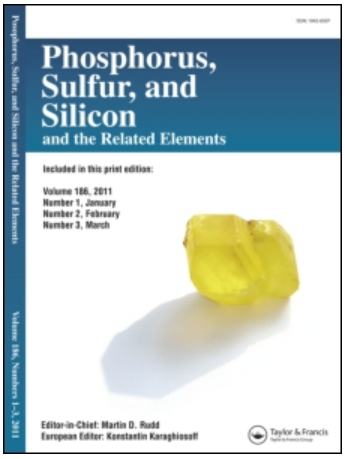

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PREPARATION AND CHARACTERIZATION OF NEW *C*-SULFONYLDITHIOFORMATES AND THEIR THIOCARBONYL *S*-IMIDES

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PREPARATION AND CHARACTERIZATION OF NEW *C*-SULFONYLDITHIOFORMATES AND THEIR THIOCARBONYL *S*-IMIDES

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Two new chlorodithioformates **2**, six new *C*-sulfonyldithioformates **3**, ten new chloromethanesulfenyl chlorides **4**, and nineteen new *C*-sulfonyldithioformate *S*-imides **5** have been prepared. Together with analogous known compounds they were fully characterized by spectroscopic means (IR, UV/VIS, MS, ^{1}C and ^{13}C NMR). According to these data and additional X-ray crystallographic structure determinations of selected **5** all known **5** possess the (*E*)-configuration and no evidence for the presence of isomeric (*Z*)-**5** could be found.

Key words: Chlorodithioformates, α-chloromethanesulfenyl chlorides, *C*-sulfonyldithioformate *S*-imides, *C*-sulfonyldithioformates, thiocarbonyl *S*-imides.

INTRODUCTION

While dithioformic acid esters **1**, X-CS-SR^1 (X = H), are subject to spontaneous trimerization and thus unattractive for synthetic purposes a number of analogs with an electron-withdrawing *C*-substituent, **1** (X = EWG), display shelf stability on one hand and synthetically useful thiocarbonyl reactivity on the other hand. Notable examples are the chlorodithioformates **2** [**1** (X = Cl)],[3] the cyanodithioformates **1** (X = CN),[4] the dialkyl/arylphosphonodithioformates **1** [X = $(R^2O)_2PO$],[5] and, finally, the *C*-sulfonyldithioformates **3** [**1** (X = R^2SO_2)] which were developed in our Århus laboratory.[6,7]

Further derivatization of **3** led to the corresponding thiocarbonyl *S*-imides **5** [R^2SO_2—C(=S=NR^3)—SR^1]. The known isolable dithioester thiocarbonyl *S*-imides fall in two categories: the stability of dithioester thiocarbonyl *S*-imides with an electron-poor thiocarbonyl carbon atom is achieved by delocalization of the partial negative charge on the nitrogen atom by a −M substituent (such as acyl or sulfonyl) on the nitrogen; in their electron-rich counterparts the presence of a bulky +I substituent on the nitrogen imparts stability by steric hindrance. A rigorous assessment of the relative importance of the mesomeric, inductive, and steric effects of the substituents present in **5** must await the outcome of further experimental scrutiny of the type carried out in the present study.

The purpose of the work presented in this paper was to extend the range of known **3** and **5**, to provide further insight into the reactivity of these two groups of compounds, and, finally, to study the E,Z-isomerism of **5**.

As far as the latter problem is concerned a previous single-crystal X-ray structure determination has established the *E*-configuration of the only observed isomer of **5t**,[8] and we now wished to examine systems where the relative sizes of the R^1S and R^2SO_2 groups are reversed (the NR^3 group being kept as bulky as possible) in order to observe cases where the E- and the Z-isomer are of comparable stability.

Another intriguing point to be addressed by the present work was the question of the relative reactivities of the C=S double bonds of **3** and **5**, respectively.

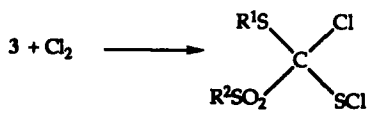
All dithioester thiocarbonyl *S*-imides described in the literature except the two **5** described so far,[8,9] are characterized by an electron-withdrawing substituent on the nitrogen. One additional thiocarbonyl *S*-imide with a tertiary alkyl substituent on nitrogen has been described.[10]

The synthesis of dithioester thiocarbonyl *S*-imides was first accomplished by Tamagaki, Oae, *et al.*[11] by treatment of 1,2-dithiole-3-thiones with *N*-chloramine salts. By a similar method Zwanenburg *et al.*[12,13] obtained the first geometrical isomers of thiocarbonyl *S*-imides, stabilized by steric hindrance, by imination of sulfines. Five- and six-membered heterocyclic thiocarbonyl *S*-imides have been prepared by Motoki *et al.*[14,15] Boberg, Wentrup, *et al.*[16–19] reported the synthesis of trithione *S*-imides from *N*,*N*-di- or *N*-monochloro substituted benzamides. Similarly, Senning *et al.*[8,9] synthesized thermally stable thiocarbonyl *S*-(*N*-*t*-butylimides) **5** by the reaction of the corresponding α-chloro sulfenyl chlorides **4** with *t*-butylamine.

