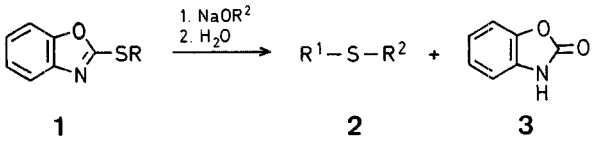
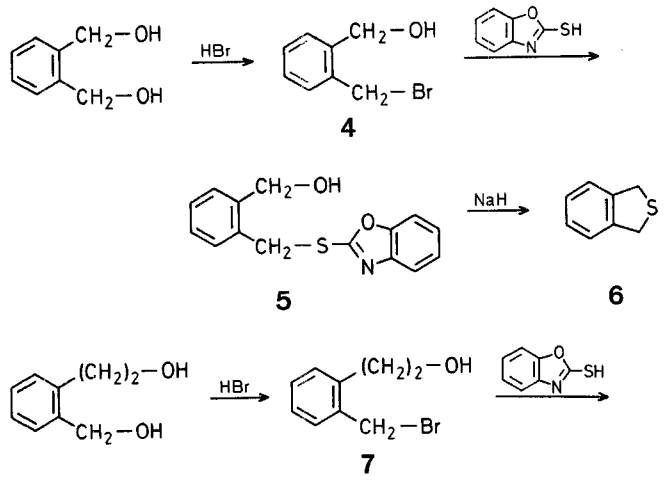
report a convenient preparation of sulfides **2** from the corresponding **1** and sodium alkoxides. This method does not use ill-smelling alkanethiols and is suitable for the preparation of various symmetrical and unsymmetrical sulfides. Furthermore, the method is efficiently applicable to the preparation of cyclic sulfides such as 1,3-dihydrobenzo[*c*]thiophene **(6)** and thioisochroman **(9)**.



1 **2** **3**

Some symmetrical and unsymmetrical sulfides **2b–e** were prepared by the reaction of the corresponding **1** with sodium alkoxide under the reaction conditions shown in the Table. The boiling points of the resulting sulfides were identical with those of the authentic samples described in the literature and their ^{1}H-N.M.R. spectral data are listed in the Table.

Cyclic sulfides **6** and **9** were prepared according to the following Scheme: Compound **6** was prepared in 64% yield from 2-[2-(hydroxymethyl)-benzylthio]-1,3-benzoxazole **(5)**, prepared by stirring 1,3-benzoxazoline-2-thione with 2-(bromomethyl)-benzyl alcohol **(4)** and potassium carbonate in dimethylformamide at room temperature. Similarly, **9** was obtained in 53% yield by the reaction of 2-[2-(hydroxylethyl)-benzylthio]-1,3-benzoxazole **(8)**, prepared from 1,3-benzoxazoline-2-thione and 2-(bromomethyl)-phenethyl alcohol **(7)**. The structure of **8** was confirmed by conversion to a crystalline derivative, 2-[(1,3-benzoxazolyl-2-thio)-methyl]-phenethyl-*N*-(1-naphthyl)-carbamate **(10)**, because **8** is a viscous oil.



A Convenient Method for the Preparation of Sulfides

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Many methods for synthesis of sulfides have appeared in the literature[1-5], most of them use ill-smelling alkanethiols.

In the course of a study on the reaction of 2-alkylthio-1,3-benzoxazoles **(1)** with nucleophilic reagents, we have found that heating of a solution of 2-benzylthio-1,3-benzoxazole **(1a)** and sodium benzyloxide in dimethylformamide at 80 °C gave dibenzyl sulfide **(2a)** and 1,3-benzoxazolin-2-one **(3)** in 56 and 35% yields, respectively. In an extension of this work, we now

