On Alkylideneamidosulfenyl Chlorides and 1-Thia-2-azoniaallene Salts

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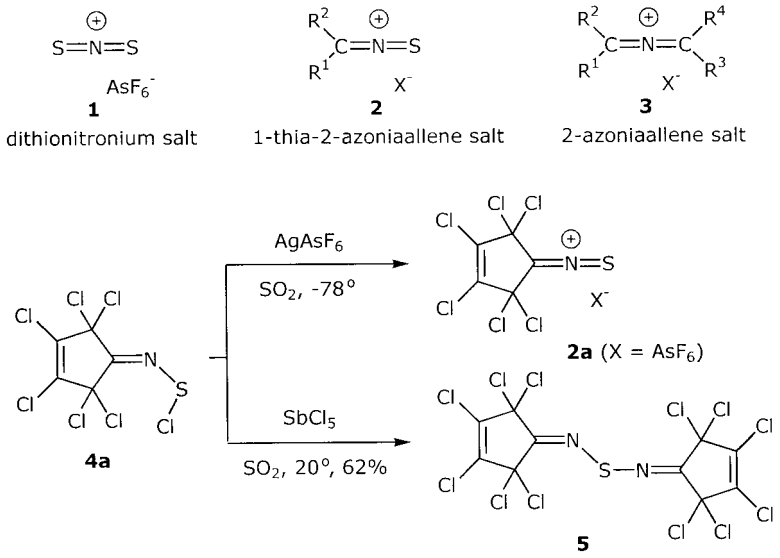
X-Ray-diffraction analysis of ^{t}Bu$_2$C=N–SCl (**4b**) revealed an almost linear C=N=S unit with an S=N bond order of *ca.* 1.9 (*Fig. 1*), in agreement with the structure of a 1-thia-2-azoniaallene chloride. With SCl_2 and $SbCl_5$, compound **4b** was transformed into the imidosulfurous dichloride **6** (*Scheme 2*). With morpholine, compounds **4b** and **6** afforded the sulfenamide **7**and the aminosulfonium salt **8**, respectively. The (diarylmethylene)amidosulfenyl chlorides **4g**,**h**,**i** reacted with $SbCl_5$ to give $SbCl_6^-$ salts of the 1,2-benzisothiazoles **9a**,**b**,**d**, most likely *via* 1-thia-2-azoniaallene intermediates **2** (*Scheme 3*).

Introduction. – While dithionitronium salts **1** [1–6] and many 2-azoniaallene salts **3** [7–15] are well-characterized stable compounds, little has been reported on 1-thia-2-azoniaallene salts **2** (*Scheme 1*). *Chivers* and co-workers isolated moisture-sensitive dark purple crystals as a product of the reaction of the amidosulfenyl chloride **4a** with $AgAsF_6$ [16]. Analytical data and ^{13}C- and ^{15}N-NMR and IR spectra were in agreement with the constitution **2a** (X = AsF_6). In solvents other than SO_2, the salt decomposed

Scheme 1

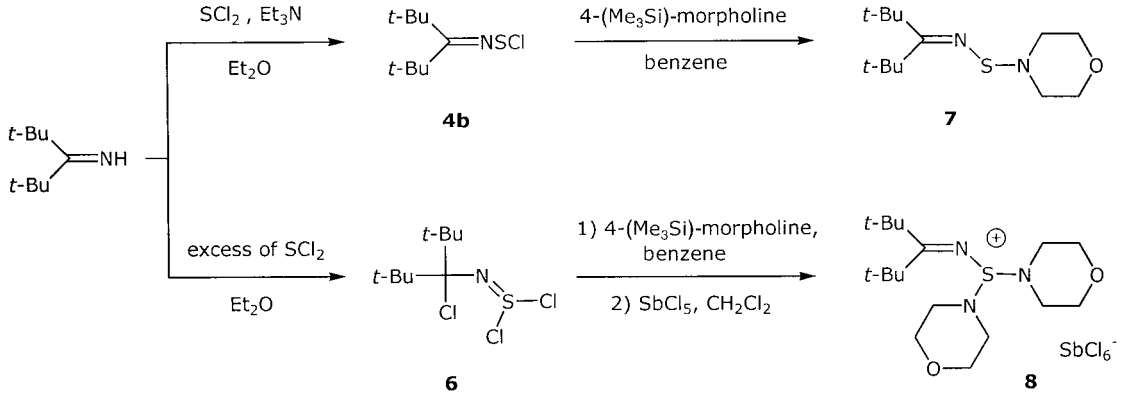


rapidly. *Haas* and *Mischo* obtained the sulfide **5** instead of a hexachloroantimonate **2a** ($X = SbCl_6$) on treatment of compound **4a** with antimony pentachloride in liquid SO_2 [17].