The required aliphatic chlorodithioformates **2** are prepared by the reaction of thiophosgene with aliphatic thiols with[20] or without [3,21–30] catalyst. The synthesis of aromatic **2** involves the reaction of thiophosgene with aromatic thiols under basic conditions[3,25,27,31,32] or the reaction of carbon disulfide with aryldiazonium chlorides.[33,34] The corresponding strongly colored (deep red to violet) *C*-sulfonyldithioformates[6] **3** have been prepared according to (1) by two-phase reaction between aqueous sulfinate anions and **2**, dissolved in

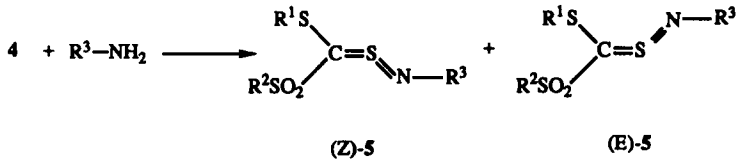
2 **3** (1)

benzene, with tetrabutylammonium hydrogen sulfate as a phase transfer catalyst[7,35] or by treatment of anhydrous sodium sulfinates, suspended in dry *N*,*N*-dimethylformamide, with **2**.[35] The properties of **3** have been investigated.[9,35–40] Chlorination of **3** according to (2) leads



4 (2)

to the corresponding α-chloro sulfenyl chlorides **4**[9,41] which react with excess *t*-alkylamines according to (3) to form *C*-sulfonyldithioformate thiocarbonyl *S*-[*N*-(*t*-alkyl)imides] **5**.[8,9,39]



(3)

The characteristically (usually yellow, orange or red) colored dithioester thiocarbonyl *S*-imides[42,43] are a class of heterocumulenes with a central tetravalent sulfur atom. Their bent structure gives rise to *E,Z*-isomerism as is also the case with their close analogs, the thiocarbonyl *S*-oxides (sulfines).[44]

RESULTS AND DISCUSSION

In the present study two new chlorodithioformates, **2a** and **2b**, were prepared. Reaction of **2b–j** (see also Table 1 with previously unreported spectral data for these compounds) with sulfinate ions in benzene/water with tetrabutylammonium hydrogen sulfate as a phase transfer catalyst led to the new **3a–f** (see Table 2a) and the known **3g–q** (see Table 2b for the spectral data of **3a–q**). The corresponding reaction of **2a** with alkane- and arenesulfinates failed, presumably due to steric hindrance. Compounds **3a–c**, **3e**, **3g–j**, **3l**, and **3n** were chlorinated to give the new **4a–j** as well as the known **4k** [see Tables 3a (for preparative details) and 3b (for spectral data)]. Finally, reaction of **4a–k** with primary *t*-alkylamines gave the corresponding new thiocarbonyl *S*-imides **5a–s** as well as the known (*E*)-**5t** [see Tables 4a (for preparative details) and 4b (for spectral data)]. The chloromethanesulfenyl chlorides **4b**, **4i**, and **4j** slowly rearrange upon standing at room temperature or during attempted recrystallization and should be used immediately without purification.[45]

Special attention was paid to the ^{13}C NMR spectroscopic characterization of both known and new compounds in the present investigation. A comparison of $\delta_{C=S}$ of **3** [from 214 ppm (for **3b**) to 225 ppm for (**3m**), see Table 2b] and **2** [(from 189 ppm (for **2g**) to 198 ppm (for **2e**), see Table 1] shows the effect of the strongly electron-withdrawing sulfonyl group of **3** on one hand and the shielding influence of the chlorine atom of **2** on the other hand.

The ^{13}C NMR signals of the α carbon atoms of **4** (see Table 3b; previously no ^{13}C NMR spectra of **4** had been recorded) lie between 93.80 (for **4i**) and 100.26 (for **4f**) ppm.

