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Studies on Organophosphorus Compounds. XV.* Synthesis of 2-Arylbenzothiazoles and 2-(α-Pyridyl)naphthothiazoles by Sulfur Oxidation in Hexamethylphosphoric Triamide (HMPA). ^{13}C NMR Studies

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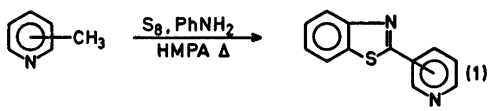
Heating primary aromatic amines in HMPA with elemental sulfur and α- or γ-picolines, benzylic esters, benzyl alcohol, acetophenone, and thiobenzanilide, respectively, produced 2-substituted thiazoles fused with aromatic rings. The following products have been synthesized: 2-(α-Pyridyl)benzothiazole, 2-(γ-pyridyl)benzothiazole, 2-(α-pyridyl)naphtho[1,2-*d*]thiazole, 2-(α-pyridyl)naphtho[2,1-*d*]thiazole, 2-benzylbenzothiazole, 6-methyl-2-phenylbenzothiazole, 2-phenylbenzothiazole, 4-methyl-2-phenylbenzothiazole, 2-(*p*-methoxyphenyl)benzothiazole. 2-Phenylbenzothiazole was obtained by heating thiobenzanilide with *o*-mercaptoaniline in HMPA. ^{13}C NMR spectra of benzothiazole, 2-phenylbenzothiazole, 2-(α-pyridyl)-benzothiazole, 2-(α-pyridyl)naphtho[1,2-*d*]thiazole, and 2-(α-pyridyl)naphtho[2,1-*d*]thiazole are reported. Proton-coupled ^{13}C NMR spectra and selective proton decoupling were used for signal assignments.

Recently much work has been done to find new ways of synthesizing 2-arylbenzothiazoles, as some of these compounds are found to be very effective antiinflammatory, analgesic, and antipyretic agents.[1–3] In an earlier report [4] we have shown that 2-phenylbenzothiazole was smoothly produced when benzyl alcohol, benzaldehyde, benzyl benzoate, *N*-benzylideneaniline, or thiobenzanilide were oxidized with elemental sulfur in the presence of aniline and hexamethylphosphoric triamide (HMPA) as co-solvent. The role of HMPA in these reactions has not been clarified but is still under investigation. Also in other reactions [4–6] elemental sulfur in HMPA is a very convenient thiation agent at elevated temperatures. A few reports have been given that 2-arylbenzothiazoles were produced from anilines and suitable aromatic compounds [7–9] but the yields reported were poor and the reaction conditions needed were rather severe. Compared to these results our synthesis of 2-phenylbenzothiazole [4] seemed so advantageous that a further investigation was started.

RESULTS AND DISCUSSION

As shown earlier α- and γ-picolines are smoothly oxidized by elemental sulfur in HMPA to the corresponding *N*,*N*-dimethylthiopicolinamides.[5] This prompted us to investigate reactions of picolines with elemental sulfur and primary aromatic amines in HMPA. Emmert [7,8] has shown that reaction of α- and γ-picolines with aniline and elemental sulfur as the main products produce the corresponding thioanilides. These reactions were performed under reflux for about 48 h. As by-products (< 25 %) the corresponding 2-pyridylbenzothiazoles were formed. In the presence of HMPA the reactions proceeded much more rapidly at lower temperatures to give high yields of the benzothiazoles, *1*, (82 and 62 % of the α- and γ-isomer, respectively).

* Part XIV: Meyer, H. J., Goldman, J., Pedersen, E. B. and Lawesson, S.-O. *Bull. Soc. Chim. Belg. 84* (1975) 735.



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In the reaction of γ-picoline no *N*-phenylthioisonicotinamide could be isolated while the reaction of α-picoline produced 5 % yield of *N*-phenyl-α-thiopicolinamide.

α-Picoline was also reacted with α- and β-naphthylamine in the presence of sulfur and with HMPA as co-solvent. In these reactions naphthothiazoles were the only products isolated and they were formed in very high yields under rather mild reaction conditions compared to similar reactions performed by Emmert *et al.*[7,8] Thus reaction of α-naphthylamine produced 2-(α-pyridyl)naphtho[1,2-*d*]thiazole, *2*, in 86 % yield.

