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Ring Transformations of 4,5- to the Isomeric 3,4-Disubstituted Isothiazolium Salts and their Oxidation to 1,1-Dioxides [1])

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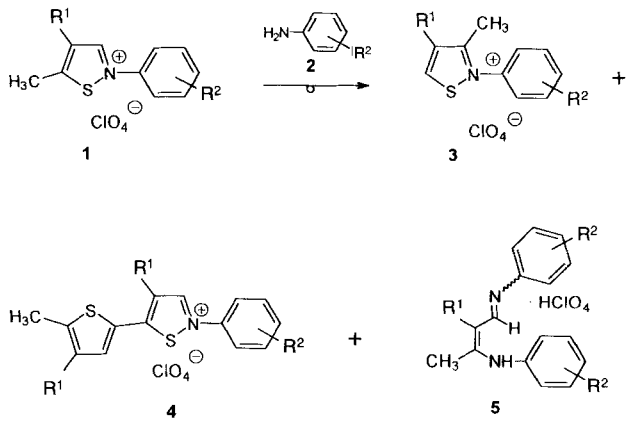
Abstract. 4,5-Disubstituted *N*-phenyl-isothiazolium salts **1** with active 5-methyl group react under the influence of anilines to form 3,4-disubstituted isothiazolium salts **3**. The influence of donor and acceptor substituents in the 2-phenyl group of **1a–h** and in the anilines **2** on the ring transformation were studied. The structure of the new salts was confirmed by X-ray analysis. The 3-hydroperoxy-2,3-dihydro-isothiazole 1,1-dioxides (**12a,d**)and the isothiazole-3(2*H*) -one 1,1-dioxides (**14a,d**) are obtained by oxidation of salts **3** with H_2O_2.

Isothiazolium salts react with the *N*-nucleophiles ammonia, primary amines, hydrazines and hydroxylamines by ring transformation to isothiazoles, pyrazoles and isoxazoles [1, 2]. Recently, a novel synthesis of 3-aminopyrroles by base-catalysed ring transformation and desulfuration of substituted 5-amino-2-methyl-isothiazolium salts was reported [3, 4]. *N*-Phenyl-isothiazolium salts **1** with active methyl- or methylene group in 5-position react in base-induced reaction with secondary amines under deprotonation and oxidative dimerisation to thieno-annelated *N*-phenyl-substituted 6aλ^4-thia-1,6-diaza-pentalenes [5, 6], spirocyclic isothiazolium salts and thianthrene derivatives [7, 8].

Interestingly, weaker bases as for instance substituted anilines **2** compete due to their basicity and nucleophilicity in the reaction with the salts **1**. Thus, isomerisation occurs by migration of sulfur to the salts **3** with alkyl substituted 3-position.

In this paper, we describe this ring transformation of isothiazolium salts **1** with substituted anilines **2** to salts of the type **3** and their oxidation to isothiazole 1,1-dioxides for the first time.

We have investigated the reaction of isothiazolium salts **1a–h** with substituted anilines **2** at room temperature, yielding stable salts **3** (10–73%). The best yields are obtained at a temperature of 50 °C, with equimolar

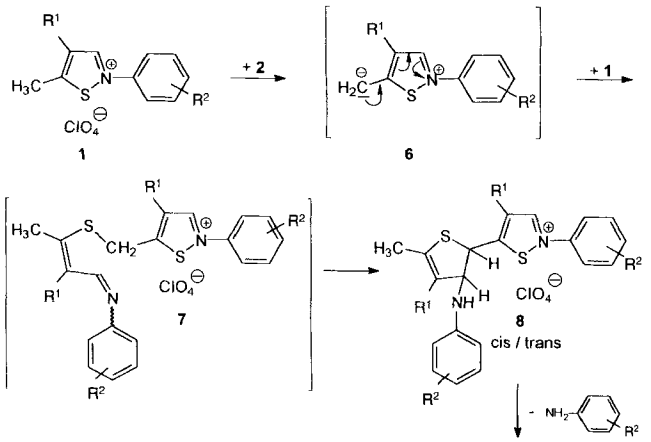


1,3,4,5	R^1	R^2	3 (%)	4 (%)	5 (%)	Overall Yield (%)
a	CH_3	4-OCH_3	87	2	8	97
b	CH_3	4-CH_3	88	1	5	94
c	CH_3	3-CH_3				
d	CH_3	H				
e	CH_3	4-Cl				
f	CH_3	4-Br				
g	C_2H_5	4-OCH_3				
h	C_2H_5	H				

Scheme 1

[1]) Presented in part at the third conference on iminium salts, Stimpfach-Rechenberg (Germany), September 17–19, 1997

amounts of **2** and with electron-donating substituents in *p*-position at the 2-phenyl ring. Aniline with substituents in *m*-position, *e.g.* **2c** (R^2 = 3-CH_3) react like the *p*-substituted to **3c**. Contrary to this, the *o*-substituted anilines (R^2 = 2-CH_3, 2-Cl) do not react with salts **1**.