Most dithioester thiocarbonyl *S*-imides described in the literature contain an electron-withdrawing substituent on the nitrogen atom which stabilizes the resonance forms **D** and **E** by delocalization of the negative charge on the nitrogen atom. Due to their +I substituent on nitrogen our thiocarbonyl *S*-imides **5a–t** are better described by the resonance forms **A**, **B**, and **C** as evident from the fact that their ^{13}C NMR $\delta_{C=S}$ signals lie in the aromatic range [i.e. from 125.90 (for **5g**) to 142.03 (for **5p**)] as expected for sp^2 carbon atoms of high electron density and far from the ^{13}C NMR $\delta_{C=S}$ signals ($\approx$168 ppm) of dithioester thiocarbonyl *S*-imides which contain an electron-withdrawing substituent on the nitrogen atom and are best

TABLE 1

The spectral properties of chlorodithioformates **2**

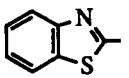
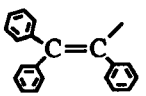
Cpd.	R^1	^1H NMR ($CDCl_3$) δ (ppm)	^{13}C NMR ($CDCl_3$) δ (ppm)	MS (70 eV) *m/z*
2a		7.55 (m, 2H); 7.95 (d, 1H); 8.15 (d, 1H)	121.76, 124.32, 126.99, 127.06, 137.23, 152.52, 158.02, 190.63 (*C*=S)	245 (M^+), 210, 169, 166, 134, 108, 76
2b		6.96-7.43 (m, 15H)	127.52, 127.73, 127.84, 128.03, 128.25, 128, 52, 128.83, 130.67, 131.13, 131.27, 137.58, 140.76, 142.30, 154.14, 194.04 (*C*=S)	366 (M^+), 331, 290, 287, 255, 178
2c[3,31]	C_6H_5	7.52 (s, 5H)	129.90, 134.43, 131.17, 131.83, 197.28 (*C*=S)	188 (M^+), 153, 109, 77
2d[3,27]	4-$O_2NC_6H_4$	7.70 (d, 2H); 8.33 (d, 2H)	124.93, 135.81, 138.82, 149.37, 194.65 (*C*=S)	233 (M^+), 198, 154, 138, 122, 108, 76
2e[3,25]	4-$CH_3C_6H_4$	2.45 (s, 3H); 7.31-7.43 (m, 4H); 7.62	21.18, 128.55, 130.59, 134.22, 141.60, 197.66 (*C*=S)	202 (M^+), 167, 123, 91, 76,
2f[32]	2,4,5-$Cl_3C_6H_2$	7.66 (s, 1H); 7.68 (s, 1H)	128.90, 129.30, 130.30, 131.80, 132.00, 137.60, 192.10 (*C*=S)	255 (M^+ – Cl), 179, 176, 83, 81, 79
2g[32]	C_6Cl_5	-	123.80, 133.20, 137.80, 138.52, 189.50 (*C*=S)	323 (M^+ – Cl), 279, 247, 212, 177, 142, 107, 76, 72
2h[3,27,30]	$(CH_3)_2CH$	1.37 (d, 6H); 3.75 (septet, 1H)	20.63, 45.54, 196.58 (*C*=S)	154 (M^+), 119, 112, 79, 76, 43
2i[3,33]	4-ClC_6H_4	7.40-7.53 (m, 4H); 7.32 (d, 2H)	129.81, 130.14, 135.75, 136.71, 196.33 (*C*=S)	222 (M^+), 187, 143, 111, 108, 83, 79, 76
2j[3,25]	CH_3	2.58 (s, 3H)	23.00, 198.10 (*C*=S)	126 (M^+), 91, 76, 59

TABLE 2a

The preparation of *C*-sulfonyldithioformates **3**

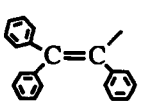
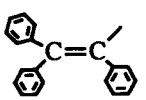
Cpd.	R^1	R^2	Reaction time (min)	Yield (%)	M.p. (°C) (solvent of recrystallization)	Molecular formula (M.wt.)	Analysis - calcd/found C	H	Cl	S
3a	C_6H_5	1-adamantyl	15	73	169-170 (acetonitrile)	$C_{17}H_{20}O_2S_3$ (352.33)	57.94 57.93	5.67 5.69	— —	27.29 26.96
3b	C_6Cl_5	1-adamantyl	10	78	238.5-239.5 (benzene)	$C_{17}H_{15}Cl_5O_2S_3$ (524.58)	38.92 39.00	2.85 2.94	33.78 33.43	18.33 18.23
3c	4-ClC_6H_4	4-$CH_3C_6H_4$	10	83	128-129 (acetonitrile)	$C_{14}H_{11}ClO_2S_3$ (342.75)	49.05 49.05	3.20 3.24	10.34 10.71	28.06 27.55
3d	4-ClC_6H_4	1-adamantyl	15	64	224-225 (acetonitrile)	$C_{17}H_{19}ClO_2S_3$ (386.78)	52.78 52.69	4.91 4.92	9.16 9.41	24.86 24.60
3e	4-$CH_3C_6H_4$	C_6H_5	15	77	91-92 diethyl ether	$C_{14}H_{12}O_2S_3$ (308.30)	54.53 54.56	3.89 3.97	— —	31.19 30.82
3f		4-$CH_3C_6H_4$	60	88	208-211 (methylene chloride/ether 1:3)	$C_{28}H_{22}O_2S_3$ (486.44)	69.13 68.66	4.52 4.74	— —	19.77 19.31