Here we describe observations relating to the ionic character (see **2**, $X = Cl$) of alkylideneamidosulfenyl chlorides **4**.

Results and Discussion. – With the exception of $(F_3C)_2C{=}NSCl$ [18–20], (dialkylmethylene)sulfenyl chlorides have not been reported. We obtained the alkylidenesulfenyl chloride **4b** by reaction of di(*tert*-butyl)ketimine with sulfur dichloride in the presence of Et_3N (*Scheme 2*) [21]. With excess sulfur dichloride in the absence of Et_3N, the imidosulfurous dichloride **6** was produced *via* **4b** [22]. Compound **4b** was characterized as the sulfenamide **7**, and the dichloride **6** as the sulfonium salt **8**. Experiments to transform the chloride **4b** into a salt with a non-nucleophilic anion, *e.g.*, $SbCl_6^-$, yielded mixtures of compounds.

Scheme 2



For the amidosulfenyl chloride **4b**, single-crystal X-ray structural analysis was carried out (*Fig. 1*, *Table 1*). For the purpose of comparison, the relevant molecular data from X-ray crystallographic analyses reported for the alkylideneamidosulfenyl halogenides **4s–f** are shown in *Fig. 2* [16][17][23][24].

Interesting features of structure **4b** are the almost linear C(1)–N–S unit, the rather short S–N bond, and the unusually long S–Cl distance of *ca.* 221 pm. The S–N bond length of **4b** (154.1(1) pm) was found to be intermediate between values reported for the S=N double bond in the dithionitronium ion $S{=}N^+{=}S$ (151.0 pm [3]) and the S–N single bonds in compounds **4c–e** (156–158 pm).

Using *Nyburg*'s equation, one calculates a S–N bond order of 1.90 for **4b**[1]). The S–Cl bond distance in SCl_2 has been reported to be 201.4(3) pm [27]. Slightly longer S–Cl bonds of 204 to 206 pm were found for the chlorides **4c–e**. The much larger S–Cl distance in **4b** (220.72(6) pm) suggests this compound to be essentially an ionic 1-thia-2-azoniaallene chloride. This view is further substantiated by the large observed S–N–C(1) bond angle of 161.7(1)°. The corresponding bond angles of the

[1]) For a bond length D_6 [Å], the following relation holds for the S–N bond order b(SN): $b(SN) = 0.429 + 6.85D_b - 3.825D_b^2$ [26].

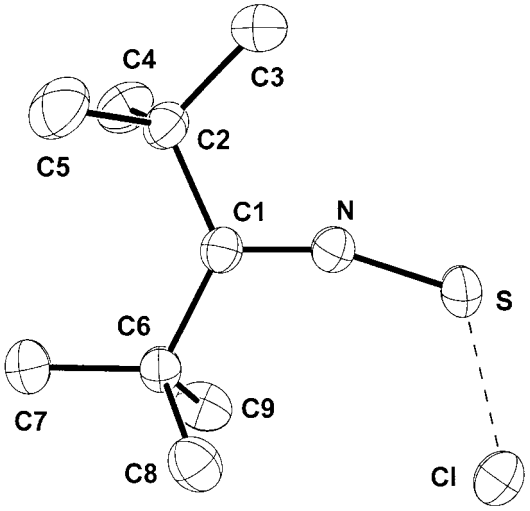


Fig. 1. *Displacement ellipsoid plot of the amidosulfenyl chloride* **4b**. Arbitrary numbering of the atoms; 50% probability ellipsoids; H-atoms are omitted for clarity.

Table 1. *Significant Bond Lengths* [pm], *Bond Angles* [°], *and Torsional Angles* [°] *for* **4b** *and Data Calculated by the AM1 Method*[a])

	Exper.	Calc. (AM1)		Exper.	Calc. (AM1)
S–Cl	220.72(6)	200	N–C(1)–C(2)	114.4(1)	118
S–N	154.1(1)	146	N–C(1)–C(6)	118.1(1)	120
N–C(1)	127.1(2)	128	Cl–S–N–C(1)	−0.9(4)	−1
C(1)–C(2)	154.2(2)	154	S–N–C(1)–C(2)	−173.6(3)	−175
C(1)–C(6)	155.0(2)	154	S–N–C(1)–C(6)	3.1(4)	2
Cl–S–N	119.79(5)	116	N–C(1)–C(2)–C(3)	−7.3(2)	−12
S–N–C(1)	161.7(1)	166	N–C(1)–C(6)–C(7)	174.5(2)	175