Scheme 2

The new red 5-thienyl-substituted salts **4** (see ref. [6, 9]) were obtained as by-product in 1–16% yield in the reaction of the isothiazolium salts **1a–h** with anilines **2** (Scheme 2). In this case, base-induced deprotonation of 5-methyl group in **1** is favoured and proceeds after nucleophilic attack of the deprotonated reaction partner **6** at the sulfur atom of the salt **1** after S–N-ring opening to **7**, ring closure and amine elimination from **8** to **4**.

Other by-products are salts of vinamidines **5** (1–17%) (Scheme 1 and 3), which were obtained from *β*-chlorvinyl aldehydes with anilines [10, 11] or 1-azaallyl anions with imidic acid derivatives [12] a long time before. The yields of compounds **4** and **5** are lower with the increase of basicity of anilines **2**.

The structure of new isothiazolium salts **3** was identified on the basis of their spectroscopic data. Apart from the correct elemental analyses, UV/Vis spectra of all salts **3** exhibit typical absorption ranges of λ = 210–225 nm and 251–272 nm, which are in agreement with those of other isothiazolium salts [5–7]. A dominant feature of the vibrational spectra of **3** are the O–Cl–O absorption bands at 1080–1100 cm^{-1}. Electrospray ionization mass spectra which are taken from **3a** and **3b**, show the expected molecular ion peaks of the cations.

The main characteristics of the ^1H NMR spectra are given by the chemical shifts for the signal of the 5-H-proton, which are at relatively low field, between δ/ppm = 9.1–9.3. The difference in the chemical shifts of 3-CH_3 and 4-CH_3 protons is smaller in the new salts **3** ($\Delta\delta$ = 0.03–0.05 ppm) than in the formerly known salts **1** ($\Delta\delta$ = 0.41–0.57 ppm).

The signals of the C-3 and C-4 atoms in the ^{13}C NMR spectra are found at 168–169 ppm and 133–138 ppm as singlets and a doublet of C-5 at 149–150 ppm of the isothiazolium moiety.

The structure of the 2-phenyl-3,4-dimethyl-isothiazolium salt **3d** was confirmed by X-ray structure analysis. (Fig. 1) The inspection of the data shows the typical isothiazolium salt structure with the S–N-bond of 1,682 Å (see ref. [13]). The 2-phenyl-ring is 86,92° out of plane of the isothiazole ring.

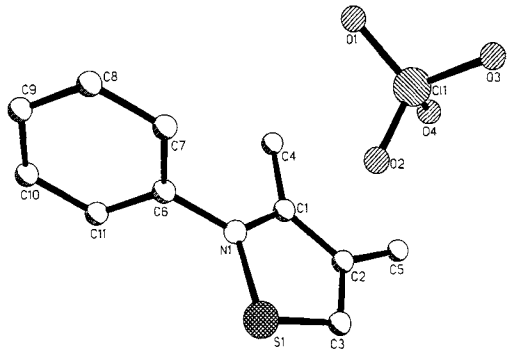
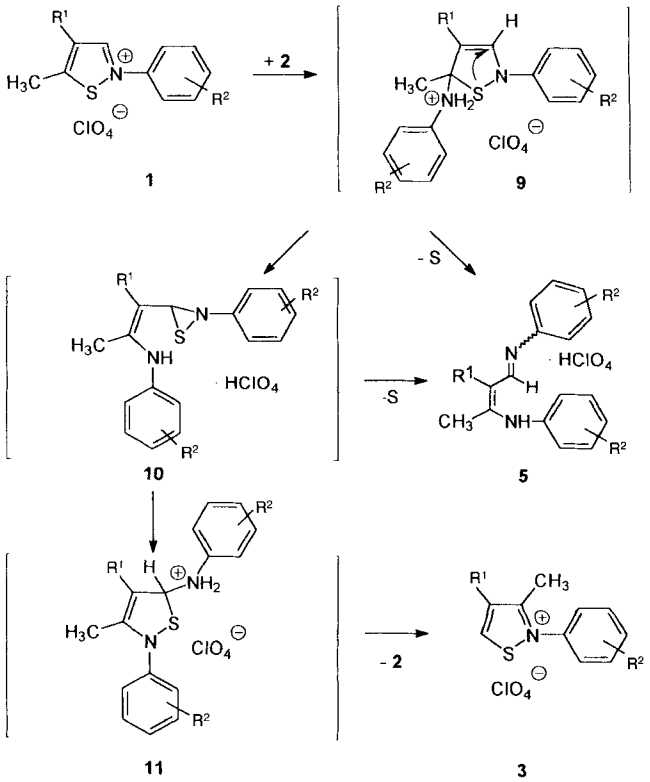


