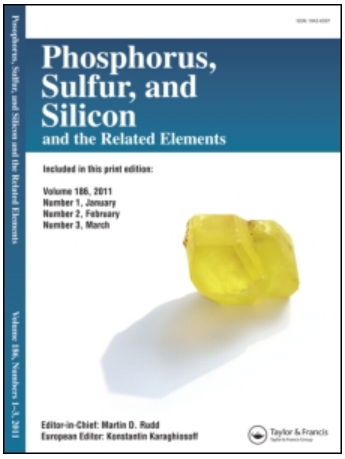


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Unexpected Formation of a 2,2'-Di(N -ethyl-acetamino)substituted Diphenyl Disulfane on Oxidation of 3-Ethyl-2-methylbenzothiazolium Tetrafluoroborate

Christian Reichardt[a]; Hans-Peter Erfurt[a]; Klaus Harms[a]
[a] Philipps University, Marburg, Germany

Online publication date: 27 October 2010

To cite this Article Reichardt, Christian , Erfurt, Hans-Peter and Harms, Klaus(2003) 'The Unexpected Formation of a 2,2'-Di(N -ethyl-acetamino)substituted Diphenyl Disulfane on Oxidation of 3-Ethyl-2-methylbenzothiazolium Tetrafluoroborate', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 5, 1081 — 1092
To link to this Article: DOI: 10.1080/10426500307848
URL: http://dx.doi.org/10.1080/10426500307848

Phosphorus, Sulfur and Silicon, 2003, Vol. 178:1081–1092

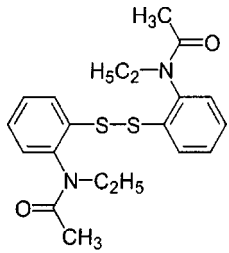
1042-6507/03 $12.00 + .00
DOI: 10.1080/10426500390208910

THE UNEXPECTED FORMATION OF A 2,2′-DI(*N*-ETHYL-ACETAMINO)SUBSTITUTED DIPHENYL DISULFANE ON OXIDATION OF 3-ETHYL-2-METHYLBENZOTHIAZOLIUM TETRAFLUOROBORATE

Christian Reichardt, Hans-Peter Erfurt, and Klaus Harms
Philipps University, Marburg, Germany

(Received August 12, 2002; accepted October 31, 2002)

Attempts at the oxidation of 3-ethyl-2-methylbenzothiazolium salt ***2*** *with a variety of oxidizing reagents did not lead to the desired isochiral* S*-oxide* ***3*** *or achiral* S,S*-dioxide* ***4****, in some cases, however, unexpectedly to the ring-opened dimeric 2,2′-di(* N*-ethyl-acetamino)substituted diphenyl disulfane* ***5****, the molecular structure of which was confirmed by x-ray analysis. The synthesis of 2-methylbenzothiazole-*S,S*-dioxide* ***14****, reported by Zincke et al. in 1915, turned out to be not reproducible.*



5

Keywords: 3-Ethyl-2-methylbenzothiazolium salts; benzothiazolium salts; heterocycles; oxidation; sulfur heterocycles

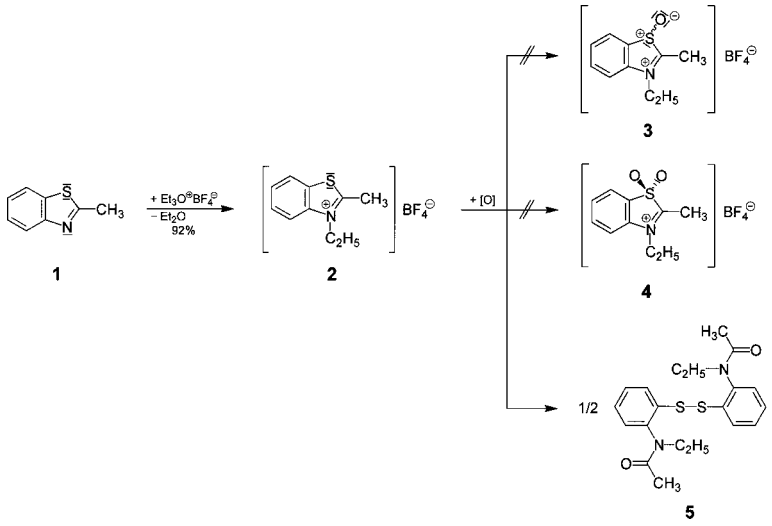
This article is part IX in the series "Chiral Polymethine Dyes."—Part VIII: Reichardt et al.[3]

X-ray crystal structure analysis by Klaus Harms.

The Fonds der Chemischen Industrie, Frankfurt (Main), is gratefully acknowledged for their financial support of this work.