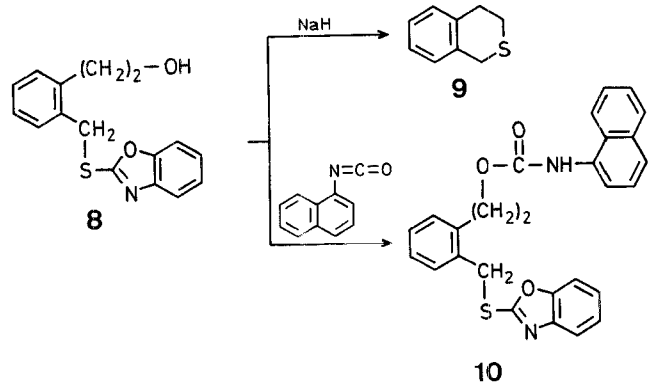

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Table. Sulfides **2a–e** prepared

Product No.	R^1	R^2	Reaction Conditions temperature/time	Yield [%]	m.p. [°C] or b.p. [°C]/torr found	reported	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
2a	$C_6H_5CH_2$	$C_6H_5CH_2$	80 °C/2.5 h	56	47°	49°[1]	3.54 (s, 4H)
2b	CH_3	$C_6H_5CH_2$	80 °C/1 h	72	193–197°/760	195–198°/760[2]	1.98 (t, 3H, J=7 Hz); 3.67 (s, 2H)
2c	C_2H_5	$C_6H_5CH_2CH_2$	80 °C/4 h	59	93–94°/5	92–94°/3[3]	1.28 (t, 3H, J=7 Hz); 2.57 (q, 2H, J=7 Hz); 2.83 (br. s, 4H)
2d	i-C_3H_7	$C_6H_5CH_2$	100 °C/2 h	64	95–98°/10	99–104°/14[4]	1.21 (d, 6H, J=7 Hz), 2.8 (m, 1H); 3.71 (s, 2H)
2e	t-C_4H_9	$C_6H_5CH_2$	100 °C/4 h	53	110–113°/10	115–116°/15[5]	1.30 (s, 9H); 3.73 (s, 2H)

Benzyl Isopropyl Sulfide (2d) from 2-Isopropylthio-1,3-benzoxazole (1d); Typical Procedure:

Sodium hydride (0.6 g, 12.5 mmol, 50% in oil) is added to a solution of benzyl alcohol (1.2 g, 11.1 mmol) in dimethylformamide (100 ml), then 2-isopropylthio-1,3-benzoxazole (**1d**; 2 g, 10.4 mmol) is added. The mixture is well stirred at room temperature for 30 min, heated at 100 °C for 2 h, poured into water (500 ml), and extracted with ether (3 × 200 ml). The ether layer is washed with 10% sodium hydroxide solution (200 ml) and saturated sodium chloride solution (200 ml), dried with magnesium sulfate, and concentrated. The residue is purified by column chromatography on silica gel eluting with cyclohexane to give **2d**; yield: 1.1 g (64%).

2-(Bromomethyl)-benzyl Alcohol (4):

1,2-Bis[hydroxymethyl]benzene (11.5 g, 83.3 mmol) is added to 48% hydrobromic acid (50 ml) and the mixture is stirred at room temperature for 2 h. The resulting precipitate is collected by suction and recrystallized from a mixture of benzene and cyclohexane to give **4**; yield: 8.8 g (53%); m.p. 66–69 °C.

C_8H_9BrO	calc.	C 47.79	H 4.51
(201.1)	found	47.62	4.23

^{1}H-N.M.R. ($CDCl_3$): δ=2.37 (broad, 1H); 4.56 (s, 2H); 4.72 (s, 2H); 7.35 ppm (broad, 4H).

I.R. (Nujol): ν=3160 cm^{-1}.

M.S.: m/e=202 (M^++2), 200 (M^+).

2-[2-(Hydroxymethyl)-phenylmethylthio]-1,3-benzoxazole (5):

A mixture of 1,3-benzoxazoline-2-thione (1.4 g, 9.3 mmol), anhydrous potassium carbonate (2 g, 14.5 mmol), and 2-(bromomethyl)-benzyl alcohol (**4**; 2 g, 9.95 mmol) in dimethylformamide (100 ml) is stirred at room temperature for 2 h, poured into water (500 ml), and extracted with ether (3 × 200 ml). The ether layer is washed with saturated sodium chloride solution (200 ml), dried with magnesium sulfate, and concentrated. The residue is recrystallized from a mixture of benzene and cyclohexane to give **5**; yield: 2.4 g (89%); m.p. 80–82 °C.

