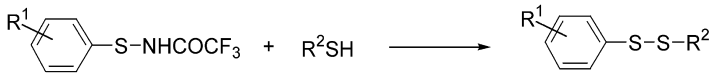
benzenethiol was stirred for 5 h, phenyl 2-(methoxycarbonyl)phenyl disulfide (**4a**)[15] was obtained in 37 or 62% yield, respectively, along with the symmetrical disulfides 2,2′-di[(methoxycarbonyl)phenyl] disulfide and diphenyl disulfide. However, **4a** was obtained in a high yield (89%) from the reaction of **3a** with benzenethiol in a short time (Table 1, entry 1, reaction time: 5 min.).

Several other *N*-trifluoroacetyl arenesulfenamides (**3**) were used to synthesize unsymmetrical disulfides (**4**) (Table 1). When **3a** was treated with the aliphatic thiol 1-dodecanethiol in dichloromethane at room temperature for 1 h, dodecyl 2-(methoxycarbonyl)phenyl disulfide (**4b**)[15] was obtained in only 13% yield, and a large amount of starting material **3a** was recovered (69%). Evidently, the low yield was due to the relatively low nucleophilic reactivity of 1-dodecanethiol compared to that of benzenethiol, and the reaction required a higher temperature to reach completion. Indeed, when the reaction was carried out in acetone at reflux for 1 h, the desired product (**4b**) was obtained in excellent yield (90%, entry 2). The reaction of *N*-(trifluoroacetyl)benzenesulfenamide (**3b**) with 4-methylbenzenethiol in dichloromethane at room temperature was complete within 5 min and gave phenyl 4-methylphenyl disulfide (**4c**)[16] in 94% yield (entry 3). Interestingly, the reaction of **3b** with 1-dodecanethiol in dichloromethane was complete within 1 h even at room temperature and gave dodecyl phenyl disulfide (**4d**)[17] in 98% yield (entry 4). Reactions of *N*-(trifluoroacetyl)-2-bromobenzenesulfenamide (**3c**), *N*-(trifluoroacetyl)-4-methylbenzenesulfenamide (**3d**), and *N*-(trifluoroacetyl)-4-nitrobenzenesulfenamide (**3e**) with aromatic thiols were similar to the reaction of **3a** with benzenethiol (entry 1) and gave unsymmetrical disulfides[18–21] in yields ranging from 73 to 98% (entries 5–8, 10, and 11). The reactivity of **3d** (bearing an electron-donating group on the aromatic ring) or **3e** (bearing an electron-withdrawing group on the aromatic ring) was similar to that of **3a** or **3b**. Although **3d** and **3e** reacted with 1-dodecanethiol to give dodecyl 4-methylphenyl disulfide (**4h**) and dodecyl 4-nitrophenyl disulfide (**4k**) in satisfactory yields (85 and 72%, respectively; entries 9 and 12), the latter reaction required high temperature to afford **4k** in such a yield. These results indicated that the reactivity of **3** in the nucleophilic substitution reaction with an aliphatic thiol depends on the electronic nature of R^1 of **3**; electron-withdrawing groups depressed the reactivity of **3** (entries 2 and 12).

2.2. Synthesis of sulfenamides

First, we investigated the nucleophilic substitution reaction of **3a** with a variety of amines to evaluate the scope of the reaction (Table 2). When the reaction of **3a** with benzylamine was carried out in THF at reflux for 6 h, the corresponding product, *N*-benzyl-2-(methoxycarbonyl)-benzenesulfenamide (**5a**),[22] was obtained in 99% yield (entry 1). However, a cyclized product, *N*-benzyl-1,2-benzisothiazolin-3-one (**6**),[22] was obtained as a by-product when the reaction was carried out in methanol or toluene at reflux (entries 2 and 3). The use of 4-chlorobenzylamine in place of benzylamine in the substitution reaction of **3a** afforded *N*-(4-chlorobenzyl)-2-(methoxycarbonyl)benzenesulfenamide (**5b**)[22] in 73% yield (entry 4). The reaction of **3a** with butylamine proceeded smoothly and afforded a high yield of the desired product, *N*-butyl-2-(methoxycarbonyl)-benzenesulfenamide (**5c**) (89%, entry 5). A good yield of *N*-cyclohexyl-2-(methoxycarbonyl)benzenesulfenamide (**5d**)[23] was obtained from the reaction of **3a** with cyclohexylamine (76%, entry 6). Sterically bulky amines, such as 2-phenyl-2-propylamine, showed lower reactivity in the substitution reaction of **3a** and gave *N*-(2-phenyl-2-propyl)-2-(methoxycarbonyl)benzenesulfenamide (**5e**)[22] in only 40% yield even when the reaction was conducted for 21 h (entry 7). The use of a secondary amine, pyrrolidine, also afforded the desired product, *N*-[(2-(methoxycarbonyl)benzenesulfenyl]pyrrolidine (**5f**),[22] in high yield (87%, entry 8). However, in the case of reaction of **3a** with anilines, such as 4-methylaniline and 4-chloroaniline, the substitution reaction did not occur, owing to poor reactivity of the aromatic amines, and the starting material **3a** was recovered.