[a]) AM1 Calculations were carried out with complete optimization of all bond lengths, bond angles, and dihedral angles [25].

amidosulfenyl chlorides **4c**–**f** range between 137.4 and 147.3°. Also in agreement with a linear C=N$^+$=S unit of **4b** in solution is the observed equivalence of the Me groups in the ^{1}H- and ^{13}C-NMR spectra. For **4e**, a variable-temperature ^{13}C-NMR study revealed fluctional behavior, which was explained on the assumption of either hindered rotation about the S–N bond or inversion at the N-center [16]. No line-broadening down to −50° was observed in the NMR spectra of **4b**.

Structures **4c**–**f** all show *syn*-periplanar C=N and C–X (X = Br, Cl) bonds. This has been explained as a consequence of negative hyperconjugation, that is, electron donation from the in-plane nonbonding orbital at N into the antibonding σ^* orbital of the S–halogen bond [16][28][29]. The orbital overlap increases with increasing C–N–S angle and with the electron-donating efficiency of the substituents at the C–N–S unit. The partial occupancy of the σ^*_{SX} orbital results in a weak and long S–X bond. It has been pointed out that the overlap of the n_N and the σ^*_{SX} orbitals is much less favorable for *anti*-periplanar bonds C=N and C–X.

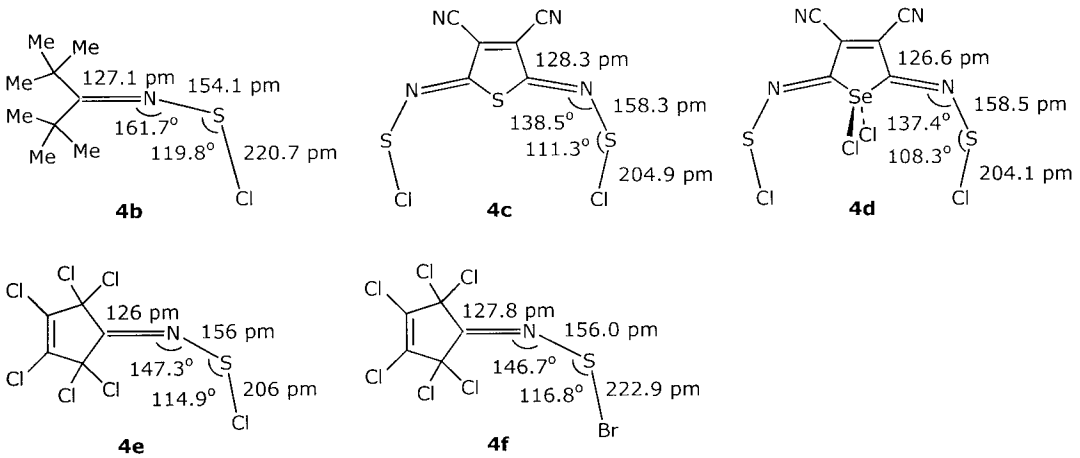


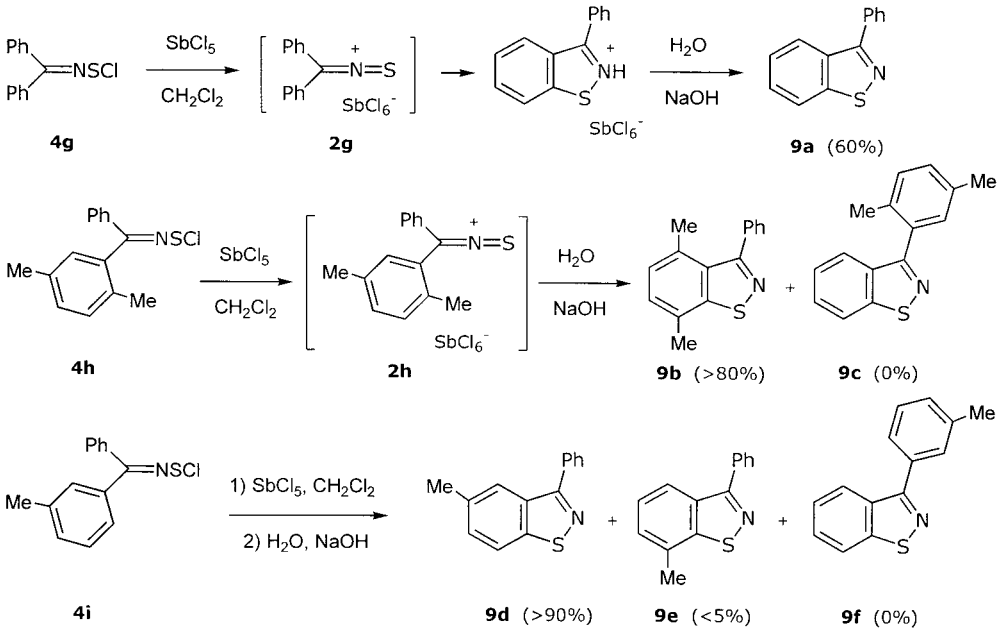
Fig. 2. *Selected molecular data from known X-ray crystallographic analyses* [16][17][23][24]