Fig. 1 Molecular structure of **3d** selected bond length (Å) and bond angles (°): S(1)–N(1) 1.682 (2), N(1)–C(1) 1.342 (3), C(1)–C(2) 1.410 (3), C(2)–C(3) 1.361 (3), S(1)–C(3) 1.684 (2), N(1)–C(6) 1.448 (3), N(1)–S(1)–C(3) 90.79 (11), C(1)–N(1)–S(1) 113.7 (2), N(1)–C(1)–C(2) 111.4 (2), C(2)–C(1)–C(4) 126.7 (2), C(3)–C(2)–C(5) 125.3 (2), C(3)–C(2)–S(1) 112.8 (2)



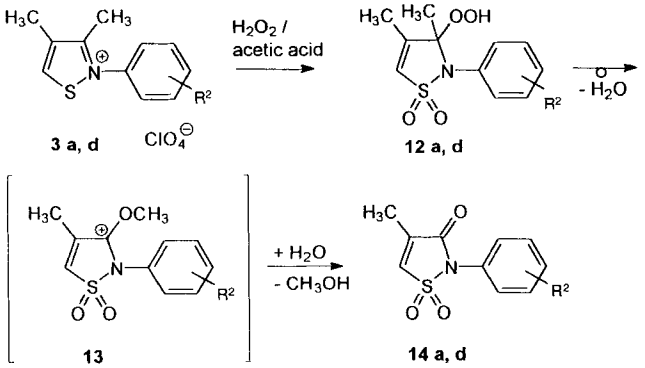
Scheme 3

In order to explain the observed reaction behaviour of salts **1** with anilines **2**, one can invoke the following mechanism (Scheme 3). Nucleophilic attack of aniline **2** at the carbon atom in 5-position leads to non-isolable intermediates **9** which react under sulfur migration to enaminothioaziridine **10**. By the following ring closure within the intermediate **10** between the aniline nitrogen and the sulfur of the thioaziridine ring under S–N-ring opening **11** arises, on the other hand sulfur extrusion to **5** is possible. Final elimination of aniline from **11** provides **3**. The postulated intermediates **9**–**11** could not be isolated.

Support for these arguments comes from the reaction of the salts **1**, *e.g.* **1d** (R^2 = H) and **1e** (R^2 = 4-Cl) with the more basic aniline **2a** (R^2 = 4-OCH_3). In this case, the isomerisation leads under aniline exchange to **3a** in 20–54% yield.

We have also found that the isothiazolium salts **3** are readily oxidized with hydrogen peroxide (30%) in acetic acid at 50 °C to 3-hydroperoxy-2,3-dihydro-isothiazole 1,1-dioxides (**12a,d**).

These stable compounds were identified by ^1H and ^{13}C NMR spectra. The most important properties of the hydroperoxides **12a,d** are the ^{13}C NMR chemical shifts of the C-3 atoms in $CDCl_3$ which appear at 98,5 ppm, and the typical symmetrical and antisymmetrical SO_2 absorption bands at 1168 cm^{-1} and 1277 cm^{-1} in the infrared spectra.



Scheme 4

14	R^2
a	4-OCH_3
d	H

Surprisingly, the oxidation of **3a,d** with hydrogen peroxide at 70 °C did not give 3-hydroperoxides (**12a,d**), but isothiazol-3(2*H*)-one 1,1-dioxides (**14a,d**) (36–47%) (Scheme 4).

The comparison of various spectroscopic data with those of typical isothiazol-3(2*H*)-one 1,1-dioxides [14] shows that all compounds **14** have the same characteristics. The IR spectra exhibit absorption bands at 1742 cm^{-1} (CO), 1188 cm^{-1} (SO_2) and 1321–1336 cm^{-1} (SO_2). The signals for the C-3 atoms are observed at 160,7–161,3 ppm, whereas those of the atoms C-4 and C-5 appear constant at 141,2–141,4 ppm and 132,1 ppm.

In order to characterize the structure of our new isothiazol-3(2*H*)-one 1,1-dioxides **14**, an X-ray structure analysis was performed for the derivative **14a** (Fig. 2). The length of the CO-bond of 1,214 Å correspond well to data for other isothiazol-3(2*H*)-one 1,1-dioxides.

