A Facile Synthesis of *N,N*-Dialkylpropanesulfenamides and -benzenesulfenamides

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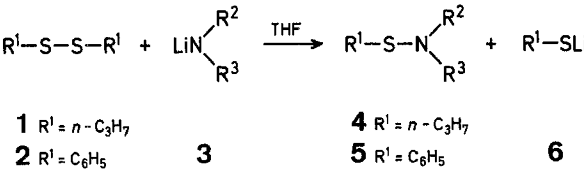
Several methods for the preparation of two classes of sulfenamides, *N,N*-dialkylalkanesulfenamides and -arenesulfenamides, have been reported. These compounds were prepared by the condensation of secondary aliphatic amines with sulfenyl chlorides[1,2], sulfenyl thiocyanates[3], or esters of thiosulfonic acids[4], and by the reaction of chloroamines with metal thiolates[5]. The oxidative condensation of the amines with metal thiolates is also known[6]. More recently, it was reported[7] that the reaction of some disulfides with amines in the presence of silver acetate or silver nitrate is capable of producing sulfenamides. Also, a new method involving the reaction of thiophthalimides with amines was reported[8]. Moreover, the electrolytic cross-coupling reaction of bis[2-benzothiazolyl] disulfide with amines has been published[9]. Thus, almost all the procedures mentioned can be used for the preparation of the title compounds. However, it appears that, except one or two procedures, all these procedures have one or more drawbacks such as the necessity to use unstable reagents, the expensiveness, or the technical difficulties in the preparation of the starting reagents.

We have found that symmetrical disulfides such as dipropyl (**1**) and diphenyl disulfide (**2**) react rapidly and cleanly with lithium dialkylamides (**3**) in tetrahydrofuran to produce the corresponding *N,N*-dialkylpropanesulfenamides (**4**) and -benzenesulfenamides (**5**), respectively. The formation of *N*-butylpropanesulfenamide (**4e**) or -benzenesulfenamide (**5e**) was also ascertained when **1** or **2** was reacted with lithium butylamide (**3**, $R^2 = n\text{-}C_4H_9$, $R^3 = H$) in tetrahydrofuran under similar conditions.

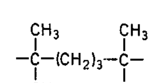


Initial attack of **3** at one of the S-atoms of **1** or **2** and simultaneous S—S bond fission is almost certain from the analogy to the mechanism proposed for the reaction between some disulfides and numerous nucleophiles[10]. The advantages of the present method are that the starting materials are relatively inexpensive and easily available, and the yields of the products are satisfactory.

_N,N_-Dialkylpropanesulfenamides (4) and -benzenesulfenamides (5); General Procedure:

A 1.56 molar solution (6.4 ml, 10.0 mmol) of butyllithium in hexane is added dropwise to a stirred solution of a secondary aliphatic amine (10.5 mmol) in tetrahydrofuran (21 ml) at −78 °C under nitrogen. The mixture is stirred for 10 min at the same temperature and further at −15 °C for 10 min. Then, a solution of **1** or **2** (9.0 mmol) in tetrahydrofuran (8 ml) is added to the mixture at −78 °C. Upon completion of the addition, the temperature is allowed to rise to −15 °C and stirring is continued for 1 h at that temperature. After removal of the cooling bath, the mixture is allowed to stand at room temperature for 30 min and is then poured into ice/water (10 ml) and ether (150 ml) with stirring. The organic layer is separated, washed with water (70

Table. *N,N*-Dialkylpropanesulfenamides (**4**) and -benzenesulfenamides (**5**) from Disulfides (**1** or **2**) and Lithium Dialkylamide (**3**)

