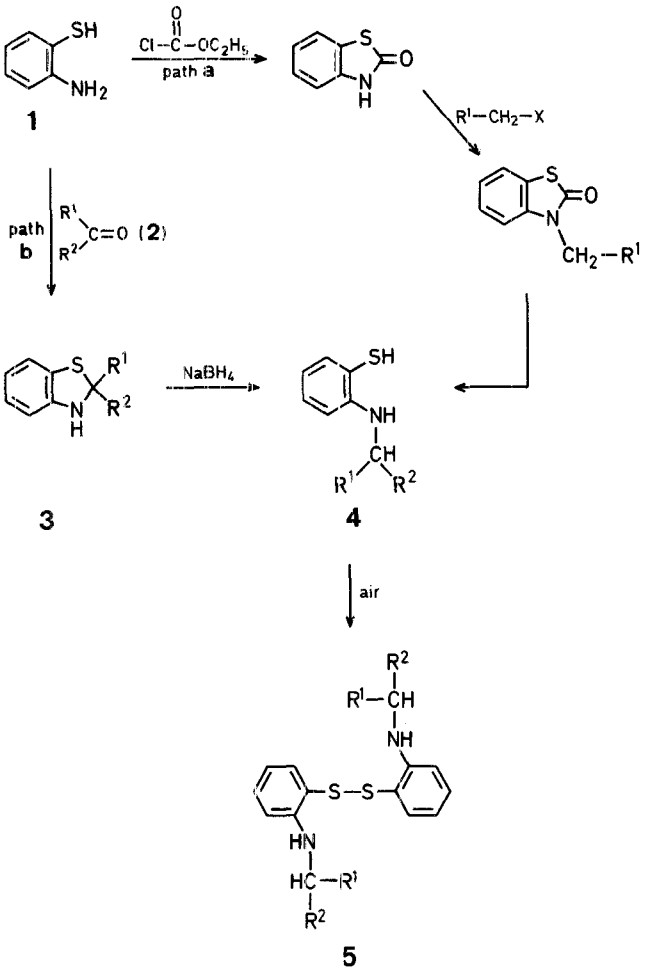
N-(*sec*-alkyl) compounds **4** in good yields. However, compounds **4** can only be isolated if work-up is performed under nitrogen. Work-up of the reaction mixture without exclusion of air generally results in oxidation of the thiols **4** to the corresponding disulfides **5** which can be isolated in likewise good yields. Disulfides **5b, d, e, i, j** were also obtained from 2-aminobenzenethiol (**1**) by a one-pot procedure.



2-Alkylaminobenzenethiols by Ring Cleavage of 2,3-Dihydro-1,3-benzothiazoles with Sodium Borohydride

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Bifunctional nucleophiles such as the title compounds are useful building blocks for the synthesis of some *N*-alkylated benzo-fused *S,N*-heterocycles. To our knowledge, a number of *N*-(*prim*-alkyl) derivatives **4** ($R^2 = H$) have been prepared according to Path **a** of the Scheme[1]. Only one 2-*sec*-alkylaminobenzenethiol [**4**, $R^1-R^2 = CH_2-CH_2-N(CH_3)-CH_2-CH_2$] has been prepared[2] by ring cleavage of the corresponding 2,3-dihydro-1,3-benzothiazole with lithium alanate. We now report that 2,3-dihydro-1,3-benzothiazoles (**3**), both mono or disubstituted at C-2, react with sodium borohydride (at least 5 mol equiv) in methanol under nitrogen to afford the corresponding *N*-(*prim*-alkyl) or

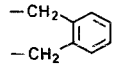
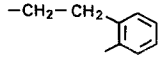
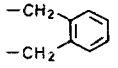
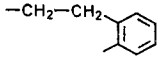
The structures of the new compounds were established by microanalysis and spectral data (I.R., ^{1}H-N.M.R., and M.S.). In particular, in the ^{1}H-N.M.R. spectra of compounds **4** and **5** the NH—CH protons are coupled, the coupling disappearing on addition of deuterium oxide. The mass spectra of compounds **5** show a strong peak at $M^+/2$; in most of the cases, only a very small molecular peak is present.

The results obtained indicate that the present method appears to be generally and successfully applicable to the preparation of 2-(*prim*-alkylamino)- and 2-(*sec*-alkylamino)-benzenethiols (**4**). In some cases, it can be carried out as a one-flask procedure from thiol **1**. Performence is easy and only readily available starting materials are required.

2-Ethoxycarbonylmethyl-2,3-dihydro-1,3-benzothiazole (**3h**) and the 2,3-dihydro-1,3-benzothiazoles **3c–g, j** are prepared by the reported[3–8] method.