In conclusion, in contrast to alkylideneamidosulfenyl chlorides **4** with electron-withdrawing substituents, the chloride **4b** substituted with electron-releasing *tert*-butyl groups has the structure of an essentially ionic 1-thia-2-azoniaallene chloride **2**.

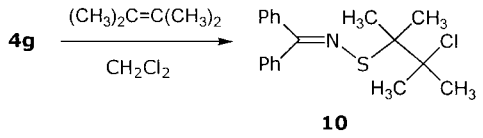
Treatment of the diphenyl derivative **4g** [21][30] with $SbCl_5$ resulted in the formation of a hexachloroantimonate, which, with aqueous NaOH solution, afforded the 1,2-benzisothiazole **9a** in 60% yield (*Scheme 3*) [31–34]. Moderate heating transformed **4g** into the hydrochloride of **9a**. Hence, in contrast to a literature report [21], the amidosulfenyl chloride **4g** cannot be purified by distillation. The formation of salts of **9a** likely proceeds *via* 1-thia-2-azoniaallene salts such as **2g**. From the corresponding reaction of the amidosulfenyl chloride **4h**, formation of the two 1,2-benzisothiazoles **9b**,**c** could be expected. In conformity with the mechanism of an intramolecular electrophilic aromatic substitution, only the more-activated dimethylphenyl moiety was attacked by the intermediate cation **2h** to afford compound **9b**. Similarly, from the methylphenyl derivative **4i**, mainly **9d** was formed. The NMR spectra of the crude product indicated the presence of small amounts of the isomer **9e** but not of **9f**. To the best of our knowledge, preparations of 1,2-benzisothiazoles **9** from amidosulfenyl chlorides **4** are unreported in the literature [35].

To test, whether 1-thia-2-azoniallene ions **2**, similar to other 2-azoniaallene ions [36][37], could act as cationic four-electron components in [3 + 2] cycloadditions with electron-rich alkenes, compound **4b** was treated with 2,3-dimethylbut-2-ene and trinorborn-2-ene. However, only tarry mixtures of products were obtained, while the diphenyl compound **4g** reacted with 2,3-dimethylbut-2-ene to afford the addition product **10** (*Scheme 4*). Chlorosulfenylations of alkenes with amidosulfenyl chlorides are well-documented [38–43].

Scheme 3



Scheme 4



We are indebted to Dr. *Martin Winkler* and to Prof. Dr. *Gerhard Müller* for their help concerning the X-ray structural analysis, and to Mr. *Siegfried Herzberger* for technical assistance.

Experimental Part

General. Solvents were dried by standard methods. All reactions were carried out with exclusion of moisture. IR Spectra: *Perkin-Elmer FTIR 1600*; in cm^{-1}. NMR Spectra: *Bruker AC-250* and *Jeol JNM-LA-400* (^1H at 250 or 400 MHz, ^{13}C at 62.9 or 100.6 MHz); 295 K; δ in ppm rel. to $SiMe_4$ as internal standard, J in Hz.

[1-(1,1-Dimethylethyl)-2,2-dimethylpropylidene]amidosulfenyl Chloride (**4b**). At 0°, a soln. of 2,2,4,4-tetramethylpentan-3-imine [44][45] (14.13 g, 100 mmol) and Et_3N (10.12 g, 100 mmol) in Et_2O (100 ml) was added dropwise to a soln. of SCl_2 (10.30 g, 100 mmol) in Et_2O (200 ml). After stirring at 0° for 30 min and then at 23° for 2 h, $Et_3N \cdot HCl$ was removed by filtration. Evaporation of the filtrate yielded an orange oil, which was dissolved in pentane (100 ml). Filtration and evaporation of the filtrate furnished a yellow semisolid residue, which was dissolved in Et_2O (50 ml). Slow evaporation of the solvent afforded yellow prisms of **4b** (2.01 g, 97%) suitable for X-ray structural analysis. B.p. 68–72°/0.1 Torr. Sublimation at 10^{-2} Torr furnished yellow prisms. M.p. 48–50°. IR (CCl_4): 2973*vs*, 2872*s*, 1481*vs*, 1463*s*, 1395*vs*, 1370*vs*, 1237*s*, 1210*m*, 1202*m*, 1049*m*, 1042*m*. ^1H-NMR ($CDCl_3$): 1.28 (Me). ^{13}C-NMR ($CDCl_3$): 29.5 (Me); 40.6 (C); 157.7 (C=N). Anal. calc. for $C_9H_{18}ClNS$ (207.8): C 52.03, H 8.73, N 6.74; found: C 51.03, H 8.56, N 6.49.