TABLE 2b

The spectral properties of *C*-sulfonyldithioformates **3**

Cpd.	R^1	R^2	^1H NMR ($CDCl_3$) δ (ppm)	^{13}C NMR ($CDCl_3$) δ (ppm)	IR (KBr) (cm^{-1}) ν_{SO_2}	$\nu_{C=S}$	MS (70 eV) *m/z*
3a	C_6H_5	1-adamantyl	1.71 (s, 6H); 2.19 (s, 9H); 7.38 (m, 2H); 7.54 (m, 3H)	28.34, 35.44, 35.54, 64.14, 129.69, 130.49, 131.30, 134.04, 220.31 (*C*=S)	1140 1300	1115	352 (M^+), 302, 262, 244, 218, 179, 153, 135, 107
3b	C_6Cl_5	1-adamantyl	1.70 (s, 6H); 2.20 (s, 9H)	28.38, 35.41, 35.45, 64.86, 130.13, 133.52, 137.27, 137.77, 213.77 (*C*=S)	1146 1340	1127	522 (M^+), 490, 427, 323, 247, 179, 135
3c	4-ClC_6H_4	4-$CH_3C_6H_4$	2.32 (s, 3H); 7.47 (m, 6H); 7.93 (d, 2H)	21.59, 127.14, 130.05, 130.15, 130.67, 133.21, 135.54, 137.90, 146.36, 223.92 (*C*=S)	1155 1320	1125	342 (M^+), 330, 298, 286, 266, 187, 167, 155, 143, 139, 123, 111, 107
3d	4-ClC_6H_4	1-adamantyl	1.70 (s, 6H); 2.18 (s, 9H); 7.30 (d, 2H); 7.50 (d, 2 H)	28.35, 35.45, 35.55, 64.29, 128.01, 130.87, 135.45, 137.97, 220.23 (*C*=S)	1144 1308	1120	386 (M^+), 278, 187, 179, 143, 135, 111, 108, 93
3e	4-$CH_3C_6H_4$	C_6H_5	2.38 (s, 3H); 7.25 (m, 4H); 7.56 (m, 2H); 7.67 (d, H); 8.07 (d, 2H)	21.32, 125.17, 129.37, 130.02, 131.23, 134.00, 134.75, 136.77, 142.03, 224.07 (*C*=S)	1155 1320	1120	308 (M^+), 290, 264, 248, 246, 232, 167, 135, 123
3f		4-$CH_3C_6H_4$	2.41 (s, 3H); 7.12 (m, 17H); 7.63 (d, 2H)	21.68, 127.73, 127.86, 127.99, 128.25, 128.35, 128.44, 128.54, 129.08, 129.57, 129.95, 130.76, 130.78, 133.72, 136.43, 140.75, 142.15, 145.48, 155.53, 218.58 (*C*=S)	1110 1235	1080	486 (M^+), 331, 287, 255, 155
3g[7]	4-$O_2NC_6H_4$	4-$CH_3C_6H_4$	2.44 (s, 3H); 7.38 (d, 2H); 7.57 (d, 2H); 7.93 (d, 2H); 8.30 (d, 2H)	21.64, 125.11, 130.13, 130.29, 130.72, 135.51, 136.50, 146.72, 149.43, 222.74 (*C*=S)	1157 1355	1120	353 (M^+), 352, 309, 277, 246, 148, 139, 122, 107