Table 1. Synthesis of unsymmetrical disulfides (**4**) by the reaction of *N*-trifluoroacetyl arenesulfenamides (**3**) with thiols[a]

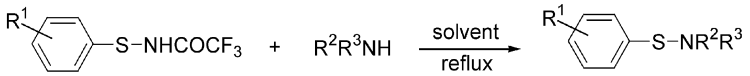


3 **4**

Entry	**3**	R^1	R^2	Solvent	Temperature	**4**	Yield (%) of **4**[b]
1	**3a**	2-CO_2Me	Ph	CH_2Cl_2	rt	**4a**	89
2[c]	**3a**	2-CO_2Me	$CH_3(CH_2)_{11}$	Acetone	Reflux	**4b**	90
3	**3b**	H	4-MeC_6H_4	CH_2Cl_2	rt	**4c**	94
4[c]	**3b**	H	$CH_3(CH_2)_{11}$	CH_2Cl_2	rt	**4d**	98
5	**3c**	2-Br	Ph	CH_2Cl_2	rt	**4e**	96
6	**3c**	2-Br	4-MeC_6H_4	CH_2Cl_2	rt	**4f**	98
7	**3d**	4-Me	Ph	CH_2Cl_2	rt	**4c**	94
8	**3d**	4-Me	4-ClC_6H_4	CH_2Cl_2	rt	**4g**	91
9[c]	**3d**	4-Me	$CH_3(CH_2)_{11}$	CH_2Cl_2	rt	**4h**	85
10	**3e**	4-NO_2	Ph	CH_2Cl_2	rt	**4i**	78
11	**3e**	4-NO_2	4-MeC_6H_4	CH_2Cl_2	rt	**4j**	73
12[c]	**3e**	4-NO_2	$CH_3(CH_2)_{11}$	Acetone	Reflux	**4k**	72

[a] Reactions were carried out in dichloromethane at room temperature for ca. 5 min, unless otherwise specified.
[b] Isolated yield.
[c] The reaction was carried out for 1 h.

Table 2. *N*-Substituted sulfenamides derived from the reaction of *N*-trifluoroacetyl arenesulfenamides (**3**) with amines[a]



3 **5**

Entry	**3**	R^1	R^2	R^3	Solvent	Time (h)	**5**	Yield of **5**[b] (%)
1	**3a**	2-CO_2Me	$PhCH_2$	H	THF	6	**5a**	99
2[c]	**3a**	2-CO_2Me	$PhCH_2$	H	MeOH	5	**5a**	61
3[d]	**3a**	2-CO_2Me	$PhCH_2$	H	Toluene	4	**5a**	74
4	**3a**	2-CO_2Me	4-$ClC_6H_4CH_2$	H	THF	7	**5b**	73
5	**3a**	2-CO_2Me	$CH_3(CH_2)_3$	H	THF	4	**5c**	89
6	**3a**	2-CO_2Me	cyclohexyl	H	THF	4	**5d**	76
7[e]	**3a**	2-CO_2Me	$PhMe_2C$	H	THF	21	**5e**	40
8	**3a**	2-CO_2Me	$-(CH_2)_4-$		THF	3	**5f**	87
9	**3f**	4-CO_2Me	$PhCH_2$	H	Toluene	2	**5g**	86
10	**3e**	4-NO_2	$PhCH_2$	H	Toluene	4	**5h**	96
11	**3g**	2-NO_2	$PhCH_2$	H	Toluene	4	**5i**	61

[a] A mixture of *N*-trifluoroacetyl sulfenamide (0.5 mmol) and 1.2 equiv. of amine in 6 mL of solvent was stirred at reflux for the period indicated.
[b] Isolated yield.
[c] 2-Benzyl-1,2-benzisothiazolin-3-one (**6**) was isolated in 20% yield.
[d] **6** was isolated in 4% yield.
[e] The starting material **3a** was recovered in 45% yield.