Address correspondence to Christian Reichardt, Department of Chemistry and Center of Material Sciences, Philipps University, Hans-Meerwein-Strasse, D-35032 Marburg, Germany. E-mail: Reichardt-Marburg@t-online.de

Whereas chiral aromatics (e.g., helicenes) and chiral polyenes (e.g., carotinoids) are well-known conjugated π-systems, chiral polymethinic π-systems have been studied in more detail only recently[3,4] in spite of the fact that chiral polymethine dyes have been already described in 1928 by König et al.[5] and 1938 by Götze.[6] Chiral polymethine dyes are of potential interest as functional dyes[7] because of their particular chiroptical properties. There are three possibilities to introduce chirality into the conjugated π-system of polymethine dyes: (a) introduction of substituents with stereogenic centers into the polymethine chain[8]or into the heterocyclic end groups;[9,10] (b) the use of heterocyclic end groups containing stereogenic centers within the heterocyclic ring system;[11,12] and (c) helical twisting of the polymethine chain by steric effects.[13–15] Recently having synthesized polymethine streptocyanine dyes with sulfinyl groups as stereogenic centers in the two end groups,[3] we thought that monochiral* 2,3-dialkylsubstituted benzothiazolium-*S*-oxide salts such as **3** (Scheme 1) with a stereogenic S—O group would be suitable candidates for the synthesis of new chiral tri- and pentamethinium thiacyanine dyes. To the best of our knowledge, up to now such benzothiazolium-*S*-oxides are not known.[17] Surprisingly, instead of the



SCHEME 1 Attempts at oxidation of benzothiazolium salt **2**.

*We prefer the designations *monochiral* (one-handed), *isochiral* (equal-handed), and anisochiral (unequal-handed) in place of the ambiguous terms *homochiral*, *racemic*, and *scalemic*, respectively, as recently recommended by H. Cornforth.[1]

desired *S*-oxide **3** (or *S*,*S*-dioxide **4**), in two cases (oxidation with peracetic acid and with 3-chloroperbenzoic acid at higher temperature), the ring-opened dimeric 2,2′-disubstituted diphenyl disulfane **5** was unexpectedly obtained.

RESULTS AND DISCUSSION

We have tried to synthesize 3-ethyl-2-methylbenzothiazolium-*S*-oxide salts such as **3** and the corresponding *S*,*S*-dioxide **4** by *S*-oxidation of 3-ethyl-2-methylbenzothiazolium tetrafluoroborate (**2**),[18] which was obtained from commercially-available 2-methylbenzothiazole (**1**) by alkylation with triethyloxonium tetrafluoroborate[19] (Scheme 1).

Because there are reports that oxidation of *N*,*S*-heterocycles without *N*-substituents leads preferably to the formation of the corresponding *N*-oxides (see for example Ochiai and Hayashi[20]), we have first protected the benzothiazol-nitrogen by alkylation. For oxidation of the *N*-alkylated benzothiazolium salt **2** to the desired isochiral ("racemic")[16] sulfoxide **3**, the following oxidation reagents were applied at various temperatures:[1,2] (a) hydrogen peroxide (without[21a] and with Jacobsen's catalyst[22]); (b) peracetic acid, formed in situ from hydrogen peroxide and acetic acid;[21b] (c) 3-chloroperbenzoic acid;[21c,23] (d) sodium periodate;[21d,24] and (e) hypofluorous acid in acetonitrile (H_3C–CN$\cdots$HOF).[21e,25]

A suspension of **2** in aqueous hydrogen peroxide ($c = 30$ cg/g)[21a] at room temperature (rt) and at 50°C led only to the recovery of unreacted **2** with 85–90% yield.[1] The same reaction in acetonitrile/water in the presence of Jacobsen's catalyst[22] (2 mole-%) at rt and at 60°C afforded likewise the unreacted educt **2** only with 84–87% yield.[1]

A suspension of **2** in acetic acid with an excess (4 equivalents) of aqueous hydrogen peroxide ($c = 30$ cg/g)[21b] led at −10°C and at rt only to the recovery of the educt with 85–90% yield. However, at higher temperatures (i.e., 50 and 70°C), a highly viscous brownish oil was isolated, which turned out to be neither the desired sulfoxide **3** nor the sulfone **4**, but the diphenyl disulfane **5** (Scheme 1; see later).[1] In order immediately to get sulfone **4**, salt **2** was treated with an excess of 10 equivalents of aqueous hydrogen peroxide in acetic acid at rt and at 70°C, however, again without success. After treatment at rt, only the educt was recovered, but at 70°C crude disulfane **5** could be again isolated as a highly viscous light-brown oil.[1]

The oxidation of **2** with 3-chloroperbenzoic acid (1 equivalent)[21c] in dichloromethane, according to a procedure given by Chioccara

et al.,[23] gave at 0°C only the unreacted educt (87%), but at 50°C in trichloromethane as solvent, crude disulfane **5** again was isolated as highly viscous brownish oil.[1] After treatment of **2** with an excess of five equivalents of 3-chloroperbenzoic acid in trichloromethane at 50°C, the formation of disulfane **5** only could be detected.[1]