2,3-Dihydro-1,3-benzothiazole〈2-spiro-2′〉indane (3a):
2-Indanone (0.47 g, 3.6 mmol) is added to a solution of 2-aminobenzenethiol (0.50 g, 4 mmol) in methanol under nitrogen. The mixture

Table. 2-Alkylaminobenzenethiols **4** and Disulfides **5** prepared

Product No.	R^1	R^2	Yield[a] [%]	m.p. [°C] (solvent)	Molecular Formula[b]	M.S. m/e (M^+)	I.R. (Nujol or neat) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3/D_2O$/TMS_{int})[c] δ [ppm]
4a			92	oil	$C_{15}H_{15}NS$ (241.3)	241	3400, 2520	2.87, 3.40 (dd, 4H); 4.33 (m, 1H); 6.5–6.8 (m, 2H); 7.1–7.4 (m, 6H)
4b	n-C_3H_7	H	90[d]	oil	$C_{10}H_{15}NS$ (181.2)	181	3370, 2520	0.93 (t, 3H); 1.1–1.9 (m, 4H); 3.10 (t, 2H); 6.4–6.7 (m, 2H); 7.0–7.4 (m, 2H)
4c		H	95	oil	$C_{13}H_{12}ClNS$ (249.7)	249	3400, 2520	4.36 (s, 2H); 6.3–6.6 (m, 2H); 6.8–7.4 (m, 6H)
4d	$-(CH_2)_4-$		86	oil	$C_{11}H_{15}NS$ (193.25)	193	3390, 2520	1.1–2.3 (m, 8H); 3.73 (m, 1H); 6.4–6.7 (m, 2H); 6.9–7.4 (m, 2H)
4e	$-(CH_2)_6-$		90	oil	$C_{13}H_{19}NS$ (221.3)	221	3390, 2520	1.2–2.4 (m, 12H); 3.48 (bs, 1H); 6.3–6.7 (m, 2H); 7.0–7.5 (m, 2H)
4f	C_2H_5	C_2H_5	81	oil	$C_{11}H_{17}NS$ (195.3)	195	3390, 2520	0.90 (t, 6H); 1.4–1.9 (m, 4H); 3.26 (m, 1H); 6.4–6.7 (m, 2H); 6.9–7.5 (m, 2H)
4i			96	oil	$C_{15}H_{15}NS$ (241.3)	241	3390, 2530	1.6–2.1 (m, 1H); 2.3–3.2 (m, 3H); 4.93 (m, 1H); 6.4–6.8 (m, 2H); 7.0–7.4 (m, 6H)
5a			83	88–90° (ethanol)	$C_{30}H_{28}N_2S_2$ (480.6)	480	3400	2.63, 3.30 (dd, 8H); 4.20 (m, 2H); 6.3–6.7 (m, 4H); 7.0–7.3 (m, 12H)
5b	n-C_3H_7	H	61[d]	156–157°[e]	$C_{20}H_{28}N_2S_2$ (360.5)	360	3400	0.90 (t, 6H); 1.1–1.7 (m, 8H); 3.00 (t, 4H); 6.3–6.6 (m, 4H); 7.0–7.3 (m, 4H)
5c		H	80	133° (ethanol)	$C_{26}H_{22}Cl_2N_2S_2$ (497.4)	248 (M/2)	3400	4.32 (s, 4H); 6.3–6.6 (m, 4H); 7.0–7.5 (m, 12H)
5d	$-(CH_2)_4-$		72[d]	127–129°[e]	$C_{22}H_{28}N_2S_2$ (384.5)	384	3390	1.0–2.2 (m, 16H); 3.66 (m, 2H); 6.2–6.7 (m, 4H); 7.0–7.3 (m, 4H)
5e	$-(CH_2)_6-$		72[d]	113–115°[e]	$C_{26}H_{36}N_2S_2$ (440.6)	440	3390	1.0–2.3 (m, 24H); 3.43 (bs, 2H); 6.3–6.6 (m, 4H); 7.0–7.4 (m, 4H)
5f	C_2H_5	C_2H_5	56	162–170°[e]	$C_{22}H_{32}N_2S_2$ (388.5)	388	3390	0.88 (t, 12H); 1.2–1.7 (m, 8H); 3.20 (m, 2H); 6.2–6.6 (m, 4H); 7.0–7.2 (m, 4H)
5g	CH_3		69	115–117°[e]	$C_{30}H_{32}N_2S_2$ (484.6)	484	3390	1.05 (d, 6H); 2.53–2.86 (2dd, 4H); 3.70 (m, 2H); 6.3–6.7 (m, 4H); 7.0–7.4 (m, 14H)
5h[f]	$-CH_2-CH_2-OH$	H	20	oil	$C_{18}H_{24}N_2O_2S_2$ (364.4)	364	3390	1.68 (m, 4H); 3.06 (t, 4H); 3.60 (t, 4H); 6.3–6.6 (m, 4H); 7.0–7.4 (m, 4H)
5i			78[d]	oil	$C_{30}H_{28}N_2S_2$ (480.6)	240 (M/2)	3380	1.4–1.8 (m, 2H); 2.3–3.0 (m, 6H); 4.7–5.0 (m, 2H); 6.3–6.8 (m, 4H); 7.0–7.4 (m, 12H)
5j		H	75[d]	147–148°[10,e]	$C_{26}H_{24}N_2S_2$ (428.5)	214 (M/2)	3400	4.23 (s, 4H); 6.3–6.6 (m, 4H); 7.0–7.4 (m, 14H)

[a] Yield of isolated crude products **4** and of pure isolated products **5**. The purity was checked by T.L.C. analysis (silica gel, light petroleum ethyl acetate 95/5 as eluent).