$C_{15}H_{13}NO_2S$	calc.	C 66.40	H 4.83	N 5.16
(271.3)	found	66.30	4.74	4.96

^{1}H-N.M.R. ($CDCl_3$): δ=4.08 (t, J=6 Hz, 1H); 4.63 (s, 2H); 4.80 (d, J=6 Hz, 2H); 7.12–7.67 ppm (m, 8H).

I.R. (Nujol): ν=3340 cm^{-1}.

M.S.: m/e=271 (M^+).

1,3-Dihydrobenzo[c]thiophene[6] (6):

Sodium hydride (1.0 g, 20.8 mmol, 50% in oil) is added to a solution of **5** (2 g, 7.4 mmol) in dimethylformamide (200 ml), the solution is heated at 80 °C for 4 h, poured into ice/water (500 ml), and extracted with ether (3 × 200 ml). The ether layer is washed with saturated sodium chloride solution (200 ml), dried with magnesium sulfate, and concentrated. The residue is purified by distillation to give **6**; yield: 0.64 g (64%); b.p. 94 °C/7 torr; Lit.[6], b.p. 108 °C/14 torr.

C_8H_8S	calc.	C 70.57	H 5.92
(136.2)	found	70.27	6.01

^{1}H-N.M.R. ($CDCl_3$): δ=4.23 (s, 4H); 7.21 ppm (s, 4H).

2-[2-(2-Hydroxyethyl)-phenylmethylthio]-1,3-benzoxazole (8):

2-(2-Hydroxyethyl)-benzyl alcohol (3 g, 19.7 mmol) is added to 48% hydrobromic acid (50 ml). The mixture is stirred at room temperature for 2 h, poured into ice/water (500 ml) and extracted with ether (3 × 200 ml). The ether layer is washed with saturated sodium chloride solution (200 ml), dried with magnesium sulfate, and concentrated. A solution of the residue in dimethylformamide (100 ml) is added to a mixture of anhydrous potassium carbonate (2 g, 14.5 mmol) and 1,3-benzoxazoline-2-thione (1.5 g, 9.9 mmol). The mixture is stirred at room temperature for 2 h, poured into water (500 ml), and extracted with ether (3 × 200 ml). The ether layer is washed with saturated sodium chloride solution (200 ml), dried with magnesium sulfate, and concentrated. The residue is purified by column chromatography on silica gel eluting with benzene/cyclohexane (1:1) to give **8** as a viscous oil; yield: 2.5 g (44%).

Compound **8** is converted to the crystalline derivative **10** by stirring a mixture of equimolar amounts of **8** and α-naphthyl isocyanate in dry benzene at room temperature for 5 days; m.p. 75–77 °C.

$C_{27}H_{22}N_2O_3S$	calc.	C 71.35	H 4.88	N 6.16
(454.5)	found	71.26	4.72	5.85

^{1}H-N.M.R. ($CDCl_3$): δ=3.20 (t, J=7 Hz, 2H); 4.51 (t, J=7 Hz, 2H); 4.70 (s, 2H); 7.20–8.03 ppm (m, 15H).

I.R. (Nujol): ν=3280, 1685 cm^{-1}.

Thioisochroman[7] (9):

Sodium hydride (1.0 g, 20.8 mmol, 50% in oil) is added to a solution of **8** (1.3 g, 4.6 mmol) in dimethylformamide (200 ml) and the solution is heated at 80 °C for 4 h. The mixture is poured into ice/water (500 ml) and extracted with ether (3 × 200 ml). The ether layer is washed with saturated sodium chloride solution (200 ml), dried with magnesium sulfate, and concentrated. The residue is purified by distillation to give **9**; yield: 0.36 g (53%); b.p. 105–110 °C/5 torr; Lit.[7], b.p. 128–130 °C/13 torr.

$C_9H_{10}S$	calc.	C 71.98	H 6.71
(150.2)	found	71.73	6.59

^{1}H-N.M.R. ($CDCl_3$): δ=2.67–3.22 (m, 4H); 3.73 (s, 2H); 7.13 ppm (s, 4H).

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