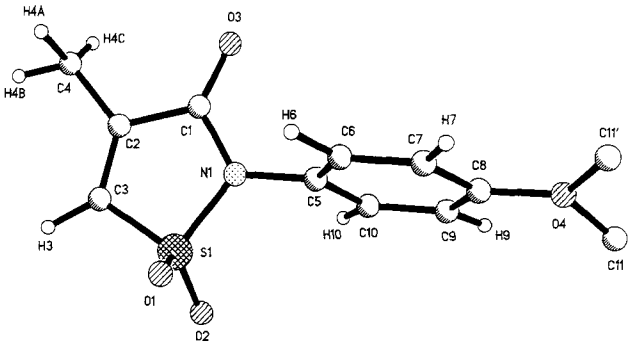


Fig. 2 Molecular structure of **14a** selected bond length (Å) and bond angles (°): S(1)–N(1) 1.672 (3), N(1)–C(1) 1.390 (5), C(1)–C(2) 1.491 (5), C(2)–C(3) 1.321 (5), S(1)–C(3) 1.740 (4), O(3)–C(1) 1.214 (4), S(1)–O(1) 1.425 (3), S(1)–O(2) 1.435 (3), O(1)–S(1)–O(2) 116.7 (2), O(2)–S(1)–N(1) 109.8 (2), N(1)–S(1)–C(3) 92.8 (2), C(1)–N(1)–S(1) 112.9 (3), N(1)–C(1)–C(2) 109.4 (3), C(1)–C(2)–C(4) 119.3 (3), C(2)–C(3)–S(1) 111.7 (3), O(3)–C(1)–C(2) 126.4 (3)
The methyl group of the methoxy substituent is disordered.

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Experimental

IR: ATI Mattson Genesis Series FTIR. – UV/Vis: Beckmann DU 650 Spectrophotometer. – NMR: Varian Unity 400 Spectrometer, TMS internal standard. – elementar analysis: Heareus- CHN–O–S-Rapid-Analyser. – MS: VG-12-250 of Analytical Instruments Manchester. – ESI-MS: PLATFORM I of Micromass. – Melting points were determined on a Boëtius micro melting point apparatus and have been corrected.

4,5-Dialkyl-2-aryl-isothiazolium perchlorates (1a–h) (General Procedure)

1a–g were prepared according ref. [5]. The isothiazolium perchlorates **1a, d–f,h** were described in [5, 6].

4,5-Dimethyl-2-(4-methylphenyl)- isothiazolium perchlorate **(1b)**

Yield 60%; *m.p.* 124–126 °C (ethanol). – IR (KBr): ν/cm^{-1} = 1116 (O–Cl–O). – UV (CH_3CN): λ_{max}/nm (lg ε) = 200.0 (4.23); 254.5 (3.84); 300.5 (3.92). – $C_{12}H_{14}ClNO_4S$ (303.74).

4,5-Dimethyl-2-(3-methylphenyl)-isothiazolium perchlorate **(1c)**

Yield 85%; *m.p.* 115–116 °C (ethanol). – IR (KBr): ν/cm^{-1} =

1092 (O–Cl–O). – UV (CH_3CN): λ_{max}/nm (lg ε) = 200.0 (4.30), 247.0 (3.77), 295.5 (3.91). – $C_{12}H_{14}ClNO_4S$ (303.74).

4-Ethyl-2-(4-methoxyphenyl)-5-methyl-isothiazolium perchlorate (**1g**)

Yield 52%; *m.p.* 112–113 °C (ethanol). – IR (KBr): ν/cm^{-1} = 1092 (O–Cl–O), 1249 (OCH_3). – UV (CH_3CN): λ_{max}/nm (lg ε) = 229.0 (3.82); 306.0 (3.54); 376.5 (4.35). – $C_{13}H_{16}ClNO_5S$ (333.77).

3,4-Dialkyl-2-aryl-isothiazolium perchlorates (3a–h) (General Procedure)

3 mmol 2-aryl-isothiazolium perchlorate **1** and 3 mmol aniline **2** are dissolved by stirring and gentle heating in 30 ml methanol. The reaction mixture is stirred at 50 °C for 8 hours. After removing the solvent up to 4 ml at room temperature, the reaction mixture is allowed to stand in the freezer for some hours. The by-product **4** is precipitated, which can be filtered off. By careful addition of 25–30 ml of ether to the filtered solution, scratching and standing at 0–5 °C for some hours the perchlorate **3** crystallizes. The residue contains **5**. The crystals were filtered off, washed with ether and purified by recrystallization from ethanol/ether.

2-(4-Methoxy-phenyl)-3,4-dimethyl-isothiazolium perchlorate (**3a**)

Yield 87%; *m.p.*103–106 °C (ethanol/ether); orange-yellow plates. – IR (KBr): ν/cm^{-1} = 1090 (Cl–O–Cl), 1260 (OCH_3). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 269.0 (3.96). – ^{1}H NMR (DMSO-d_6): δ/ppm = 9.25 (s, 1H, CH=N); 7.61; 7.18 (4H, J_{AB} = 8 Hz, *o*/*m*-H); 3.84 (s, 3H, OCH_3); 2.37 (s, 3H, CH_3); 2.34 (s, 3H, CH_3). – ^{13}C NMR (DMSO-d_6): δ/ppm = 169.0 (C-3); 162.4 (*p*-C); 149.4 (C-5); 134.5 (C-4); 128.5 (*o*-C); 127.6 (*i*-C); 115.8 (*m*-C); 56.2 (OCH_3); 16.0 (CH_3); 14.4 (CH_3).