From the above results, it seems that THF was an effective solvent for the substitution reaction of **3** with amines. However, further attempts to synthesize sulfenamides using other *N*-trifluoroacetyl arenesulfenamides in THF gave none of the desired products. The pK_a values of **3** measured by titration showed that *para*-substituted arenesulfenamides (**3e**, **3f**) were more acidic than *ortho*-substituted ones (**3a**, **3d**) (Table 3). This result suggests that the N–H proton of **3e** or **3f** is easily transferred to benzylamine to form a salt in THF.

Table 3. pK_a values of *N*-trifluoroacetyl arenesulfenamides (**3**)

3	pK_a
3a	7.9
3d	7.6
3e	6.3
3f	6.8
3g	7.0

When the substitution reactions of **3e**, **3f**, and **3g** with benzylamine were carried out in toluene (a nonpolar solvent) at reflux for 2–4 h, the corresponding products[24,25] were obtained in good yields (entries 9–11). These results showed that the proton transfer from **3** to amine was inhibited in nonpolar solvent.

3. Conclusion

N-Trifluoroacetyl arenesulfenamides (**3**) were readily prepared by a chlorine-free procedure. These stable, crystalline solids were effective precursors for the synthesis of unsymmetrical disulfides and *N*-substituted sulfenamides. Reactions of **3** with a variety of aromatic thiols in dichloromethane at room temperature were generally complete within 5 min and gave unsymmetrical diaryl disulfides in high yields. Aralkyl disulfides were isolated in high yields from the reaction of **3** with aliphatic thiols. Since the reaction of **3** with thiols proceeded under neutral reaction conditions in a short time, thiol–disulfide exchange did not occur during reaction. The reaction of **3** with amines proceeded smoothly in THF or toluene and provided N-substituted sulfenamides in good to excellent yields.

4. Experimental

4.1. General

Melting points were determined on a Mettler FP90 microscopic plate and are uncorrected. ^1H and ^{13}C NMR spectra were obtained with a JEOL LA-500 spectrometer, and chemical shifts (δ) are reported in parts per million relative to internal tetramethylsilane (^1H NMR) or $CDCl_3$ (^{13}C NMR). IR spectra were recorded on a JASCO FTIR-5300 spectrophotometer. HRMS analysis was performed by the Analytical Center at the National Institute of Advanced Industrial Science and Technology with a Hitachi M-80B mass spectrometer. *N*-Trifluoroacetyl arenesulfenamides (**3**) were prepared by the method described in our previous paper.[14]

4.2. General procedure for the synthesis of unsymmetrical disulfides (4)

A thiol (0.6 mmol) was added to a solution of **3** (0.5 mmol) in 6 mL of dichloromethane at room temperature. The mixture was stirred for ca. 5 min, and then the solvent was removed under reduced pressure. The crude product was chromatographed on a silica gel column with dichloromethane/hexane (2:1) mixture as an eluent.

4.2.1. 2-Bromophenyl 4-methylphenyl disulfide (4f). Pale yellow oil with bp 80°C/6.7 Pa. ^1H NMR (500 MHz, $CDCl_3$): δ 7.69 (dd, J=8.0, 1.5 Hz, 1H), 7.50 (dd, J=8.0, 1.2 Hz, 1H), 7.37 (dt, J=8.2, 2.2 Hz, 2H), 7.28 (ddd, J=8.0, 7.3, 1.2 Hz, 1H), 7.10 (dt, J=8.2, 2.2 Hz, 2H), 7.05 (ddd, J=8.0, 7.3, 1.5 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.6, 137.5, 132.8, 132.5, 129.9, 128.1, 128.0,

127.7, 127.1, 121.0, 21.0; IR (neat): 3054, 2919, 1574, 1489, 1443, 1427, 1017, 804, 747 cm^{-1}; HRMS: calcd for $C_{13}H_{11}BrS_2$: 309.9486, 311.9465; found: 309.9480, 311.9473. Anal. calcd for $C_{13}H_{11}BrS_2$: C, 50.16; H, 3.56; found: C, 50.55; H, 3.41.