In the ^{1}H NMR spectrum of *2* a significant steric interaction is observed in the *peri*-hydrogen H-8 which appears as a multiplet at $\delta_8 \sim 9.0$. Further the assignment of structure *2* has been confirmed by ^{13}C NMR spectroscopy.

β-Naphthyl amine similarly produced 2-(α-pyridyl)naphtho[2,1-*d*]thiazole, *3*, in 83 % yield. Structure *3* was assigned by ^{13}C NMR spectroscopy.

Structural assignments by ^{13}C NMR. ^{13}C NMR studies of benzothiazoles have only been reported for 2-methylbenzothiazole.[15] However, only the signals of the quaternary carbon atoms and of the CH_3-group were assigned. It was our hope to obtain a complete assignment of the ^{13}C NMR spectra of the naphthothiazoles *2* and *3* to confirm the proposed structures conclusively.

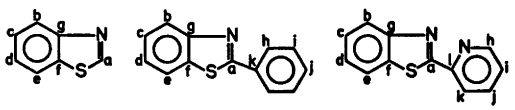
Benzothiazole, 4. ^{1}H NMR parameters for benzothiazole have been reported by Tobiason and Goldstein,[16] so an assignment of the signals from the proton bearing carbon atoms were straight-forward by selective decoupling of the protons. As the chemical shifts in the ^{1}H NMR spectrum are highly concentration dependent.[16] selective proton decoupling was performed at different concentrations. The chemical shifts are given in Table 1. The shift values for the quaternary carbon atoms δ 133.73(f) and δ 153.31(g) were in good agreement with the values given for 2-methylbenzothiazole [δ 135.5(f) and δ 153.3(g)].

2-Phenylbenzothiazole, 5. The signals of low intensity from the quaternary carbon atoms in the decoupled spectrum, δ(a), δ(f), δ(g), and δ(k) were easily assigned and δ(a), δ(f), and δ(g) (167.99, 135.12, 154.22) correspond nicely to the corresponding shifts in 2-methylbenzothiazole (166.4, 135.5, 153.3)[15] and 2-(α-pyridyl)benzothiazole, *6* (169.32, 136.15, 154.30). For δ(b), δ(c), δ(d), and δ(e) we found almost the same values as the corresponding signals in benzothiazole, *4*, and in 2-(α-pyridyl)-benzothiazole, *6* ($\Delta\delta < 0.45$). Further the corresponding selective proton decoupling frequencies appeared in the same order in the three compounds *4*, *5*, and *6*. The high intensity in the proton decoupled spectrum assigned two of the signals as δ(h) and δ(i) because of the equivalency of the two *ortho*-positions and the two *meta*-positions in the phenyl ring. It is known from other 2-phenyl substituted heterocycles that $\delta_{ortho} < \delta_{meta}$, and from ^{1}H NMR it has been shown that $\delta_{Hortho} < \delta_{Hmeta}$.[17] This gave the individual assignment of δ(h) and δ(i).

2-(α-Pyridyl)benzothiazole, 6. The signals from the benzothiazole part of the molecule were assigned according to the principles given above for 2-phenylbenzothiazole and the δ-values were in good agreement with the two compounds as seen in Table 1. Long-range ^{13}CH coupling constants for the pyridine and 2-bromopyridine have been determined by Hansen and Jakobsen.[18] From the undecoupled ^{13}C NMR spectrum of *6*, first order long-range ^{13}CH coupling constants were found which fitted very well with the reported constants. The chemical shifts of the α-carbon and of the γ-carbon in pyridine [18] have typical down-field values. The corresponding shifts for *6* were δ 149.57 [h; δ (pyridine) = 150.10] and δ 136.88 [j; δ (pyridine) = 135.85]. From the ^{1}H NMR spectrum of *6* δ_H(h), δ_H(i), and δ_H(k) were assigned. So selective proton decoupling easily afforded the corresponding carbon-13 shift values. The complete assignment is summarized in Table 1.

*2-(α-Pyridyl)naphtho[1,2-*d*]thiazole, 2.* ^{13}C NMR signals from the pyridine part of the molecule were easily assigned by first order long-range ^{13}CH coupling constants, selective proton decoupling, and typical down-field values for δ 149.51 (l) and 136.82 (h). The chemical shifts thus assigned differed very

Table 1. ^{13}C NMR chemical shifts of benzothiazoles.