3h[7]	C_6Cl_5	4-ClC_6H_4	7.55 (d, 2H); 8.00 (d, 2H);	129.22, 130.02, 130.27, 131.33, 133.52, 134.58, 137.98, 142.38, 216.32 (*C*=S)	1160 1340	1123	466 (M^+ - S), 463, 434, 422, 323, 251, 247, 212, 159,175, 111
3i[7]	C_6Cl_5	C_6H_5	7.50 (m, 3H); 7.90 (d, 2H)	128.37, 129.61, 129.94, 133.41, 135.16, 136.10, 137.80, 137.99, 216.90 (*C*=S)	1157 1345	1123	464 (M^+ - CS_2), 429, 323, 212, 141, 125, 77, 60
3j[7]	2,4,5-$Cl_3C_6H_2$	4-$CH_3C_6H_4$	2.44 (s, 3 H); 7.37 (d, 2H); 7.51 (s, H); 7.62 (s, H); 7.93 (d, 2H)	21.66, 127.93, 130.01, 130.12, 130.27, 132.27, 132.59, 132.95, 137.14, 137.69, 146.60, 220.18 (*C*=S)	1158 1336	1122	410 (M^+), 334, 350, 255, 211, 179, 139, 123
3k[7]	C_6H_5	4-ClC_6H_4	7.35 (m, 2H); 7.51 (m, 5H); 8.01 (d, 2H)	128.44, 129.77, 129.77, 130.46, 131.42, 134.18, 135.02, 141.87, 222.99 (*C*=S)	1160 1336	1123	328 (M^+), 284, 175, 155
3l[7,35]	C_6Cl_5	4-$CH_3C_6H_4$	2.46 (s, 3H); 7.36 (d, 2H); 7.95 (d, 2H)	21.67, 129.48, 129.93, 130.31, 132.81, 133.31, 137.66, 137.95, 146.71, 217.40 (*C*=S)	1160 1340	1130	446 (M^+ - S), 323, 246, 155, 139, 91
3m[35]	CH_3	4-$CH_3C_6H_4$	2.42 (s, 3H); 2.64 (s, 3H); 7.33 (d, 2H); 7.89 (d, 2H)	21.02, 21.62, 130.06, 130.43, 133.53, 146.14, 224.88 (*C*=S)	1160 1330	1120	246 (M^+), 202, 186, 167, 155, 139, 135, 123, 91
3n[7,35]	$(CH_3)_2CH$	4-ClC_6H_4	1.40 (d, 6H); 3.75 (septet, H); 7.50 (d, 2H); 7.92 (d, 2H	20.62, 43.86, 129.97, 131.40, 135.11, 141.70, 221.18 (*C*=S)	1163 1328	1122	294 (M^+), 286, 262, 251, 250, 175, 159, 114, 111
3o[7,35]	C_6H_5	C_6H_5	7.50 (m, 8H); 8.07 (d, 2H)	128.47, 129.33, 129.84, 130.31, 131.27, 134.05, 134.77, 136.41, 223.47 (*C*=S)	1155 1327	1120	294 (M^+), 218, 153, 141, 125, 121, 109, 77
3p[35]	4-ClC_6H_4	4-ClC_6H_4	7.28 (d, 2H); 7.45 (d, 2H); 7.53 (d, 2H); 7.98 (d, 2H)	126.77, 129.85, 130.84, 131.46, 134.84, 135.54, 138.26, 142.05, 222.79 (*C*=S)	1155 1319	1123	362 (M^+), 330, 318, 286, 254, 187, 159, 143, 111, 108
3q[7,35]	C_6H_5	4-$CH_3C_6H_4$	2.4 (s, 3H); 7.38 (m, 7H); 7.92 (d, 2H)	21.44, 128.54, 129.80, 130.00, 130.21, 130.14, 132.19, 133.96, 146.13, 224.01 (*C*=S)	1152 1325	1120	308 (M^+), 200, 155, 153, 139, 123, 109, 91, 77, 60

TABLE 3a

The preparation of α-chloromethanesulfenyl chlorides **4**

Cpd.	R^1	R^2	Yield (%)	M.p. (°C) (solvent of recrystallization)	Molecular formula (M.wt.)	Analysis – calcd/found C	H	Cl	N	S
4a	C_6Cl_5	C_6H_5	88	167-169 (CH_2Cl_2/ether 1:3)	$C_{13}H_5Cl_7O_2S_3$ (537.44)	29.05 28.98	0.93 0.96	46.17 46.16	— —	17.89 17.61
4b	C_6Cl_5	1-adamantyl	85	135-136.5 (CH_2Cl_2/ether 1:3)	$C_{17}H_{15}Cl_7O_2S_3$ (595.48)	34.28 34.24	2.51 2.52	41.67 41.75	— —	16.15 15.85
4c	4-ClC_6H_4	4-$CH_3C_6H_4$	82	133-135 (CH_2Cl_2/ether 1:3)	$C_{14}H_{11}Cl_3O_2S_3$ (413.65)	40.64 40.48	2.65 2.85	25.71 25.59	— —	23.25 23.11
4d	C_6Cl_5	4-$CH_3C_6H_4$	87	168-170 (CH_2Cl_2/ ether 1:1)	$C_{14}H_7Cl_7O_2S_3$ (551.45)	30.49 30.06	1.26 1.32	44.90 44.79	— —	17.44 16.90
4e	4-$CH_3C_6H_4$	C_6H_5	89	113-114 (CH_2Cl_2/ether 1:3)	$C_{14}H_{12}Cl_2O_2S_3$ (379.20)	44.69 44.49	3.16 3.22	18.69 19.14	— —	25.36
4f	C_6Cl_5	4-ClC_6H_4	83	175-177 (CH_2Cl_2/ether 1:2)	$C_{13}H_4Cl_8O_2S_3$ (572.89)	27.30 27.47	0.69 0.74	49.58 49.53	— —	16.81 16.66
4g	2,4,5-$Cl_3C_6H_2$	4-$CH_3C_6H_4$	88	124-126 (CH_2Cl_2/ether 1:3)	$C_{14}H_9Cl_5O_2S_3$ (482.55)	34.84 34.17	1.86 1.85	36.73 36.89	— —	19.93 18.78