4.2.2. Dodecyl 4-methylphenyl disulfide (4h). Colorless oil with bp 80°C/8.0 Pa. ^1H NMR (500 MHz, $CDCl_3$): δ 7.43 (dt, J=8.7, 2.5 Hz, 2H), 7.13 (dt, J=8.3, 2.5 Hz, 2H), 2.72 (t, J=7.3 Hz, 2H), 2.33 (s, 3H), 1.65 (quint, J=7.3 Hz, 2H), 1.35–1.24 (m, 18H), 0.88 (t, J=7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.9, 134.2, 129.7, 128.3, 38.9, 31.9, 29.63, 29.57, 29.5, 29.3, 29.2, 28.7, 28.5, 22.7, 21.0, 14.1; IR (neat): 2924, 2853, 1489, 1464, 1017, 912, 804, 741, 486 cm^{-1}; HRMS: calcd for $C_{19}H_{32}S_2$: 324.1945; found: 324.1962. Anal. calcd for $C_{19}H_{32}S_2$: C, 70.31; H, 9.94; found: C, 70.62; H, 9.71.

4.2.3. Dodecyl 4-nitrophenyl disulfide (4k). Pale yellow crystal with mp 32.5–33.5°C (from pentane). ^1H NMR (500 MHz, $CDCl_3$): δ 8.18 (dt, J=8.9, 2.5 Hz, 2H), 7.66 (dt, J=8.9, 2.5 Hz, 2H), 2.76 (t, J=7.3 Hz, 2H), 1.66 (quint, J=7.3 Hz, 2H), 1.39–1.27 (m, 18H), 0.88 (t, J=7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.3, 146.1, 125.8, 124.0, 39.1, 31.9, 29.63, 29.55, 29.5, 29.3, 29.1, 28.9, 28.4, 22.7, 14.1; IR (neat): 3098, 2926, 2853, 1458, 1518, 1468, 1339, 1109, 1078, 851, 741 cm^{-1}; HRMS: calcd for $C_{18}H_{29}NO_2S_2$: 355.1640; found: 355.1635. Anal. calcd for $C_{18}H_{29}NO_2S_2$: C, 60.80; H, 8.22; N, 3.94; found: C, 61.13; H, 8.26; N, 3.86.

4.3. General procedure for the synthesis of *N*-substituted sulfenamides (5)

An amine (0.6 mmol) was added to a solution of **3** (0.5 mmol) in 6 mL of THF. The mixture was stirred at reflux for 7 h, and then the solvent was removed under reduced pressure. The crude product was chromatographed on a silica gel column with dichloromethane as an eluent.

4.3.1. *N*-Butyl-(2-methoxycarbonyl)benzenesulfenamide (5c). Colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (dd, J=7.6, 1.4 Hz, 1H), 7.83 (dd, J=8.3, 1.2 Hz, 1H), 7.52 (ddd, J=8.3, 7.2, 1.4 Hz, 1H), 7.14 (ddd, J=7.6, 7.2, 1.2 Hz, 1H), 3.91 (s, 3H), 2.97 (q, J=7.1 Hz, 2H), 2.59 (br s, 1H), 1.58 (quint, J=7.4 Hz, 2H), 1.39 (sext, J=7.4 Hz, 2H), 0.92 (t, J=7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 149.5, 132.4, 131.3, 123.8, 123.5, 122.5, 52.1, 51.6, 32.8, 20.1, 13.9; IR (neat): 3339, 2955, 2928, 2861, 1709, 1460, 1435, 1271, 1250, 745 cm^{-1}; HRMS: calcd for $C_{12}H_{17}NO_2S$: 239.0980; found: 239.0973.

4.3.2. *N*-Benzyl-(4-methoxycarbonyl)benzenesulfenamide (5g). Colorless crystal with mp 62–63.5°C (from hexane). ^1H NMR (500 MHz, $CDCl_3$): δ 7.98 (dt, J=8.6, 1.8 Hz, 2H), 7.37–7.29 (m, 7H), 4.12 (d, J=5.8 Hz, 2H), 3.90 (s, 3H), 3.11 (t, J=5.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 149.0, 139.0, 130.0, 128.6, 128.2, 127.8, 126.7, 121.9, 56.4, 52.0; IR (neat): 3329, 3029, 2949, 2851, 1717, 1593, 1435, 1277, 1109, 760 cm^{-1}; HRMS: calcd for $C_{15}H_{15}NO_2S$: 273.0823; found: 273.0832. Anal. calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12; found: C, 65.82; H, 5.39; N, 5.03.

4.4. Determination of pK_a values

The compound (**3**, 0.3 mmol) was dissolved in 50% aqueous methanol, and the solution was titrated with 0.06 M sodium hydroxide. The pH of the solution was measured after each addition (0.1 mL) of titrant (all measurements were made at room temperature). The pK_a values were calculated from the pH readings.

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