4 *5* *6*

δ_X	*4*	*5*	*6*
a	153.75	167.99	169.32
b	123.63	123.27	123.58
c	126.10	126.28	126.21
d	125.47	125.16	125.59
e	121.81	121.60	121.96
f	133.73	135.12	136.15
g	153.31	154.22	154.30
h		128.99	149.57
i		127.57	125.15
j		130.91	136.88
k		133.68	120.71
l			151.40

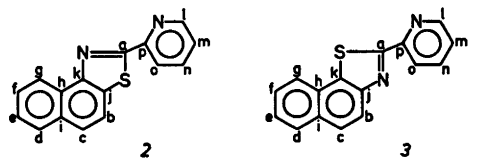
little from the corresponding shifts in the pyridine ring of *6*. The maximum difference was $\Delta\delta = 0.37$. Of the five remaining quaternary signals only assignment of δ(i) and δ(j) could cause some doubt. However, δ(i) was expected to be of higher intensity than δ(j) as C(i) is surrounded by two geminal protons while C(j) has only one geminal proton. Using additivity rules the assignment thus obtained fits very well with the calculated values for δ(i) and δ(j) as indicated in Table 3. Because of steric interaction the peri-proton Hg absorbs at very low field [δ_H 9.0(g)], so C(g) was easily assigned by selective proton decoupling. As C(b) is the only proton bearing carbon which has no $^3J_{CH}$ couplings it appears as the only sharp doublet in the undecoupled spectrum. As pointed out by Ernst [19] small $^3J_{CH}$– values are expected when the coupling nuclei are locked in a *cis*-conformation compared to *trans*-conformations. The assignment of C(c) is thus obtained. ($^3J_{C(c)H(d)}^{cis} \sim 4.5$ Hz). C(d) has both a $^3J_{CH}^{cis}$- and a $^3J_{CH}^{trans}$-coupling and from the long-range splittings of the remaining 3 signals C(d) is assigned leaving C(e) and C(f) unassigned. As expected δ(d), δ(e), and δ(f) deviate very little from the corresponding shifts in naphthalene. δ (naphthalene) 128.10(α) and δ 128.10(d); δ (naphthalene) 126.00(β) and $\{\delta(e), \delta(f)\} = \{126.11, 126.95\}$.

*2-(α-Pyridyl)naphtho[2, 1-*d*]thiazole, 3.* As this compound resembles compound *2*, the same principles of assignment could be used, only that the *peri*-proton Hg in *3* was not shifted as far down-field as in compound *2*. The assigned δ-values are summarized in Table 2.

With 2-(α-pyridyl)benzothiazole, *6*, as model compound the δ-values of the substituted ring of the naphthalene part of compounds *2* and *3* were calculated as follows: δ_x^{calc} (*2* or *3*) = $\delta_x(6) + \delta_x$ (naphthalene $- \delta_c$ (benzene). Deviations from the observed δ-values are defined as $\Delta\delta_x = \delta_x^{obs} - \delta_x^{calc}$ and summarized in Table 3. From these values it can be seen that additivity rules are fulfilled quite well except for δ(k). As underlined by Ernst [19] this discrepancy is probably of steric origin due to interaction with the *peri*-hydrogen H(g).

As presented in an earlier paper [4] reaction of benzyl benzoate with aniline and sulfur in HMPA produced 2-phenylbenzothiazole and benzanilide. As benzanilide was formed in rather high yields we suggested that the benzothiazole was formed mainly from the alcoholic part of the ester. To verify this suggestion *p*-methoxybenzyl benzoate, *7*, was reacted under

Table 2. ^{13}C NMR chemical shifts of naphthothiazoles.



2 *3*

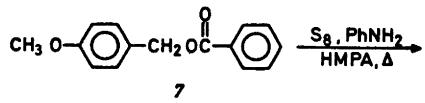
δ_X	*2*	*3*
a	168.10	168.20
b	119.29	121.84
c	126.37	127.41
d	128.10	128.88
e, f	126.11, 126.95	126.20, 127.01
g	123.78	125.29
h	128.96	128.26
i	132.02	131.20
j	133.18	152.40
k	150.61	133.73
l	149.51	149.57
m	124.78	124.89
n	136.82	136.91
o	120.52	120.38
p	151.75	151.44

Table 3. ^{13}C NMR chemical shift deviations from calculated values in naphthothiazoles.