$C_{12}H_{14}ClNO_5S$	Calcd.:	C 45.07	H 4.41	N 4.38	S 10.03
(319.74)	Found:	C 44.90	H 4.44	N 4.47	S 9.66.

3,4-Dimethyl-2-(4-methyl-phenyl)-isothiazolium perchlorate (**3b**)

Yield 77%; *m.p.*112–115 °C (ethanol/ether); yellow plates. – IR (KBr): ν/cm^{-1} = 1090 (Cl–O–Cl). – UV (CH_3CN): λ_{max}/nm (lg ε) = 260.0 (3.67). – $C_{12}H_{14}ClNO_4S$ (303.74).

3,4-Dimethyl-2-(3-methyl-phenyl)-isothiazolium perchlorate (**3c**)

Yield 87%; *m.p.*140–141 °C (ethanol/ether); yellow solid.– IR (KBr): ν/cm^{-1} = 1094 (Cl–O–Cl). – UV (CH_3CN): λ_{max}/nm (lg ε) = 269.5 (3.93). $C_{12}H_{14}ClNO_4S$ (303.74).

3,4-Dimethyl-2-phenyl-isothiazolium perchlorate (**3d**)

Yield 77%; *m.p.*158–160 °C (ethanol/ether); yellow plates. – IR (KBr): ν/cm^{-1} = 1080 (Cl–O–Cl). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 272.5 (3.86). – ^{1}H NMR (DMSO-d_6): δ/ppm= 9.33 (s, 1H, CH=N); 7.71 (m, 5H, arom. H); 2.42 (s, 3H, CH_3); 2.38 (s, 3H, CH_3). – ^{13}C NMR (DMSO-d_6): δ/ppm = 168.3 (C-3); 150.8 (C-5); 135.2 (*i*-C); 133.1 (C-4); 131.6 (*p*-C); 130.3 (*m*-C); 126.8 (*o*-C); 15.5 (CH_3); 13.1 (CH_3).

$C_{11}H_{12}ClNO_4S$	Calcd.:	C 45.60	H 4.17	N 4.83	S 11.07
(289.71)	Found:	C 45.36	H 4.25	N 4.99	S 11.08.

Crystal Structure Analysis of 3d [15]

STADI 4 (Fa. Stoe) diffractometer, $C_{11}H_{12}ClNO_4S$ (289.73), crystal size: 0.6×0.4×0.1mm, Mo-K_α (λ = 0.71073 Å), T = 293 K, monoclinic crystal system, space group $P2_1/c$, unit cell dimensions a = 14.7260 (11) Å, b = 7.4123 (6) Å, c = 12.4645 (10) Å, β = 106.9670 (10)°, V = 1301.3 (2) Å^3, Z = 4, ρ = 1.479 mg/m^3, μ(Mo-K_α) = 0.459 mm^{-1}, 6886 reflections collected, 2653 independent reflections, θ–range for data collection 1.45–26.48°, index ranges: $-18 \le h \le 11$, $-9 \le k \le 8$, $-15 \le l \le 15$, refinement method: Full-matrix least squares on F^2, R/R_w: 0.0419/0.1007, largest diff. peak and hole: 0.440/−0.391e Å^{-3}, programs: SHELXL93, SHELXS, SCHAKAL

2-(4-Chlorophenyl)-3,4-dimethyl-isothiazolium perchlorate (**3e**)

Yield 38%; *m.p.*114–115 °C (ethanol/ether); beige plates. – IR (KBr): ν/cm^{-1} = 1080 (Cl–O–Cl). – UV (CH_3CN): λ_{max}/nm (lg ε) =220.0 (4.07), 251.0(4.02). – $C_{11}H_{11}Cl_2NO_4S$ (324.16).

2-(4-Bromophenyl)-3,4-dimethyl-isothiazolium perchlorates (**3f**)

Yield 44%; *m.p.* 143–147 °C (ethanol/ether); beige plates. – IR (KBr): ν/cm^{-1} = 1080 (Cl–O–Cl). – UV (CH_3CN): λ_{max}/nm (lg ε) = 224.0 (4.10), 268.5 (4.00). $C_{11}H_{11}BrClNO_4S$ (368.61).