4h	$4\text{-}O_2NC_6H_4$	$4\text{-}CH_3C_6H_4$	79	139-140 (CH_2Cl_2/ether 1:4)	$C_{14}H_{11}Cl_2NO_4S_3$ (424.18)	39.63 39.87	2.59 2.67	16.71 17.08	3.30 3.34	22.67 22.51
4i	C_6H_5	1-adamantyl	78	129-130 (diethyl ether)	$C_{17}H_{20}Cl_2O_2S_3$ (423.23)	48.24 48.05	4.72 4.03	16.71 16.91	— —	22.72 22.05
4j	$(CH_3)_2CH$	$4\text{-}ClC_6H_4$	63	33 (diethyl ether)	$C_{10}H_{11}Cl_3O_2S_3$ (365.61)	32.84 33.64	3.00 3.13	29.08 27.45	— —	26.30 25.47

TABLE 3b

The spectral properties of α-chloromethanesulfenyl chlorides **4**

Cpd.	R^1	R^2	^1H NMR ($CDCl_3$) δ (ppm)	^{13}C NMR ($CDCl_3$) δ (ppm)	IR (KBr) $\nu_{SO_2}(cm^{-1})$		MS (70 eV) *m/z*
4a	C_6Cl_5	C_6H_5	7.62 (m, 2H); 7.65 (m, H); 8.17 (d, 2H)	100.01 (α-C), 126.65, 128.98, 132.55, 132.86, 133.05, 135.50, 138.52, 141.59	1160	1340	534 (M^+), 457, 323, 287, 247, 141, 125
4b	C_6Cl_5	1-adamantyl	1.75 (s, 6H); 2.16 (s, 6H); 2.27 (s, 3H)	28.95, 35.54, 35.81, 73.40, 93.93 (α-C), 130.23, 133.01, 138.42, 141.52	1143	1337	592 (M^+), 557, 522, 478, 291, 279, 212, 199, 183, 179, 177, 135, 79
4c	$4\text{-}ClC_6H_4$	$4\text{-}CH_3C_6H_4$	2.47 (s, 3H); 7.38 (m, 6H); 7.98 (d, 2H)	21.69, 98.79 (α-C), 124.63, 129.64, 129.77, 129.88, 132.14, 138.73, 139.14, 147.12	1162	1340	257 ($M^+ - C_6H_7SO_2$), 222, 187, 155, 143, 139, 111, 91, 79
4d	C_6Cl_5	$4\text{-}CH_3C_6H_4$	2.43 (s, 3H); 7.36 (d, 2H); 7.93 (d, 2H)	21.94, 100.25 (α-C), 126.82, 129.43, 129.68, 132.55, 133.06, 138.47, 141.64, 147.11	1159	1337	478 (M^+- 2Cl), 323, 247, 155, 139, 123
4e	$4\text{-}CH_3C_6H_4$	C_6H_5	2.33 (s, 3H); 7.12 (d, 2H);7.31 (d, 2H); 7.60 (m, 2H); 7.72 (m, H); 8.11 (d, 2H)	21.41, 98.76 (α-C), 122.31, 128.83, 130.03, 132.04, 133.04, 135.27, 137.74, 142.53	1150	1325	378 (M^+), 346, 343, 264, 255, 237, 205, 167, 125, 123, 91, 77
4f	C_6Cl_5	$4\text{-}ClC_6H_4$	7.60 (d, 2H); 8.09 (d, 2H)	100.26 (α-C), 126.59, 129.57, 131.23, 133.36, 133.98, 138.89 , 141.76, 142.96	1157	1335	568 (M^+), 533, 478, 466, 323, 279, 244, 212, 175, 159, 155, 139, 127
4g	$2,4,5\text{-}Cl_3C_6H_2$	$4\text{-}CH_3C_6H_4$	2.49 (s, 3H); 7.40 (d, 2H); 7.55 (s, H); 7.68 (s, H); 7.98 (d, 2H)	21.70, 98.93 (α-C), 125.68, 129.62, 129.78, 131.67, 131.80, 132.43, 137.78, 140.31, 140.58, 147.23	1158	1338	480 (M^+), 366, 325 ($M^+ - C_6H_7SO_2$), 255, 211, 176, 155, 139, 91