Oxidation of **2** with sodium periodate[21d] in acetone/water at 0 and 50°C, according to a procedure given by Leonard et al. for the oxidation of sulfanes to sulfoxides,[24] resulted likewise in the recovery of unreacted educt only.[1]

Eventually, the oxidation of **2** at 0°C with the strongly oxidizing hypofluorous acid/acetonitrile complex,[21e,25] which oxidizes even thiophene easily to thiophene-*S*,*S*-dioxide, afforded with an equivalent amount of oxidizing agent only the unreacted educt, however, with a five-fold excess a nonseparated mixture of **2** (ca. 20%) and **5** (ca. 80%) according to its ^{1}H and ^{13}C NMR spectrum.[2]

Obviously, the quaternary imonium cation of salt **2** is very resistant to all five oxidation reagents, applied at various reaction conditions: neither the sulfoxide **3** nor the sulfone **4** could be prepared this way. However, in two cases (with peracetic acid and 3-chloroperbenzoic acid at higher temperatures) a viscous brownish oil was unexpectedly isolated, the molecular structure of which could not unambiguously determined by its elemental analysis and spectroscopic measurements alone. The oil, which did not crystallize by itself, was dissolved in small amounts of various solvents and the solutions were slowly concentrated by evaporation in vacuo in an exsiccator in the presence of silica gel or P_4O_{10}. Finally, in one case, a slow crystallization process started under high vacuum. After two days, the crystals were separated, washed with petroleum ether (b.p. 40–60°C)/diethyl ether (5:1), and dried to afford colorless needles with m.p. 104°C, resistant to air and water. One of them was suitable for an x-ray analysis, the result of which is shown in Figure 1.[26]

Unexpectedly, this oxidation product, mostly obtained as a poorly crystallizing oil, turned out to be the ring-opened dimeric 2,2′-di(*N*-ethyl-acetamino)substituted diphenyl disulfane **5**, crystallizing with a half equivalent of water as semihydrate (Scheme 1). Elemental analysis, IR, mass, ^{1}H, and ^{13}C NMR spectra are in agreement with this molecular structure (see Experimental). The bond lengths, bond angles, and torsion angles around the C–S–S–C moiety of **5** are practically equal to that found for the unsubstituted diphenyl disulfane.[27] Only the torsion angle for C(1)–S(1)–S(2)–C(11) in **5** differs with −90.72° somewhat from that found for the unsubstituted diphenyl disulfane (–85.99°),[27] the increase obviously caused by the two voluminous 2,2′-substituents.

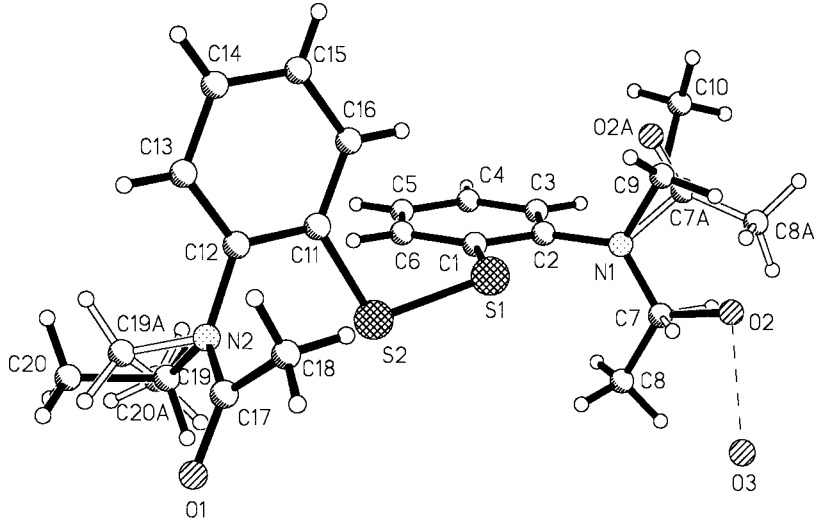
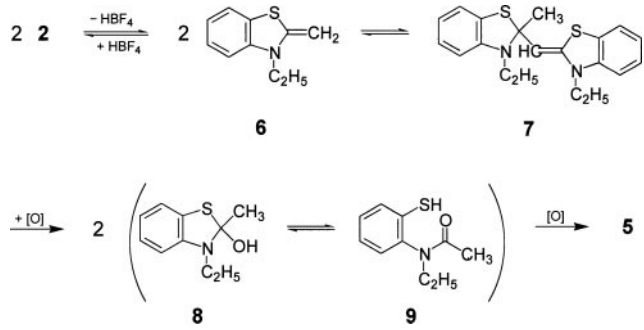