Compound	$\delta\Delta_X$[a] b	c	h	i	j	k
2	−0.18	1.17	0.15	0.58	−0.48	−3.30
3	0.75	1.59	1.07	0.38	0.59	−2.03

[a] $\Delta\delta_X = \delta_X$ (*2* or *3*) $- \delta_X$ (naphthalene) $+ \delta_X$ (benzene) $- \delta_X$ (*6*); δ_X (naphthalene): $\delta_\alpha = 128.10$; $\delta_\beta = 126.00$, $\delta_\gamma = 133.72$; δ_C (benzene) $= 128.49$.

similar conditions. Two main products were formed: benzanilide, *8*, in 64 % yield and 2-(*p*-methoxyphenyl)benzothiazole, *9*, in 78 % yield. Only traces of 2-phenylbenzothiazole were formed.



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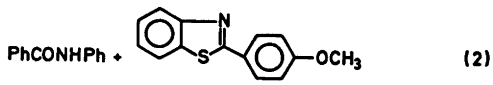
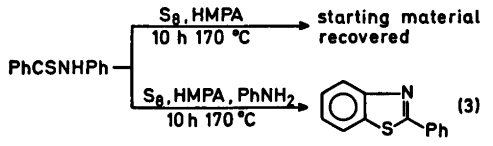


(2)

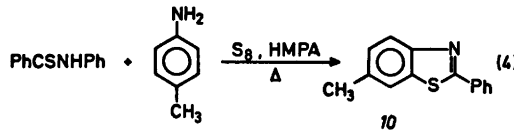
8 *9*

Often 2-arylbenzothiazoles are produced by oxidation of the corresponding thioanilides by potassium hexacyanoferrate(III) (Jacobsen oxidation).[10] As thioanilides could be isolated in many of our reactions and by short reaction times in good yields they were believed to be intermediates. However, a direct oxidation of these thioanilides by elemental sulfur cannot account for the formation of the thiazoles. No reaction took place when thiobenzanilide was heated with sulfur in HMPA. But by addition of aniline to this reaction mixture 2-phenylbenzothiazole was formed (82 %).[4]



(3)

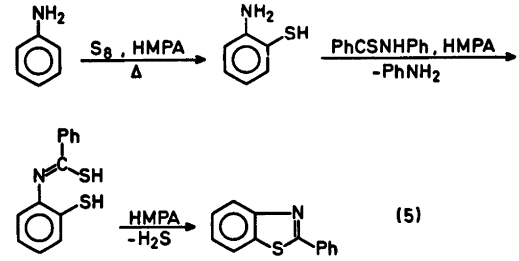
In fact we were able to react benzanilide with sulfur in HMPA above 200 °C to give thiobenzanilide (69 %) without producing any 2-phenylbenzothiazole.[11] Another indication that a simple oxidation of the thioanilides cannot account for the formation of the benzothiazoles was that reaction of thiobenzanilide with elemental sulfur in the presence of *p*-toluidine and HMPA did not produce any 2-phenylbenzothiazole, but 6-methyl-2-phenylbenzothiazole, *10*, was formed in 76 % yield.



(4)

10

We thus suggest that thioanilides are produced as intermediates, and *trans*-amidation of these with *ortho*-thiolated anilines, followed by H_2S elimination, produces the corresponding thiazoles. It is well-known that reaction of anilines with sulfur at elevated temperatures produces 2-mercaptoanilines or the corresponding polysulfides.[12,13]

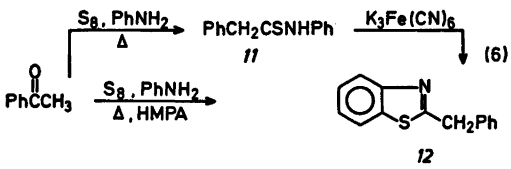


(5)

When *o*-mercaptoaniline was heated with thiobenzanilide at 170 °C in HMPA 2-phenylbenzothiazole was formed (60 %).

Reaction of benzyl alcohol with *o*-toluidine and sulfur in HMPA produced the expected 4-methyl-2-phenylbenzothiazole (68 %). In a similar experiment *o*-chloroaniline was reacted with benzyl alcohol. This reaction had to be run at rather high temperatures and the chlorine atom was substituted by sulfur to give 2-phenylbenzothiazole (43 %) and from reaction of benzyl alcohol with sulfur and HMPA was isolated *N*,*N*-dimethylthiobenzamide (46 %).