4h	$4\text{-}O_2NC_6H_4$	$4\text{-}CH_3C_6H_4$	2.45 (s, 3H); 7.38 (d, 2H); 7.56 (d, 2H); 7.94 (d, 2H); 8.30 (d, 2H)	21.73, 98.60 (α-C), 124.03, 129.53, 129.92, 132.16, 134.23, 138.52, 147.46, 149.76,	1155	1340	423 (M^+), 368, 336, 353 308, 268, 233, 198, 155, 139, 109, 91
4i	C_6H_5	1-adamantyl	1.68 (s, 6H); 2.10 (s, 6H); 2.18 (s, 3H); 7.48 (m, 3H); 7.79 (d, 2H)	28.69, 35.33, 35.51, 72.86, 93.80 (α-C) , 128.96, 130.00, 131.45, 137.54	1136	1329	276 (M^+- CS_2Cl_2), 262, 186, 153, 135, 109, 77
4j	$(CH_3)_2CH$	$4\text{-}ClC_6H_4$	1.34 (d, 6H); 3.38 (septet, 1H); 7.53 (d, 2H); 7.94 (d, 2H)	23.46, 42.11, 97.36 (α-C), 128.97, 131.01, 133.09, 141.94	1152	1337	304 (M^+- CSO), 210, 189, 175, 159, 154, 119, 111, 75, 44, 43, 42
4k[9]	C_6H_5	$4\text{-}CH_3C_6H_4$	2.48 (s, 3H); 7.39 (m, 7H); 7.99 (d, 2H)	21.90, 98.73 (α-C), 126.08, 129.22, 129.57, 129.89, 131.69, 132.10, 137.86, 146.79	1145	1325	264 (M^+ -$CSCl_2$), 223, 188, 155, 153, 141, 139, 109, 91, 77

TABLE 4a

The preparation of *C*-sulfonyldithioformate thiocarbonyl *S*-imides **5**

Cpd.	R^1	R^2	R^3	Yield (%)	M.p. (°C) (solvent of recrystallization)	Molecular formula (M.wt.)	Analysis – calcd/found C	H	Cl	N	S
5a	C_6Cl_5	4-$CH_3C_6H_4$	1-adamantyl	78	137-138.5 (diethyl ether)	$C_{24}H_{22}Cl_5NO_2S_3$ (629.65)	45.77 45.86	3.49 3.59	28.15 27.69	2.22 2.11	15.27 14.76
5b	C_6Cl_5	4-$CH_3C_6H_4$	*t*-octyl	87	166-166.5 (ethanol)	$C_{22}H_{24}Cl_5NO_2S_3$ (607.63)	43.48 43.17	3.94 4.01	29.17 28.99	2.30 2.22	15.82 15.40
5c	4-ClC_6H_4	4-$CH_3C_6H_4$	*t*-butyl	83	120-121 (ethanol)	$C_{18}H_{20}ClNO_2S_3$ (413.79)	52.24 52.20	4.83 4.80	8.56 8.97	3.38 3.31	23.24 23.31
5d	C_6Cl_5	4-$CH_3C_6H_4$	*t*-amyl	89	136-137.5 (ethanol)	$C_{19}H_{18}Cl_5NO_2S_3$ (565.60)	40.34 40.37	3.18 3.36	31.33 31.45	2.47 2.55	17.00 16.40
5e	C_6Cl_5	4-ClC_6H_4	*t*-octyl	75	170-171.5 (diethyl ether)	$C_{21}H_{21}Cl_6NO_2S_3$ (628.07)	40.15 40.12	3.34 3.45	33.86 33.72	2.22 2.25	15.31 14.85
5f	C_6Cl_5	4-$CH_3C_6H_4$	*t*-butyl	84	118-120 (ethanol)	$C_{18}H_{16}Cl_5NO_2S_3$ (551.59)	39.19 38.57	2.90 2.95	32.13 32.49	2.53 2.58	17.43 16.88
(E)-**5g**[48]	C_6Cl_5	1-adamantyl	1-adamantyl	61	204-205 (diethyl ether)	$C_{27}H_{30}Cl_5NO_2S_3$ (673.68)	48.13 47.78	4.45 4.51	26.31 26.09	2.07 2.14	14.27 14.47
5h	C_6Cl_5	4-ClC_6H_4	*t*-butyl	77	143-145 (diethyl ether)	$C_{17}H_{13}Cl_6NO_2S_3$ (572.00)	35.69 35.68	2.27 2.31	37.18 37.22	2.44 2.40	16.81 16.53
(E)-**5i**[48]	C_6Cl_5	C_6H_5	*t*-butyl	87	141-142 (ethanol)	$C_{17}H_{14}Cl_5NO_2S_3$ (537.58)	37.97 37.84	2.60 2.68	32.97 32.90	2.60 2.68	17.89 17.70
5j	C_6H_5	1-adamantyl	1-adamantyl	73	145-146 (diethyl ether)	$C_{27}H_{35}NO_2S_3$ (501.43)	64.66 64.18	6.98 7.30	— —	2.79 2.47	19.18 18.05