FIGURE 1 Ball-and-stick-model of the molecular structure of disulfane **5** in the crystal. – Selected bond lengths [pm]: C(1)–S(1) 178.4(3), S(1)–S(2) 202.07(15), S(2)–C(11) 179.0(3), C(2)–N(1) 141.9(5), N(1)–C(7) 133.4(9), C(7)–O(2) 125.9(8), C(12)–N(2) 142.9(4), N(2)–C(17) 137.3(5), C(17)–O(1) 121.5(5). – Selected bond angles [°]: C(1)–S(1)–S(2) 105.58(13), C(11)–S(2)–S(1) 105.59(12), C(2)–C(1)–S(1) 115.0(3), C(12)–C(11)–S(2) 115.0(2), C(2)–N(1)–C(7) 124.5(5), C(12)–N(2)–C(17) 121.6(3), N(1)–C(7)–O(2) 113.8(10), N(2)–C(17)–O(1) 121.1(4). – Selected torsion angles [°]: S(2)–S(1)–C(1)–C(2) −165.1(3), S(1)–S(2)–C(11)–C(12) –167.9(2), C(1)–S(1)–S(2)–C(11) –90.72(18), S(1)–C(1)–C(2)–N(1) 1.5(5), S(2)–C(11)–C(12)–N(2) 0.5(4), C(2)–N(1)–C(7)–O(2) –179.7(4), C(12)–N(2)–C(17)–O(1) 176.2(4). – The two 2,2′-*N*-ethylacetamino-substituents are disordered. O(3) represents the oxygen atom of the water of crystallization, the H-atoms of which were not localized. For further details see Experimental and ref.[26].

The diphenyl disulfane **5** was already described by Clark in 1925: After treatment of an aqueous solution of the corresponding iodide (**2** with I^- as anion) with ammonia, the mixture was kept in the dark, exposed to atmospheric oxygen for two months and the crystalline deposit formed (m.p. 103°C) was collected.[28] However, at that time the molecular structure of **5** was proven only by elemental analysis. The corresponding bis(*N-methyl*-acetamino) derivative of **5** was isolated in 1968 by Vorsanger during his UV/Vis spectroscopical studies of the methylene base obtained by deprotonation of 2,3-dimethylbenzothiazolium salts.[29,30] A plausible reaction path for the formation of disulfane **5** by oxidation of **2** is given in Scheme 2. The quaternary imonium salt **2** is at higher temperatures in equilibrium with its methylene base, which

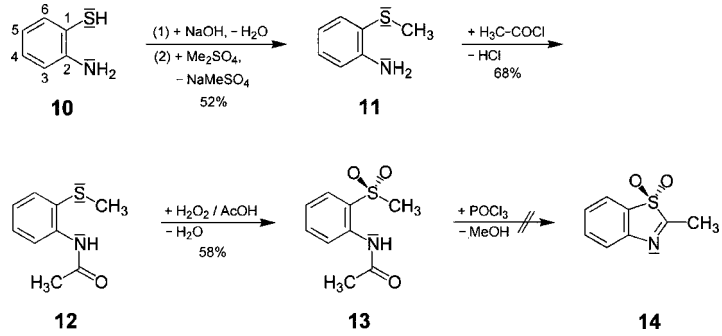


SCHEME 2 Possible reaction path for the formation of disulfane **5** by oxidation of **2**, according to Vorsanger.[29]

dimerizes to **7**,[29,30] the oxidation of which leads to the semi-thioketal **8**. Its ring-opened isomer **9** is then oxidized to give the disulfane **5**.

In conclusion, a selective or stereoselective *S*-oxidation of benzothiazolium salts such as **2** to the desired isochiral sulfoxide **3** or the sulfone **4** seems to be not possible by means of the aforementioned five reagents, even not with rather strong oxidizing reagents. Under forced reaction conditions, however, the ring-opened disulfane **5** is unexpectedly always formed.[1,2]

In order to get at least sulfone **4**, we have tried to synthesize 2-methylbenzothiazole-*S*,*S*-dioxide **14**, the *N*-alkylation of which should easily lead to **4** (Scheme 3). Sulfone **14** was supposedly prepared in 1915 by Zincke et al. by heating the 2-(acetamino)phenyl methyl sulfone **13** with phosphorus oxytrichloride at 130°C for 1 h, to give **14** as "glänzende, glashelle Plättchen" with m.p. 149–150°C.[31] The only proof



SCHEME 3 Attempt at the synthesis of 2-methylbenzothiazol-*S*,*S*-dioxide **14**, according to Zincke et al.[31]

for its molecular structure was an analysis of the sulfur content of the product obtained (calculated 17.70% S; found 17.80% S[30]).

Starting with 2-aminothiophenol **10**, we have synthesized the *S*,*S*-dioxide **13** via the thioether **11** and its *N*-acetyl derivative **12** (Zincke et al. used at that time a somewhat different route[31]). Unfortunately, all attempts to reproduce the ring-closure reaction of **13** to **14** under the given reaction conditions failed.[1] The sulfone **14** obviously is not available this way. To the best of our knowledge, this compound has not been prepared up to now.