(Diphenylmethylene)amidosulfenyl Chloride (**4g**) [21][30]. At 5°, a soln. of α-phenylbenzenemethanimine [46] (18.12 g, 100 mmol) and Et_3N (10.12 g, 100 mmol) in toluene (50 ml) was added dropwise to a soln. of SCl_2

(10.30 g, 100 mmol) in toluene (150 ml). After stirring at 23° for 4 h, $Et_3N \cdot HCl$ was removed by filtration. Evaporation of the filtrate afforded a turbid orange-brown oil (21.98 g), which according to ^{1}H-NMR ($CDCl_3$) consisted mainly of **4g** (*ca.* 80%) and $Ph_2C{=}N{-}S{-}N{=}CPh_2$ (*ca.* 20%). The oil was dissolved in pentane (200 ml). Filtration from $Ph_2C{=}N{-}S{-}N{=}CPh_2$ and evaporation of the filtrate afforded **4g** (12.39 g, 50%). Orange-brown oil of > 90% purity. IR (CCl_4): 3064v*s*, 3033*s*, 1492v*s*, 1445v*s*, 1316v*s*, 1288v*s*, 1183*s*. ^{1}H-NMR ($CDCl_3$): 7.38 (br., Ph). ^{13}C-NMR ($CDCl_3$): 128.2, 128.6 (C_o, C_m); 129.7, 134.3 (C_{ipso}, C_p); 151.0 (C=N).

Attempts to purify **4g** by distillation [21] resulted in the formation of the hydrochloride of **9a**.

[1-Chloro-1-(1,1-dimethylethyl)-2,2-dimethylpropyl]imidosulfurous Dichloride (**6**). At 0°, a soln. of 2,2,4,4-tetramethylpentan-3-imine (14.13 g, 100 mmol) in CH_2Cl_2 (100 ml) was added dropwise to SCl_2 (100 g). After stirring at 23° for 3 h, the mixture was evaporated. The yellow mushy residue was suspended in Et_2O (40 ml). Filtration and evaporation of the filtrate afforded **6** (22.90 g, 82%). Yellow volatile oil for which a correct elemental analysis could not be obtained. IR (CCl_4): 2978v*s*, 1477v*s*, 1396v*s*, 1372v*s*, 1333v*s*. ^{1}H-NMR ($CDCl_3$): 1.29 (Me). ^{13}C-NMR ($CDCl_3$): 29.8 (Me); 46.4 (C); 106.9 (CCl). EI-MS (70 eV): 207 (13, $[M - Cl_2]^+$), 150 (42, $[^t$BuCNSCl$]^+$), 116 (47, $[^t$BuCHNS$]^+$). Anal. calc. for $C_9H_{18}Cl_3NS$ (278.7): C 38.79, H 6.51, N 5.03; found: C 39.64, H 6.53, N 6.03.

N-*[2,2-Dimethyl-1-(1,1-dimethylethyl)propylidene]morpholine-4-sulfenamide* (**7**). At 5°, a soln. of 4-(trimethylsilyl)morpholine [47] (0.80 g, 5 mmol) in benzene (100 ml) was added dropwise to a soln. of **4b** (1.04 g, 5 mmol) in benzene (5 ml). Stirring at 23° for 24 h, filtration, and evaporation of the filtrate yielded a brown residue, which was suspended in warm pentane (10 ml). Filtration, evaporation of the filtrate, followed by crystallization of the residue from petroleum ether afforded **7** (0.72 g, 56%). Colorless prisms. M.p. 97–99°. IR (CCl_4): 2961v*s*, 2911v*s*, 2854v*s*, 1572*s*, 1481v*s*, 1451v*s*, 1390v*s*, 1369v*s*. ^{1}H-NMR ($CDCl_3$): 1.23 (3 Me); 1.27 (3 Me); 3.21 (*m*, 2 CH_2); 3.73 (*m*, 2 CH_2). ^{13}C-NMR ($CDCl_3$): 28.2, 30.3 (Me); 41.7, 45.8 (C); 53.7, 67.6 (CH_2); 169.9 (C=N). Anal. calc. for $C_{13}H_{26}N_2OS$ (258.4): C 60.42, H 10.14, N 10.84; found: C 60.49, H 10.15, N 10.83.