[b] The microanalyses showed the following maximum deviations from the calculated values: C ±0.29, H ±0.39, N ±0.30.

[c] ^{1}H-N.M.R. spectra recorded in $CDCl_3$ as solvent showed broad peaks for SH and NH at δ = 4.5–5.3 ppm.

[d] Yield based on **1**.

[e] m.p. of hydrochloride.

[f] The starting material was 2-ethoxycarbonylmethyl-2,3-dihydro-1,3-benzothiazole (**3h**).

is refluxed for 20 min, and the solvent then evaporated under reduced pressure. The residue is the essentially pure compound **3a** which can be recrystallized from 2-propanol/petroleum ether; yield: 0.81 g (95%); m.p. 125–127°C.

$C_{15}H_{13}NS$	calc.	C 75.30	H 5.47	N 5.85
(239.3)	found	75.34	5.44	5.97

I.R.(Nujol): ν = 3340 cm^{-1} (N—H).

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): δ = 3.40 (s, 5H); 6.4–7.3 ppm (m, 8H).

2-Propyl-2,3-dihydro-1,3-benzothiazole (3b):
A mixture of 2-aminobenzenethiol (0.50 g, 4 mmol) and butanal (0.28 g, 3.8 mmol) is stirred under nitrogen at room temperature for 30 min. Then, methanol (20 ml) is added and stirring is continued for 30 min. The solvent is evaporated to give product **3b** as a pale yellow oil; yield: 0.69 g (98%).

$C_{10}H_{13}NS$	calc.	C 67.02	H 7.31	N 7.82
(179.2)	found	66.88	7.24	7.88

I.R. (neat): ν = 3360 cm^{-1} (N—H).

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): δ = 0.88 (t, 3H); 1.1–1.9 (m, 4H); 3.97 (s, 1H, NH); 5.17 (t, 1H); 6.5–7.1 ppm (m, 4H).

2,3-Dihydro-1,3-benzothiazole〈2-spiro-1′〉indane (3i):
A solution of 2-aminobenzenethiol (1.00 g, 8 mmol), 1-indanone (1.06 g, 8.1 mmol), and 2 catalytic amount of *p*-toluenesulfonic acid in toluene (50 ml) is refluxed for 3 h under nitrogen, while the water formed is continuously separated. The solvent is then evaporated to give the essentially pure product **3i** as a thick oil; yield: 1.87 g (98%).

$C_{15}H_{13}NS$	calc.	C 75.27	H 5.47	N 5.85
(239.3)	found	75.51	5.64	5.83

I.R. (neat): ν = 3340 cm^{-1} (N—H).

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): δ = 2.1–3.0 (m, 4H); 4.10 (s, 1H); 6.4–7.6 ppm (m, 8H).

2-Alkylaminobenzenethiols (4a–f, i); General Procedure:
All operations including work-up are carried out under nitrogen. To a stirred solution of benzothiazoline **3a–f, i** (4 mmol) in methanol (30 ml), sodium borohydride (0.74 g, 20 mmol) is added portionwise over 15 min. Additional small amounts of sodium borohydride are added, depending on the reactivity of the benzothiazoline while monitoring the progress of the reaction by T.L.C. (silica gel, petroleum ether/ethyl acetate 95/5 as eluent). Removal of the solvent is followed by dilution with icewater (50 ml), acidification with acetic acid, and extraction with ether (3 × 50 ml). The combined extracts are washed with water (3 × 30 ml), dried with sodium sulfate, and concentrated. The residual pale yellow oil is the essentially pure product **4** as estimated by ^{1}H-N.M.R. spectrometry.

Bis[2-alkylaminophenyl] Disulfides (*N,N′*-Dialkyl-2,2′-dithiodianilines (5):

Compounds **5a, c, f, g, h:** The procedure for the preparation of compounds **4** is followed up to the point were the combined ether extracts are dried with sodium sulfate. The ether solution is stirred with exposure to air overnight and then concentrated. The residual yellow oil is purified by chromatography (silica gel, petroleum ether/ethyl acetate 95/5 as eluent).

Compounds **5b, d, e, i, j** (One-Flask Procedure): The 2-aminobenzenethiol **1** (4 mmol) and the carbonyl compound **2** (4 mmol) are allowed to react as described in the general procedure for the preparation of compounds **4**. The solvent is then evaporated and methanol (30 ml) is added to the residue. This methanolic solution is treated with sodium borohydride under nitrogen according to the general procedure.

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