EXPERIMENTAL

General methods, equipment, and materials are the same as given in Reichardt et al.[3]

Attempts at the Synthesis of 3 by Oxidation of 2 with Peracetic Acid[21b]

(a) *At Room Temperature*: Aqueous hydrogen peroxide (c = 30 cg/g; 1.3 mL, 32 mmol) was added with stirring to a suspension of tetrafluoroborate **2** (2.13 g, 8.0 mmol) in glacial acetic acid at rt. Stirring was continued until a clear solution was formed (ca. 2 h). After neutralization with a saturated aqueous $NaHCO_3$ solution, the reaction mixture was extracted with dichloromethane. The extract was dried with $MgSO_4$ and the solvent was distilled off, to afford ca. 1.8 g (85%) of the starting compound **2**.

(b) *At 70°C*: Aqueous hydrogen peroxide (c = 30 cg/g; 1.5 mL, 37 mmol) was added with stirring to a suspension of tetrafluoroborate **2** (2.50 g, 9.4 mmol) in glacial acetic acid (5 mL, 85 mmol) at rt. Stirring was continued until a clear solution was formed. Then, the reaction mixture was heated slowly to 70°C and kept at this temperature for 2 h. After cooling to rt and neutralization with saturated aqueous $NaHCO_3$ solution, the diluted acetic acid was distilled off (after a negative peroxide test) and the residue was dissolved in dichloromethane. After drying with $MgSO_4$, the solvent was distilled off to yield crude **5** (ca. 1.3 g, ca. 71%) as a highly viscous light-brown oil.

Attempts at the Synthesis of 3 by Oxidation of 2 with 3-Chloroperbenzoic Acid[21c,23]

(a) *At 0°C*: A solution of 3-chloroperbenzoic acid (1.50 g, 8.75 mmol) in dry dichloromethane (50 mL) was added with stirring to a solution of tetrafluoroborate **2** (2.45 g, 8.73 mmol) in dry dichloromethane at 0°C during 60 min. Stirring was continued for ca. 30 min without cooling

until rt was reached. The reaction mixture was washed with saturated aqueous $NaHCO_3$ solution and water (100 mL), dried with $MgSO_4$, and the solvent was distilled off (after a negative peroxide test). The residue, partly oily and partly colorless crystals, was dried in vacuo, to give crude educt **2** (ca. 2.0 g, ca. 87%), according to its ^1H and ^{13}C NMR spectrum.

(b) *At Room Temperature with a Five-Fold Excess of Oxidizing Reagent*: A solution of 3-chloroperbenzoic acid (11.52 g, 67.0 mmol) in dry trichloromethane was added with stirring to a solution of tetrafluoroborate **2** (3.54 g, 13.4 mmol) in dry trichloromethane (50 mL) at rt during 2 h. Within 1 h, the reaction mixture was heated to 50°C and kept at this temperature for 2 h with stirring, to give a clear yellow solution. After cooling to rt the mixture was neutralized by washing with saturated aqueous $NaHCO_3$ solution (150 mL) and eventually with water (150 mL). The organic phase was dried with $MgSO_4$, the solvent was distilled off (after a negative peroxide test), and the residue was dried in vacuo to give crude **5** (1.95 g, 75%) as highly viscous brownish oil, identical with that obtained after oxidation of **2** with peracetic acetic at 70°C, according to its ^1H and ^{13}C NMR, IR, and mass spectra.

Analytical Data of Disulfane 5

The viscous brownish oil obtained, which did not crystallize by itself, and the crystalline compound (colorless needles with m.p. 104°C; ref.[28] 103°C), obtained from this oil as described in the general section, gave the following results, which are in complete agreement with the molecular structure of **5**: ^1H NMR (CD_3COCD_3): $\delta = 1.13$ (t, 6H, $^3J = 7.2$ Hz, CH_2—CH_3), 1.72 (s, 6H, CO—CH_3), 3.29 (d of q, 2H, $^3J = 7.1$ Hz, CH_2—CH_3; additional splitting because of restricted rotation for steric reasons), 4.08 (d of q, 2H, $^3J = 7.1$ Hz, CH_2—CH_3; additional splitting because of restricted rotation for steric reasons), 7.29–7.64 (m, 8H, aromatic H). – ^{13}C NMR (CD_3COCD_3): $\delta = 13.4$ (CH_2—*C*H_3), 22.6 (CO—*C*H_3), 43.4 (*C*H_2—CH_3), 127.5, 129.0, 130.3, and 131.2 (aromatic C), 136.0 (*C*—S—S—*C*), 141.1 (*C*—N), 169.6 (*C*O—CH_3). – IR (KBr): $\tilde{\nu} = 1663$ cm^{-1} (C=O). – MS (FD): m/z(%) = 388 (100) [M$^+$]. – $C_{20}H_{24}N_2O_2S_2$ (388.5): calcd. C 61.83, H 6.23, N 7.21; found C 61.54, H 6.41, N 7.19.

X-Ray Molecular Structure of 5 (Figure 1)[*]

(a) *Crystal data*: $C_{20}H_{24}N_2O_2S_2 \cdot 0.5\ H_2O$ with $M_r = 388.54 + 9.00 = 397.54$ g/mol; crystal habitus: colorless needle; crystal size: ca.