{[2,2-Dimethyl-1-(1,1-dimethylethyl)propylidene]amino}di(morpholin-4-yl)sulfonium Hexachloroantimonate (**8**). From 4-(trimethylsilyl)morpholine (4.78 g, 30 mmol) and **6** (2.79 g, 10 mmol) as described for **7**. After stirring for 15 min, the precipitate was isolated by filtration and dissolved in CH_2Cl_2 (40 ml). At −30°, a soln. of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (40 ml) was added dropwise. Stirring was continued at −30° for 30 min, then at 0° for 30 min, and finally at 23° for 15 min. Et_2O (90 ml) was added dropwise. The precipitate was dissolved in CH_2Cl_2 (54 ml)/MeCN (16 ml). Filtration and slow addition of Et_2O (200 ml) to the filtrate afforded **8** (5.68 g, 84%). Colorless powder. M.p. 165–167° (dec.). IR (CH_2Cl_2): 1563v*s*. ^{1}H-NMR (CD_3CN): 1.45 (6 Me); 3.38–3.78 (several *m*, 8 CH_2). ^{13}C-NMR (CD_3CN): 30.4 (br., Me); 47.2 (br., C); 47.7, 67.2 (CH_2); 203.2 (C=N). Anal. calc. for $C_{17}H_{34}Cl_6N_3O_2SSb$ (679.0): C 30.07, H 5.05, N 6.19; found: C 29.96, H 5.01, N 6.16.

3-Phenyl-1,2-benzisothiazole (**9a**) [33][34]: At −40°, a soln. of $SbCl_5$ (1.50 g, 5 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a soln. of **4g** (1.24 g, 5 mmol) in CH_2Cl_2 (10 ml). The orange mixture was stirred at −40° for 30 min, then at 0° for 1 h. Filtration afforded the salt **9a** · $HSbCl_6$ (1.63 g, 60%). Orange powder. ^{1}H-NMR (CD_3CN): 7.67 (*m*, 4 arom. H); 7.85 (*m*, 3 arom. H); 8.26 (*m*, 3 arom. H); 11.81 (br., NH). ^{13}C-NMR (CD_3CN): 121.9, 127.4, 128.2, 130.2, 130.3, 132.0, 132.3, 132.5, 152.1 (arom. C); 166.0 (C=N).

The salt (2.73 g, 5 mmol) was dissolved in MeCN (20 ml). A soln. of NaOH (1.40 g, 35 mmol) in H_2O (20 ml) was added dropwise. Stirring at 23° for 30 min, filtration, concentration of the filtrate to 5 ml, extraction with $CHCl_3$ (3 × 15 ml), and workup afforded a powder, which crystallized at −15° from EtOH (3 ml) to furnish **9a** (0.55 g, 52%). Fawn-colored needles. M.p. 66–68° ([33]: m.p. 70°). IR (CCl_4): 3064*s*, 3030*m*, 1593*s*, 1470v*s*, 1443*s*, 1350v*s*, 1322*s*, 1305*s*. ^{1}H-NMR ($CDCl_3$): 7.40–8.18 (several *m*, arom. C). ^{13}C-NMR ($CDCl_3$): 119.9, 124.8, 125.0, 127.5, 128.7, 128.8, 129.3, 133.7, 135.2, 153.5, 164.3 (arom. C, C=N).

4,7-Dimethyl-3-phenyl-1,2-benzisothiazole (**9b**). a) At 0–5°, a soln. of 2,5-dimethyl-α-phenylbenzenemethanimine [48][2]) (20.93 g, 100 mmol) and Et_3N (10.12 g, 100 mmol) in Et_2O (100 ml) was added dropwise to a soln. of SCl_2 (10.30 g, 100 mmol) in Et_2O (200 ml). After stirring at 5° for 24 h, $Et_3N \cdot HCl$ was removed by filtration and washed with Et_2O. Evaporation afforded an orange oil, which was taken up in pentane (100 ml). Filtration and evaporation of the filtrate furnished an orange oily mixture of compounds (25.94 g) containing *[(2,5-dimethylphenyl)phenylmethylene]amidosulfenyl chloride* (**4h**; *ca.* 75%). ^{1}H-NMR ($CDCl_3$): 2.16, 2.34 (Me); 6.98–7.64 (several *m*, arom. C). ^{13}C-NMR ($CDCl_3$): 18.86, 20.95 (Me); 152.02 (C=N).