4-Ethyl-2-(4-methoxyphenyl)-3-methyl-isothiazolium perchlorate (**3g**)

Yield 97%; *m.p.* 91–93 °C (ethanol/ether); colourless prisms. – IR (KBr): ν/cm^{-1} = 1109 (O–Cl–O),1259 (OCH_3). – UV (CH_3CN): λ_{max}/nm (lg ε) = 224.5 (4.06), 268.0 (3.99). – ^{1}H NMR (DMSO-d_6): δ/ppm = 9.20 (s, 1H, CH=N); 7.66, 7.21 (4H, J_{AB}= 8Hz, *o*/*m*-H); 3.86 (s, 3H, OCH_3); 2.75 (q, 2H, CH_2); 2.42 (s, 3H, CH_3); 1.27 (t, 3H, CH_3). – ^{13}C NMR (DMSO-d_6): δ/ppm = 167.9 (C-3); 161.2 (*p*-C); 149.5 (C-5); 138.7 (C-4); 128.0 (*o*-C); 127.6 (*i*-C); 115.4 (*m*-C); 55.4 (OCH_3); 20.8 (CH_2); 15.2 (CH_3); 13.1 (CH_3).

$C_{13}H_{16}ClNO_5S$	Calcd.:	C 46.78	H 4.83	N 4.20	S 9.61
(333.77)	Found:	C 46.54	H 4.85	N 4.42	S 10.18.

4-Ethyl-3-methyl-2-phenyl-isothiazolium perchlorate (**3h**)

Yield 85%; *m.p.* 130–135 °C (ethanol/ether); yellow prisms. – IR (KBr): ν/cm^{-1} = 1099 (O–Cl–O). – UV (CH_3CN): λ_{max}/nm (lg ε) = 269.0 (3.83). – $C_{12}H_{14}ClNO_4S$ (303.7).

2-Aryl-4-methyl-5-thienyl-isothiazolium perchlorates (4a–h).

The 5-thienyl-isothiazolium perchlorates **4a–h** are obtained as by-products at the synthesis of the salts **3a–h**.

2-(4-Methoxyphenyl)-4-methyl-5-(2',3'-dimethyl-thien-5'-yl)-isothiazolium perchlorate (**4a**)

Yield 2%; *m.p.* 185–190 °C (ethanol); reddish-brown needles. – IR (KBr): ν/cm^{-1} = 1090 (Cl–O–Cl), 1250 (OCH_3). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 401.0 (4.29). – $C_{17}H_{18}ClNO_5S_2$ (415.9).

4-Methyl-2-(4-methylphenyl)-5-(2'3'-dimethyl-thien-5'-yl)-isothiazolium perchlorate (**4b**)

Yield 1%; *m.p.* 165–170 °C (ethanol); reddish-brown needles.

– IR (KBr): ν/cm^{-1} = 1090 (Cl–O–Cl). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 405.5 (4.25). – $C_{17}H_{18}ClNO_4S_2$ (399.9).

4-Methyl-2-(3-methylphenyl)-5-(2',3'-dimethyl-thien-5'-yl)-isothiazolium perchlorate (**4c**)

Yield 5%; *m.p.* 125–127 °C (raw product); red-brown solid. – IR (KBr): ν/cm^{-1} = 1104 (Cl–O–Cl). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 376.0 (4.00). – $C_{17}H_{18}ClNO_4S_2$ (399.9).

4-Methyl-5-(2',3'-dimethyl-thien-5'-yl)-2-phenyl-isothiazolium perchlorate (**4d**)

Yield 5%; *m.p.* 198–200 °C (ethanol); reddish-brown needles. – IR (KBr): ν/cm^{-1} = 1090 (Cl–O–Cl). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 406.0 (4.32). – $C_{16}H_{16}ClNO_4S_2$ (385.8).

2-(4-Chlorophenyl)-4-methyl-5-(2',3'-dimethyl-thien-5'-yl)-isothiazolium perchlorate (**4e**)

Yield 8%; *m.p.* 245–248 °C (ethanol); reddish-brown needles. – IR (KBr): ν/cm^{-1} = 1090 (Cl–O–Cl). – UV (CH_3CN): λ_{max}/nm (lg ε) = 401.0 (4.29). – ^{1}H NMR (DMSO-d_6): δ/ppm = 9.60 (s, 1H, CH=N); 7.89; 7.82 (4H, J_{AB}= 9.0 Hz, *o*/*m*-H); 7.81 (s, 1H, 4'-H); 2.53 (s, 3H, 4-CH_3); 2.49 (s, 3H, 3'-CH_3); 2.21 (s, 3H, 2'-CH_3). – ^{13}C NMR (DMSO-d_6): δ/ppm = 159.6 (C-5); 158.5 (C-3); 144.2 (C-2'); 136.8 (C-5'); 135.9 (C-4'); 135.6 (*p*-C); 135.3 (*i*-C); 130.5 (*m*-C); 128.9 (C-3'); 124.7 (*o*-C); 121.8 (C-4); 13.5 (2'-CH_3); 13.2 (3'-CH_3); 12.7 (4-CH_3). – $C_{16}H_{15}Cl_2NO_4S_2$ (420.3).