[*]Further crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC–169579. Copies of the data can be obtained free of charge on application to CCDC.[26]

$0.4 \times 0.2 \times 0.1$ mm; monoclinic crystal system with space group $C2/c$ and $Z = 8$, $a = 2794.9(2)$, $b = 737.5(1)$, and $c = 2041.4(1)$ pm, $\alpha = \gamma = 90^\circ$ and $\beta = 94.470(10)^\circ$; $V = 4195.0(7) \cdot 10^{-30}$ m^3; $\rho_{\text{calcd.}} = 1.259$ Mg/m^3; $F(000) = 1688$; linear absorption coefficient $\mu = 2.453$ mm^{-1}.

(b) *Data collection*: Type of diffractometer: Enraf-Nonius CAD 4; Cu-K_α radiation [$\lambda = 154.178$ pm at 293(2) K] with software CAD4-EXPRESS for data collection and cell refinement and XCAD4 (Harms, 1993) for data reduction; scan method: ω-θ-scans, scan angle: 0.75°; θ range for data collection: 3.17 to 65.10°; index ranges $0 \le h \le 32$, $0 \le k \le 8$, $-23 \le l \le 23$.

(c) *Solution and refinement*: Reflections collected 3644, symmetry-independent reflections 3563 ($R_{\text{int}} = 0.0469$), observed reflections 2647 [$I > 2\sigma(I)$], reflections used for refinement 3563, extinction coefficient $X = 0.00034(11)$. Program system used: SHELXS-97, SHELXL-97, and SHELXTL. Empirical absorption correction, direct methods, difference Fourier analysis, full-matrix refinement at F^2 with all independent reflections, weighting scheme $w = [\sigma^2(F_0^2) + (0.1246\ P)^2 + 3.0398\ P]^{-1}$, with $P = (F_0^2 + 2F_c^2)/3$. Goodness-of-fit parameter (based on F^2) $S = 1.036$. Hydrogen atoms were introduced in calculated positions with fixed isotropic U's; non-hydrogen atoms were refined anisotropically. R index (all data): wR_2 (based on F^2) = 0.2069; R index conventional [$I > 2\sigma(I)$] = 0.0630. Completeness to $\theta = 65.10^\circ$: 99.6%.

Attempts at the Synthesis of 2-Methylbenzothiazole-*S,S*-dioxide 14

See Scheme 3.

(2-Aminophenyl) Methyl Sulfane (11)

In a three-necked, round-bottomed 500-mL flask, equipped with two dropping funnels, reflux condenser, and magnetic stirrer, a solution of NaOH (60.0 g, 1.50 mmol) in distilled water (100 mL) and methanol (100 mL) was placed under a nitrogen atmosphere. At rt, 2-aminothiophenol (**10**) (62.6 g, 0.50 mmol) was added dropwise with stirring within 1 h. Through the second dropping funnel, freshly distilled dimethyl sulfate (70.0 g, 0.56 mmol) was added at 30–40°C with stirring and the mixture was heated at reflux for 2 h. After cooling to rt, the precipitate formed was filtered off and the red-violet filtrate was extracted three times with diethyl ether (3×100 mL). The combined red-violet ethereal extracts were dried with $MgSO_4$ and the solvent was distilled off until the boiling point reached ca. 65°C. The fractional distillation was continued in vacuo with a glass filter pump to yield **11** (36.5 g, 52%)

as colorless liquid of b.p. 126°C/15 Torr (ref.[32] 141.5–143.0°C/36 Torr). – ^{1}H NMR ($CDCl_3$): $\delta = 2.34$ (s, 3H, CH_3), 4.26 (broad s, 2H, NH_2), 6.67–7.37 (m, aromatic H). – ^{13}C NMR ($CDCl_3$): $\delta = 18.1$ (CH_3), 115.0 (C-3), 118.9 (C-5), 120.3 (C-1), 129.0 (C-4), 133.5 (C-6), 147.3 (C-2). – IR (KBr): $\tilde{\nu} = 3359$ (NH_2) cm^{-1}.– MS (FD): m/z (%) = 139 (100) [M$^+$]. – C_7H_9NS (139.2): calcd. C 60.39, H 6.52, N 10.06; found C 60.24, H 6.48, N 9.95.