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[2]) Prepared in the manner described for benzophenone imine (= α-phenylbenzenemethanimine) [46] from 2,5-dimethylbenzonitrile and bromobenzene. Yield 83%. B.p. 124–126°/0.02 Torr. ^{1}H-NMR ($CDCl_3$): 2.07, 2.32 (Me). ^{13}C-NMR ($CDCl_3$): 19.27, 20.87 (Me); 179.00 (C=N).

Table 2. *Crystallographic Data of Compound* **4b**

Crystallized from	Et_2O
Empirical formula	$C_9H_{18}ClNS$
Formula weight [g mol^{-1}]	207.75
Crystal color, habit	yellow, prisms
Crystal dimensions [mm]	$0.50 \times 0.20 \times 0.20$
Temp. [K]	183
Crystal system	triclinic
Space group	*P*-1 (No. 2)
Z	2
Reflections for cell determination	25
θ Range for cell determination [°]	2.20–27.50
Unit-cell parameters *a* [pm]	814.7(2)
b [pm]	842.7(2)
c [pm]	903.1(2)
α [°]	96.68(1)
β [°]	94.65(1)
γ [°]	109.07(1)
V [pm^3]	$577.3(2) \cdot 10^6$
D_x [g cm^{-3}]	1.195
$\mu(\mathrm{Mo}K_\alpha)$ [m^{-1}]	466
$\theta_{(\max)}$ [°]	17.97
Total reflections measured	2824
Symmetry-independent reflections	2637
Reflections used [$I > 2\sigma(I)$]	2175
Parameters refined	181
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0297$, $wR_2 = 0.0775$
R indices (all data)	$R_1 = 0.0443$, $wR_2 = 0.0837$
Goodness-of-fit on F^2	1.017
$\Delta\rho$ (max; min) [10^{-6} e pm^{-3}]	0.291; −0.338

b) At −40°, a soln. of $SbCl_5$ (29.90 g, 100 mmol) in CH_2Cl_2 (150 ml) was added dropwise to a soln. of crude **4h** (27.58 g, 100 mmol) in CH_2Cl_2 (150 ml). At 5°, the salt **9b** · $HSbCl_6$ soon started to crystallize. ^{1}H-NMR (CD_3CN): 2.23, 2.66 (Me); 12.00 (br., NH). ^{13}C-NMR (CD_3CN): 20.05, 20.78 (Me); 129.67, 129.79, 129.93, 130.07, 130.36, 132.27, 133.29, 136.01, 138.90, 151.58 (arom. C); 169.66 (C=N).

After 12 h at 5°, evaporation afforded **9b** · $HSbCl_6$ as a pale brown solid, which was dissolved in MeCN (250 ml). A soln. of NaOH (28.00 g, 700 mmol) in H_2O (250 ml) was added dropwise. After stirring for 30 min, MeCN was distilled off, and the remaining aq. mixture was repeatedly extracted with $CHCl_3$. Workup of the combined org. extracts afforded a brown oil, which was dissolved in AcOEt (100 ml). Filtration, evaporation of the filtrate, and crystallization at −15° of the oily residue from AcOEt (10 ml)/Et_2O (10 ml) furnished **9b** (7.18 g, 30%). Yellow prisms. M.p. 83–84°. IR (CCl_4): 3064*s*, 3028*s*, 2977*s*, 2928*s*, 2861*m*, 1581*s*, 1481v*s*, 1458v*s*, 1445v*s*, 1382*s*, 1348v*s*, 1318*s*. ^{1}H-NMR ($CDCl_3$): 2.16, 2.59 (Me); 7.08–7.20 (2*m*, H–C(5), H–C(6)); 7.48 (br., Ph). ^{13}C-NMR ($CDCl_3$): 19.89, 20.97 (Me); 127.56, 127.66, 127.75, 128.02, 128.71, 129.08, 132.99, 133.08, 138.19, 154.33 (arom. C); 166.73 (C=N). Anal. calc. for $C_{15}H_{13}NS$ (239.3): C 75.27, H 5.48, N 5.85; found: C 74.89, H 5.29, N 5.77.