Product	R^1	R^2	R^3	Yield[a] [%]	b.p. [°C]/ torr	Molecular Formula[b] or Lit. b.p. [°C]/torr	^{1}H-N.M.R. (CCl_4/TMS) δ [ppm]
4a	n-C_3H_7	C_2H_5	C_2H_5	69	59°/19	$C_7H_{17}NS$ (147.3)	0.98 (t, 3H, $J=7$ Hz); 1.09 (t, 6H, $J=7$ Hz); 1.0–2.0 (m, 2H); 2.43 (t, 2H, $J=7$ Hz); 2.73 (q, 4H, $J=7$ Hz)
4b	n-C_3H_7	n-C_3H_7	n-C_3H_7	75	124°/75	74°/5[3]	0.85 (t, 6H, $J=6$ Hz); 0.95 (t, 3H, $J=6$ Hz); 1.2–1.8 (m, 6H); 2.45 (t, 2H, $J=6$ Hz); 2.68 (t, 4H, $J=6$ Hz)
4c	n-C_3H_7	i-C_3H_7	i-C_3H_7	88	42°/3.5	$C_9H_{21}NS$ (175.3)	0.8–1.2 (m, 3H); 1.07 (d, 12H, $J=6$ Hz); 1.2–1.8 (m, 2H); 2.43 (t, 2H, $J=6$ Hz); 2.8–3.5 (m, 2H)
4d	n-C_3H_7	i-C_4H_9	i-C_4H_9	96	105°/17.5	$C_{11}H_{25}NS$ (203.4)	0.87 (d, 12H, $J=6$ Hz); 0.98 (t, 3H, $J=6$ Hz); 1.2–2.4 (m, 4H); 2.50 (d, 4H, $J=6$ Hz); 2.51 (t, 2H, $J=6$ Hz)
4e	n-C_3H_7	n-C_4H_9	H	92	83°/17	$C_7H_{17}NS$ (147.3)	0.7–1.2 (m, 6H); 1.2–1.9 (m, 6H); 2.43 (t, 2H, $J=7$ Hz); 2.5–3.0 (m, 3H)
5a	C_6H_5	C_2H_5	C_2H_5	79	123°/19.5	90°/3.5[2]	1.13 (t, 6H, $J=6$ Hz); 2.89 (q, 4H, $J=6$ Hz); 6.8–7.3 (m, 5H)
5b	C_6H_5	n-C_3H_7	n-C_3H_7	88	92°/2.5	68–70°/0.02[11]	0.85 (t, 6H, $J=7$ Hz); 1.2–1.9 (m, 4H); 2.82 (t, 4H, $J=7$ Hz); 6.8–7.2 (m, 5H)
5c	C_6H_5	i-C_3H_7	i-C_3H_7	62	88°/3.2	71.5–73°/0.35[7]	1.11 (d, 12H, $J=6$ Hz); 3.0–3.7 (m, 2H); 6.8–7.3 (m, 5H)
5d	C_6H_5	i-C_4H_9	i-C_4H_9	93	164°/17	$C_{14}H_{23}NS$ (237.4)	0.88 (d, 12H, $J=6$ Hz); 1.6–2.4 (m, 2H); 2.61 (d, 4H, $J=6$ Hz); 6.8–7.3 (m, 5H)
5e	C_6H_5	n-C_4H_9	H	92	149°/18	87°/0.02[11]	0.7–1.1 (m, 3H); 1.1–1.7 (m, 4H); 2.5–3.1 (m, 3H); 6.9–7.4 (m, 5H)
5f	C_6H_5	 $-\overset{CH_3}{\underset{CH_3}{C}}-(CH_2)_3-\overset{CH_3}{\underset{CH_3}{C}}-$		80	92°/3.3	$C_{15}H_{23}NS$ (249.4)	1.1–1.4 (m, 14H); 1.5–1.8 (m, 4H); 6.7–7.5 (m, 5H)

[a] Yield of distilled product, based on **1** or **2**.

[b] The microanalyses were in satisfactory agreement with the calculated values (C ±0.29, H ±0.29, N ±0.30).

ml), then with saturated aqueous sodium hydroxide solution (70×3 ml), and dried with magnesium sulfate. Evaporation of the solvents gives a residue, which is distilled under reduced pressure to afford pure **4** or **5** (Table).

Compounds **4e** and **5e** are prepared similarly except that the primary *n*-butylamine is used in place of the secondary aliphatic amine.

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