*2-(*N*-Acetamino)phenyl Methyl Sulfane (12):*

In a three-necked, round-bottomed 1 L-flask with stirrer, reflux condenser, and dropping funnel, a solution of sulfane **11** (35.4 g, 25.4 mmol) in dry benzene (400 mL) was placed. Under cooling with an ice-bath, acetyl chloride (24.0 g, 25.3 mmol) was added dropwise with stirring. The mixture was then stirred at 90°C for 1 h. After cooling to rt, the precipitate formed was filtered off, and washed in succession with water (200 mL), aqueous HCl ($c = 5$ cg/g; 200 mL), aqueous NaOH ($c = 5$ cg/g; 200 mL), and water (200 mL). After two-fold recrystallization from ethanol and drying in vacuo, **12** (31.3 g, 68%) was obtained as colourless needles with m.p. 104°C (ref.[33] 104–106°C). – ^{1}H NMR ($CDCl_3$): $\delta = 2.18$ (s, 3H, CH_3—CO), 2.33 (s, 3H, CH_3—S), 7.02–8.21 (m, aromatic H), 8.22 (broad s, 1H, NH). – ^{13}C NMR ($CDCl_3$): $\delta = 18.8$ (CH_3—S), 24.8 (CH_3—CO), 120.9 (C-3), 124.4 (C-5), 125.5 (C-1), 128.6 (C-4), 132.5 (C-6), 138.2 (C-2), 168.4 (C=O). – IR (KBr): $\tilde{\nu} = 3228$ (NH) cm$^-$1, 1656 (C=O). – MS (EI): m/z (%) = 183 (2) [M$^+$ + 2H], 182 (5) [M$^+$ + H], 181 (55) [M$^+$], 139 (82) [M$^+$–CH_3CO + H], 134 (42) [M$^+$–SCH_3], 124 (100) [M$^+$–CH_3CO + H—CH_3], 43 (32) [CH_3CO^+]. – $C_9H_{11}NOS$ (181.3): calcd. C 59.64, H 6.12, N 7.73; found C 59.68, H 5.88, N 7.83.

*2-(*N*-Acetamino)phenyl Methyl Sulfone (13)*[30]

To a solution of sulfane **12** (14.5 g, 78.8 mmol) in glacial acetic acid (65 mL), placed inside a three-necked, round-bottomed 250-mL flask equipped with stirrer, dropping funnel, and reflux condenser, was added with stirring aqueous hydrogen peroxide ($c = 30$ cg/g; 65 mL, 1.7 mol). The mixture was slowly heated to 85°C within 1 h and kept at this temperature for 2 h. The reaction mixture was given in an open Erlenmeyer flask and concentrated by heating it at 40°C. The brownish, partly crystalline residue was three times recrystallized from 2-propanol and dried in vacuo, to afford sulfone **13** (9.8 g; 58%) as colorless needles with m.p. 139°C (ref.[31] 139–140°C). – ^{1}H NMR ($CDCl_3$): $\delta = 2.18$ (s, 3H, CH_3—SO_2), 3.00 (s, 3H, CH_3—CO), 7.19–8.39 (m, 4H, aromatic H), 9.43 (broad s, 1 H, NH). – ^{13}C NMR ($CDCl_3$): $\delta = 25.1$ (CH_3—CO), 44.3 (CH_3—SO_2), 123.0, 124.2, 127.2, 129.3, 135.4, and 137.1 (aromatic C), 168.6 (C=O). – IR (KBr): $\tilde{\nu} = 3320$ (NH) cm^{-1}, 1683 (C=O), 1306 and 1148 (SO_2). – MS (EI): m/z (%) = 214 (2) [M$^+$ + H], 213 (20) [M$^+$], 171

(100) [M^+–CH_3CO + H], 134 (30) [M^+–SO_2CH_3], 43 (32) [CH_3CO^+]. – $C_9H_{11}NO_3S$ (213.3): calcd. C 50.69, H 5.20, N 6.57; found C 50.46, H 5.10, N 6.43.

Attempts at the Synthesis of 2-Methylbenzothiazole-1,1-dioxide (14)[31]

Sulfone **13** (1.0 g, 4.8 mmol) and phosphorus oxytrichloride (3 mL, 32 mmol) were slowly heated to 130°C within 2 h and kept at this temperature for 1 h, to give an orange-yellow solution. After cooling to RT, the reaction mixture was poured onto ice (ca. 10 g) in order to hydrolyze unreacted $POCl_3$. The flocculent brownish precipitate formed (ca. 5 mg only), which should be **14** according to Zincke et al.,[31] was filtered off and dried. Its FD mass spectrum does not show the peak of the molecular ion at $m/z = 181$, corresponding to $M_r = 181.2$ for $C_8H_7NO_2S$ (**14**). The aqueous filtrate was extracted with dichloromethane, the extract was dried with $MgSO_4$, and the solvent was distilled off, to give unreacted educt **13** (0.87 g, 85%) as brownish solid. The reaction was several times repeated, also with longer reaction times, but always with the same negative result.[1]