5-Methyl-3-phenyl-1,2-benzisothiazole (**9d**) [49]: a) *[(3-Methylphenyl)phenylmethylene]amidosulfenyl chloride* (**4i**) was prepared from (3-methyl-α-phenylbenzenemethanimine [48][3]) (19.53 g, 100 mmol) as described for **4h**. The resulting brown oil of **4i** (24.56 g) was contaminated with (3-MeC_6H_4)C(Ph)=N–S–N=

[3]) Prepared in the manner described for 'benzophenone imine' [46] from 3-methylbenzonitrile and bromobenzene. Yield 78%. B.p. 115–119°/0.03 Torr. ^{1}H-NMR ($CDCl_3$): 2.37 (Me). ^{13}C-NMR ($CDCl_3$): 21.34 (Me); 178.39 (C=N).

C(Ph)(3-MeC_6H_4) (*ca.* 10%). ^{1}H-NMR ($CDCl_3$): 2.33 (Me); 7.36 (*s*, arom. H); 7.13–7.40 (several *m*, arom. H). ^{13}C-NMR ($CDCl_3$): 21.36 (Me); 125.74–137.82 (10 signals, arom. C); 151.11 (C=N).

b) At −40°, a soln. of $SbCl_5$ (29.90 g, 100 mmol) in CH_2Cl_2 (150 ml) was added dropwise to a soln. of crude **4i** (26.18 g, 100 mmol) in CH_2Cl_2 (150 ml). At 5°, **9d**·$HSbCl_6$ started to crystallize. ^{1}H-NMR (CD_3CN): 2.59 (Me); 7.75–7.95 (6 arom. H); 8.25 (*s*, H–C(4)); 8.31 (*d*, 1 H); 12.61 (br., NH). ^{13}C-NMR (CD_3CN): 21.49 (Me); 122.40–147.67 (10 signals, arom. C); 166.36 (C=N).

After 12 h at 5°, the solvent was evaporated. Neutralization of the residue was carried out as described for **9b**: **9d** (21.40 g, 95%). Dark brown oil, which crystallized at 5°. Two crystallizations from either MeOH or hexane furnished pale yellow needles. M.p. 72–74° ([49]: m.p. 70°). IR (CCl_4): 3065*s*, 2925*s*, 1901*w*, 1607*m*, 1478v*s*, 1446*s*, 1420*s*, 1349v*s*, 1295v*s*. ^{1}H-NMR ($CDCl_3$): 2.50 (Me); 7.35–7.86 (several *m*, 7 arom. H); 7.94 (*s*, H–C(4)). ^{13}C-NMR ($CDCl_3$): 21.44 (Me); 119.51, 124.27, 128.67, 128.76, 129.21, 129.53, 134.25, 134.97, 135.31, 150.98 (arom. C); 163.91 (C=N).

*3-Chloro-*N*-(diphenylmethylene)-2,3,3-trimethylbutane-2-sulfenamide* (**10**). At −20°, a soln. of 2,3-dimethylbut-2-ene (1.01 g, 12 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a soln. of **4g** (2.48 g, 10 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at −20° for 1 h and then at 0° for 1 h. Evaporation and crystallization of the residue from hexane (40 ml) afforded **10** (2.98 g, 90%). Fine prisms. At 25°, a soln. of **10** in $CDCl_3$ slowly decomposed. M.p. 110–112° (dec.). IR (CCl_4): 1491v*s*, 1457*s*, 1444v*s*, 1379v*s*, 1371*s*. ^{1}H-NMR ($CDCl_3$): 1.65 (2 Me); 1.76 (2 Me); 7.28–7.55 (10 arom. H). ^{13}C-NMR ($CDCl_3$): 24.1 (2 Me); 29.8 (2 Me); 58.2 (C); 78.6 (C); 127.3, 127.5, 128.1, 128.7, 128.9, 129.1, 137.8, 139.3 (Ph); 161.1 (C=N). Anal. calc. for $C_{19}H_{22}ClNS$ (331.9): C 68.76, H 6.68, N 4.22; found: C 68.65, H 6.63, N 4.43.

Crystal-Structure Determination of **4b** (see *Table 2* and *Fig. 1*)[4]): All measurements were performed on an *Enraf-Nonius-CAD4* diffractometer with graphite-monochromated MoK_α radiation (λ 71.069 pm). The $\omega/2\theta$ scan mode was employed for data collection. Data collection and refinement parameters are given in *Table 2*, and a view of the molecule is shown in *Fig. 1*. The structure was solved by direct methods with subsequent difference *Fourier* synthesis and full-matrix least-squares refinement on F^2 by using the programs SHELXS-86 and SHELXL-93, resp. [50], which revealed the positions of all non-H- and H-atoms.

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[4]) Crystallographic data for the structure **4b** reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-180463. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)-(0)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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