2-(4-Bromophenyl)-4-methyl-5-(2',3'-dimethyl-thien-5'-yl)-isothiazolium perchlorate (**4f**)

Yield 16%; *m.p.* 276–280 °C (ethanol); reddish-brown needles. – IR (KBr): ν/cm^{-1} = 1090 (Cl–O–Cl). – UV (CH_3CN): λ_{max}/nm (lg ε) = 401.5 (4.34). – $C_{16}H_{15}BrClNO_4S_2$ (464.7).

4-Ethyl-5-(3'-ethyl-2'-methyl-thien-5'-yl)-2-(4-methoxyphenyl)-isothiazolium perchlorate (**4g**)

Yield 1%; *m.p.* 105–106 °C; brown solid. – IR (KBr): ν/cm^{-1} = 1093 (Cl–O–Cl). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 240.5 (4.11); 388.0 (3.70). – $C_{19}H_{22}ClNO_5S_2$ (443.9).

4-Ethyl-5-(3'-ethyl-2'-methyl-thien-5'-yl)-2-phenyl-isothiazolium perchlorate (**4h**)

Yield 1%; *m.p.* 168–169 °C (methanol); reddish-brown needles. – IR (KBr): ν/cm^{-1} = 1101 (Cl–O–Cl). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 271.5 (3.94); 378.0 (3.58). – $C_{18}H_{20}ClNO_4S_2$ (413.9).

2-Aryl-3-hydroperoxy-3,4-dimethyl-2,3-dihydro-isothiazole 1,1-dioxides (12a,d) (General Procedure)

1mmol 3,4-dialkyl-2-aryl-isothiazolium perchlorate **3** is dissolved in 6 ml acetic acid and under stirring 4 ml hydrogen peroxide is added dropwise at room temperature. The reaction mixture is stirred for 8 hours at 50 °C. By slow removal of the solvent at room temperature **12a,d** are obtained as colourless crystals, which are filtered off and washed with distilled water. Purification by recrystallisation from ethanol is possible.

3-Hydroperoxy-2-(4-methoxyphenyl)-3,4-dimethyl-2,3-dihydro-isothiazole 1,1-dioxide (**12a**)

Yield 81%; *m.p.* 103–107 °C (dec.); colourless needles. – IR (KBr): ν/cm^{-1} = 1168 (SO_2),1251 (OCH_3), 1277 (SO_2). – UV (ethanol): λ_{max}/nm (lg ε) = 229.5 (4.06); 270.5 (3.01). – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.41; 6.91 (4H, J_{AB}= 8.8Hz, *o*/*m*-H); 6.60 (s, 1H, 5-H); 3.80 (s, 3H, OCH_3); 2.05 (s, 3H, 4-CH_3); 1.30 (s, 3H, 3-CH_3). – ^{13}C NMR ($CDCl_3$): δ/ppm = 160.9 (*p*-C); 149.8 (C-4); 133.5 (*o*-C); 124.7 (C-5); 122.9 (*i*-C); 115.4 (*m*-C); 98.3 (C-3); 56.1 (OCH_3); 19.8 (CH_3); 13.7 (CH_3). – MS (*m/z*): 285 (M^+,1); 251 (38); 187 (26); 172 (47); 147 (100); 92 (32). – $C_{12}H_{15}NO_5S$ (285.3)

Calcd.:	C 50.51	H 5.30	N 4.91	O 28.04	S 11.24
Found:	C 50.48	H 5.19	N 5.16	O 27.90	S 11.08.

3-Hydroperoxy-2-phenyl-3,4-dimethyl-2,3-dihydro-isothiazole 1,1-dioxide (**12d**)

Yield 67%; *m.p.* 127–128 °C (dec.); colourless plates. – IR (KBr): ν/cm^{-1} = 1167 (SO_2) 1277 (SO_2). – UV (ethanol): λ_{max}/nm (lg ε) = 224.5 (3.62); 264.5 (2.59). – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.56–7.54 (m, 2H, *o*-H); 7.46–7.41 (m, 3H, *m*/*p*-H); 6.61 (s, 1H, 5-H); 2,10 (s, 3H, 4-CH_3); 1.36 (s, 3H, 3-CH_3). – ^{13}C NMR ($CDCl_3$): δ/ppm = 149.5 (4-C); 131.6 (*p*-C); 131.0 (*i*-C); 130.2 (*m*-C); 129.6 (*o*-C); 124.9 (C-5); 98.5 (C-3); 19.8 (CH_3); 13.6 (CH_3).– MS (*m/z*): 255 (M^+, 1); 237 (2); 221 (46); 156 (93); 144 (41); 118 (46); 77 (100).

$C_{11}H_{13}NO_4S$ (255.3)

Calcd.:	C 51.75	H 5.13	N 5.49	O 25.07	S 12.56
Found:	C 51.54	H 5.48	N 5.59	O 24.80	S 12.34.