2-Phenylthioacetanilide, *11*, has been prepared in a Kindler reaction from acetophenone, aniline, and sulfur.[14] The thioanilide was then further oxidized by potassium hexacyanoferrate(III) to give 2-benzylbenzothiazole, *12*. In the presence of HMPA the benzothiazole, *12*,



was directly formed from acetophenone. It has earlier been reported that acetophenones are oxidized and degraded to *N,N*-dimethylthiobenzamides by heating with sulfur in HMPA.[5] As a by-product the degraded compound 2-phenylbenzothiazole was also formed in the reaction above.

EXPERIMENTAL

^{1}H NMR spectra were recorded at 60 MHz on a Varian A-60 spectrometer. TMS was used as internal reference standard. ^{13}C NMR spectra were recorded at 20 MHz on a Varian CFT-20 instrument. $CDCl_3$ was used as solvent and the concentration was 15 % W/V. TMS was added as internal reference. Silica gel 60 (Merck) was used for column chromatography. Commercial HMPA dried over molecular sieves (3A) was used. Elemental analyses were performed by Novo Industry A/S, Copenhagen, M.p.'s and b.p.'s are uncorrected.

2-(α-Pyridyl)benzothiazole, *6*. α-Picoline (9.3 g), sulfur (19.2 g), aniline (30 ml), and HMPA (10 ml) were heated together at 160–175 °C for 7.5 h. Non-reacted aniline and HMPA were removed by ether extraction (3 × 100 ml) from diluted hydrochloric acid (250 ml). The combined ether phases were washed with water (2 × 50 ml), dried ($MgSO_4$), and the ether evaporated. Column chromatography (ether/light petroleum) gave three pure products. *α-Thiopicolinanilide* (1.0 g, 5 %), m.p. 53 °C (lit.[8] m.p. 52 °C). NMR ($CDCl_3$): δ 7.2–8.9 (9 H, m), 12.6 (1 H, broad m). *N-Methyl-α-thiopicolinamide* (0.6 g, 4 %), m.p. 77 °C (lit.[20] m.p. 79 °C). NMR ($CDCl_3$): δ 3.4 (3 H, d), 7.3–8.8 (4 H, m), ~10.4 (1 H, broad). *2-(α-Pyridyl)-benzothiazole* (17.4 g, 82 %), m.p. 133 °C (lit.[8] m.p. 133–133.5 °C). NMR ($CDCl_3$): δ 7.1–8.7 (m). The ^{13}C NMR spectrum is summarized in Table 1.

2-(γ-Pyridyl)benzothiazole. γ-Picoline (9.3 g), sulfur (19.2 g), aniline (30 ml), and HMPA (10 ml) were heated together at 165–185 °C for 7 h. The reaction mixture was worked up as above. Column chromatography (ether/light petroleum) gave two pure products. *2-(N-Phenylamino)benzothiazole* (1.2 g), m.p. 159 °C (lit.[21] m.p. 161 °C). NMR ($CDCl_3$): δ 7.4 (9 H, m), 11.2 (1 H, broad). *2-(γ-Pyridyl)benzothiazole* (13.2 g, 62 %), m.p. 132–133 °C (lit.[7] m.p. 134–135 °C). NMR ($CDCl_3$): δ 7.2–8.2 (6 H, m), 8.8 (2 H, m).

2-(α-Pyridyl)naphtho[1,2-d]thiazole, *2*. α-Picoline (4.7 g), sulfur (9.6 g), α-naphthylamine (14.3 g), and HMPA (5 ml) were heated together at 165–170 °C for 7 h. The reaction mixture was very stiff, and was therefore dissolved in 25 ml of boiling acetone. Non-reacted aniline and HMPA were removed by ether extraction (3 × 100 ml) from diluted hydrochloric acid (250 ml). The combined ether phases were washed with water (2 × 50 ml) and dried ($MgSO_4$) and the ether evaporated. Column chromatography (ether/light petroleum) yielded *2-(α-pyridyl)naphtho[1,2-d]thiazole* (11.3 g, 86 %), m.p. 137 °C (lit.[8] m.p. 137–138 °C). NMR ($CDCl_3$): δ 7.1–8.7 (9 H, m), 9.0 (1 H, m). The ^{13}C NMR spectrum is summarized in Table 2.