REFERENCES

[1] H.-P. Erfurt, Diploma Thesis, Philipps University, Marburg, 1996.
[2] H.-P. Erfurt, Ph.D. Thesis, Philipps University, Marburg, 1999.
[3] C. Reichardt, H.-P. Erfurt, K. Harms, and G. Schäfer, *Eur. J. Org. Chem.*, 439 (2002).
[4] a) C. Reichardt, *J. Phys. Org. Chem.*, **8,** 761 (1995); b) A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra, and G. B. Behera, *Chem. Rev.*, **100,** 1973 (2000).
[5] W. König, *Z. Angew. Chem.*, **41,** 615 (1928).
[6] J. Götze, *Ber. Dtsch. Chem. Ges.*, **71,** 2289 (1938).
[7] a) J. Griffiths, *Chem. Unserer Zeit*, **27,** 21 (1993); b) Z. Yoshida and T. Kitao, *Chemistry of Functional Dyes* (Mita Press, Tokyo, 1989).
[8] C. Reichardt and U. Budnik, *Chem. Ber.*, **123,** 2023 (1990).
[9] C. Reichardt and U. Budnik, *Liebigs Ann. Chem.*, 927 (1994).
[10] C. Reichardt, U. Budnik, K. Harms, G. Schäfer, and J. Stein, *Liebigs Ann. Chem.*, 329 (1995).
[11] C. Reichardt, H.-D. Engel, R. Allmann, D. Kucharczyk, and M. Krestel, *Chem. Ber.*, **123,** 565 (1990).
[12] C. Reichardt, W. Amann, K. Harms, G. Schäfer, and J. Stein, *J. Prakt. Chem.*, **340,** 513 (1998).
[13] V. Buß, D. Ulbrich, and C. Reichardt, *Liebigs Ann.*, 1823 (1996).
[14] V. Buß, F. Terstegen, and S. Falzewski, *Chem. Phys.*, **243,** 179 (1999).
[15] G. Nuding, E. Zimmermann, and V. Buß, *Tetrahedron Lett.*, **42,** 2649 (2001).
[16] J. W. Cornforth, *Aust. J. Chem.*, **46,** 157 (1993), and *Aldrichimica Acta*, **27**(3), 71 (1994).
[17] a) J. V. Metzger, *Thiazoles and Their Benzo Derivatives,* in *Comprehensive Heterocyclic Chemistry*, edited by A. R. Katritzky and C. W. Rees (Pergamon Press, Oxford,

1984), vol. 6, part 4B (ed. K. T. Potts), pp. 235–331; b) U. Zoller in *The Syntheses of Sulphones, Sulphoxides and Cyclic Sulphides*, edited by S. Patai and Z. Rappoport (Wiley, Chichester, 1994), pp. 389–527; c) A. Dondoni and P. Merino, "Benzothiazole" in *Encyclopedia of Reagents for Organic Syntheses*, edited by L. A. Paquette (Wiley, Chichester, 1995), vol. 1, pp. 298–300; d) M. Mikolajczyk, J. Dabrowski, and P. Kielbasinski, *Chiral Sulfur Reagents* (CRC Press, London, 1997).

[18] C. Reichardt, *Liebigs Ann. Chem.*, **715,** 74 (1968).

[19] H. Meerwein, *Org. Synth*., **46,** 113 (1966); *Org. Synth., Coll. Vol. V,* 1080 (1973).

[20] E. Ochiai and E. Hayashi, *J. Pharm. Soc. Jpn.,* **67,** 34 (1947); *Chem. Abstr.*, **45,** 9533 (1951).

[21] L. A. Paquette, ed., *Encyclopedia of Reagents for Organic Synthesis* (Wiley, Chichester, 1995); a) A. S. Rao and H. R. Mohan, *Hydrogen Peroxide*, vol. 4, p. 2731; b) A. S. Rao and H. R. Mohan, *Peracetic Acid*, vol. 6, p. 3933; c) A. S. Rao and H. R. Mohan, *3-Chloroperbenzoic Acid*, vol. 2, p. 1192; d) A. G. Wee and J. Slobodian, *Sodium Periodate*, vol. 7, p. 4613; e) S. Rozen, *Hypofluorous Acid*, vol. 4, p. 2789.

[22] M. Palucki, P. Hanson, and E. N. Jacobsen, *Tetrahedron Lett.*, **33,** 7111 (1992).

[23] F. Chioccara, L. Oliva, G. Prota, and E. Novellino, *Synthesis*, 744 (1978).

[24] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27,** 282 (1962).

[25] S. Rozen, *Chem. Rev.*, **96,** 1717 (1996).

[26] CCDC, 12 Union Road, Cambridge/UK, CB2 1E2; E-mail: deposit@ccdc.cam.ac.uk

[27] M. Sacerdoti, G. Gilli, and P. Domiano, *Acta Crystallogr., Sect. B*, **31,** 327 (1975).

[28] L. M. Clark, *J. Chem. Soc.*, **127,** 973 (1925).

[29] J.-J. Vorsanger, *Bull. Soc. Chim. Fr.*, **35,** 955 (1968).

[30] J. R. Owen, *Eastman Organic Chemical Bulletin*, **43,** 3 (1971); *Chem. Abstr.,* **76**, 114815u (1972).

[31] a) Th. Zincke and G. Siebert, *Ber. Dtsch. Chem. Ges.*, **48,** 1242 (1915); b) G. Siebert, Ph.D. Thesis, Philipps University, Marburg, 1914.

[32] E. Bayer and E. Breitmaier, *Chem. Ber.*, **101,** 1579 (1968).

[33] R. J. Crawford and C. Woo, *J. Org. Chem.*, **31,** 1655 (1966).