2-Aryl-4-methyl-isothiazol-3(2*H*)-one 1,1-dioxides (14a,d) (General Procedure)

To the stirred solution of 1mmol 3,4-dialkyl-2-aryl-isothiazolium perchlorate **3** in 6 ml acetic acid is added dropwise 4 ml hydrogen peroxide (30%) at room temperature. After this the mixture is stirred at 70 °C for 6 hours, while the reaction mixture loses colour. After slow removal of the solvent, colourless needles of **14** were isolated, which are recrystallized from ethanol.

2-(4-Methoxyphenyl)-4-methyl-isothiazol-3(2H)-one 1,1-dioxide (**14a**)

Yield 36%; *m.p.* 160–162 °C; colourless needles. – IR (KBr): ν/cm^{-1} = 1188 (SO_2), 1253 (OCH_3), 1336 (SO_2), 1742 (C=O). – UV (ethanol): λ_{max}/nm (lg ε) = 226.5 (4.12), 271.0 (3.15). – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.34; 7.01 (4H, J_{AB}= 9Hz, *o*/*m*-H); 7.15 (s, 1H, 5-H); 3.83 (s, 3H, OCH_3); 2.20 (s, 3H, 4-CH_3). – ^{13}C NMR ($CDCl_3$): δ/ppm = 161.3 (C-3); 160.8 (*p*-C); 141.2 (C-4); 132.0 (C-5); 130.4 (*o*-C); 121.1 (*i*-C); 115.7 (*m*-C); 56.0 (OCH_3); 12.3 (4-CH_3). – MS (m/z): 253 (M^+, 92); 149 (100); 134 (70); 106 (38); 78 (24).

$C_{11}H_{11}NO_4S$ (253.3)

Calcd.:	C 52.16	H 4.38	N 5.53	O 25.27	S 12.66
Found:	C 52.54	H 4.78	N 5.89	O 25.60	S 12.24.

Crystal Structure Analysis of 14a [16]

Siemens CCD (SMART) diffractometer, $C_{11}H_{11}NO_4S$ (253.27), crystal size: 0.6×0.2×0.1mm, Mo-K_α (λ = 0.71069 Å), T = 293 K, monoclinic crystal system, space group $P2_1/c$, unit cell dimensions a = 16.040 (5) Å, b = 5.289 (5) Å, c = 14.772 (5) Å, β = 110.960 (5)°, V = 1170.3 (12) Å^3, Z = 4, ρ = 1.437 mg/m^3, μ(Mo-K_α) = 0.279 mm^{-1}, 5945 reflections

collected, 2345 independent reflections, θ–range for data collection 1.36–27.26°, index ranges: $-20 \leq h \leq 10, -6 \leq k \leq 6, -17 \leq l \leq 18$, refinement method: Full-matrix least squares on F^2, R/R_w: 0.0625/0.1568, largest diff. peak and hole: 0.412/ −0.317e $Å^{-3}$, programs: SHELXL97, SHELXS, SCHAKAL

2-Phenyl-4-methyl-isothiazol-3(2H)-one-1,1-dioxide (**14d**)

Yield 47%; *m.p.* 172–173 °C; colourless needles. – IR (KBr): ν/cm^{-1} = 1189 (SO_2), 1321 (SO_2), 1742 (C=O). – UV (ethanol): λ_{max}/nm (lg ε) = 214.5 (3.97), 266.0 (2.81). – ^1H NMR ($CDCl_3$): δ/ppm = 7.53–7.44 (m, 5H, arom. H); 7.16 (s, 1H, 5-H); 2.23 (s, 3H, 4-CH_3). – ^{13}C NMR ($CDCl_3$): δ/ppm = 160.7 (C-3); 141.4 (C-4); 132.1 (C-5); 130.6 (*p*-C); 130.5 (*o*-C); 129.5 (*i*-C); 128.7 (*m*-C); 12.5 (4-CH_3). – MS (*m/z*): 223 (M^+, 60); 159 (23); 130 (54); 119 (76); 91 (100).

$C_{10}H_9NO_3S$ (223.2)

Calcd.:	C 53.80	H 4.06	N 6.27	O 21.50	S 14.36
Found:	C 54.02	H 4.15	N 6.31	O 21.50	S 14.51.

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[15] Further details of the crystal structure analysis of **3d** are available on request from Fachinformationszentrum Karlsruhe D-76344 Eggstein-Leopoldshafen, on quoting the depository number CSD-408226, the names of the authors and journal citation.

[16] Further details of the crystal structure analysis of **14a** are available on request from Cambridge Crystallographic Database Centre by contacting the CCDC Technical Editors at deposit @Chemcrys.cam.ac.uk, on quoting the depository number CCDC-101078, the names of the authors and journal citation.

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