2-(α-Pyridyl)naphtho[2,1-d]thiazole, *3*. α-Picoline (4.7 g), sulfur (9.6 g), β-naphthylamine (14.3 g), and HMPA (5 ml) were heated together at 170 °C for 7 h. The reaction mixture was worked up as for compound *2*, yielding *2-(α-pyridyl)naphtho[2,1-d]thiazole* (10.9 g, 83 %), m.p. 146–147 °C. NMR ($CDCl_3$): δ 7.1–8.7 (m). The ^{13}C NMR spectrum is summarized in Table 2. (Found: C 72.86; H 3.98; N 10.56; S 12.89. $C_{16}H_{10}N_2S$ requires: C 73.28; H 3.82; N 10.69; S 12.21).

2-(p-Methoxyphenyl)benzothiazole. *p*-Methoxybenzyl benzoate (12.1 g), sulfur (9.6 g), aniline (30 ml) and HMPA (10 ml) were heated together for 5 h at 170 °C. The same working-up procedure as for compound *6* gave two pure products. *2-(p-Methoxyphenyl)benzothiazole*, m.p. 122 °C (lit.[22] m.p. 121.5–122 °C). NMR ($CDCl_3$): δ 3.8 (3 H, s); 6.8–8.1 (8 H, m). (Found: C 69.75; H 4.55; N 5.80; S 13.30; $C_{14}H_{11}NOS$ requires: C 69.71; H 4.52; N 5.81; S 13.28 %). *Benzanilide* (6.3 g, 64 %), m.p. 161–162 °C (lit.[23] m.p. 160–161 °C). Spectral data were in accordance with an earlier prepared sample. On TLC small amounts of 2-phenylbenzothiazole (< 200 mg) were recognized, but we were unable to purify this compound adequately for further identification.

6-Methyl-2-phenylbenzothiazole. Thiobenzanilide (2.1 g), sulfur (1.6 g), *p*-toluidine (10 g), and HMPA (5 ml) were heated together at 170 °C for 10 h. The same working-up procedure as for compound *6* afforded *6-methyl-2-phenylbenzothiazole* (1.7 g, 76 %), m.p. 121–122 °C (lit.[24] m.p. 122–123 °C). NMR ($CDCl_3$): 2.4 (3 H, s); 7.1–8.1 (8 H, m).

2-Phenylbenzothiazole, *A*. Thiobenzanilide (1.1 g), *o*-mercaptoaniline (1 g) and HMPA (5 ml) were heated together at 170 °C for 10 h. Column chromatography (ether/light petroleum) of the reaction mixture afforded *2-phenylbenzothiazole* (0.67 g, 61 %), m.p. 113 °C (lit.[4] m.p. 113 °C). Spectral data were in accordance with an earlier prepared sample.[4]

2-Phenylbenzothiazole, *B*. Benzyl alcohol (5.4 g), sulfur (9.6 g), *o*-chloroaniline (25 ml), and HMPA (10 ml) were heated together at 175 °C for 12 h. The same working-up procedure as

for compound *6* afforded two pure products. *2-Phenylbenzothiazole* (4.5 g, 43 %). N,N-*Dimethylthiobenzamide* (3.8 g, 46 %), m.p. 67 °C (lit.[5] m.p. 67 °C). Spectral data were in accordance with an earlier prepared sample.[5]

4-Methyl-2-phenylbenzothiazole. Benzyl alcohol (5.4 g), sulfur (9.6 g), *o*-toluidine (25 ml), and HMPA (10 ml) were heated together at 170 °C for 10 h. The same working-up procedure as for compound *6* afforded *4-methyl-2-phenylbenzothiazole* (7.6 g, 67 %), m.p. 53 °C. NMR ($CDCl_3$): δ 2.8 (3 H, s), 7.2–8.2 (8 H, m). (Found: C 74.69; H 5.00; N 6.19; S 14.22; $C_{14}H_{11}NS$ requires: C 74.67; H 4.89; N 6.22; S 14.22).

2-Benzylbenzothiazole. Acetophenone (6.0 g), sulfur (12.8 g), aniline (20 ml), and HMPA (7 ml) were heated together at 185 °C for 6 h. The same working-up procedure as for compound *6* afforded two pure products from the rather complex reaction mixture, *2-phenylbenzothiazole* (1.6 g, 16 %). *2-Benzylbenzothiazole* (3.9 g, 35 %), b.p. 138 °C/0.25 mmHg (lit.[25] b.p. 157–163 °C/0.5 mmHg. Picrate m.p. 140–141 °C (lit.[14] m.p. 139–139.5). NMR ($CDCl_3$): 4.4 (2 H, s), 7.2–8.1 (9 H, m).

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