5k	C_6H_5	4-$CH_3C_6H_4$	*t*-amyl	89	102-103 (ethanol)	$C_{19}H_{23}NO_2S_3$ (393.35)	58.01 57.84	5.84 6.03	— —	3.55 3.69	24.45 23.47
5l	C_6H_5	4-$CH_3C_6H_4$	1-adamantyl	72	141-141.5 (diethyl ether)	$C_{24}H_{27}NO_2S_3$ (457.40)	63.01 62.85	5.90 5.99	— —	3.06 3.03	21.02 20.74
(E)-**5m**[48]	4-$O_2NC_6H_4$	4-$CH_3C_6H_4$	*t*-butyl	77	116-118 (diethyl ether)	$C_{18}H_{20}N_2O_4S_3$ (424.32)	50.94 51.03	4.71 4.80	— —	6.59 6.54	22.66 22.20
5n	C_6H_5	4-$CH_3C_6H_4$	*t*-octyl	81	66-67 (ethanol)	$C_{22}H_{29}NO_2S_3$ (435.38)	60.68 60.75	6.66 6.76	— —	3.21 3.30	22.09 21.83
5o	4-$O_2NC_6H_4$	4-$CH_3C_6H_4$	*t*-amyl	83	180-182 (diethyl ether)	$C_{19}H_{22}N_2O_4S_3$ (438.33)	52.05 51.95	5.01 5.05	— —	6.38 6.34	21.94 21.59
5p	2,4,5-$Cl_3C_6H_2$	4-$CH_3C_6H_4$	*t*-butyl	85	122-123 (ethanol)	$C_{18}H_{18}Cl_3NO_2S_3$ (482.67)	44.78 44.95	3.72 3.88	22.03 22.65	2.90 2.87	19.92 19.22
5q	4-$CH_3C_6H_4$	C_6H_5	*t*-butyl	83	59-62 (diethyl ether)	$C_{18}H_{21}NO_2S_3$ (379.34)	56.98 56.11	5.53 5.49	— —	3.69 3.60	25.35 23.66
5r	$(CH_3)_2CH$	4-ClC_6H_4	*t*-amyl	69	65-67 (petroleum ether/diethyl ether 1:3)	$C_{15}H_{22}ClNO_2S_3$ (379.76)	47.43 47.61	5.79 6.15	9.33 8.78	3.68 4.18	25.32 26.28
5s	C_6Cl_5	1-adamantyl	*t*-butyl	72	150-152.5 (diethyl ether)	$C_{21}H_{24}Cl_5NO_2S_3$ (595.62)	42.34 41.89	4.02 4.50	29.75 29.43	2.35 2.11	16.14 15.99

TABLE 4b

The spectral properties of *C*-sulfonyldithioformate thiocarbonyl *S*-imides **5**

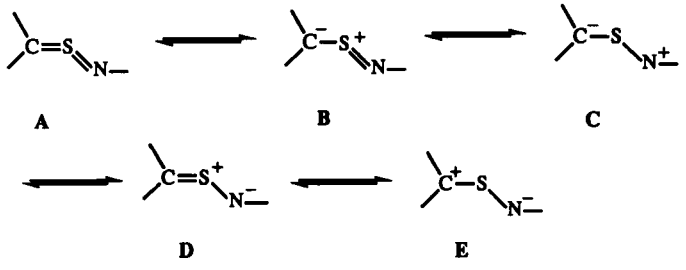
Cpd.	R^1	R^2	R^3	^1H NMR ($CDCl_3$) δ (ppm)	^{13}C NMR ($CDCl_3$) δ (ppm)	IR (KBr) (cm^{-1}) ν_{SO_2}	$\nu_{S=N}$	MS (70 eV) *m/z*
5a	C_6Cl_5	4-$CH_3C_6H_4$	1-adamantyl	1.75 (m, 12H); 2.17 (s, 3H); 2.39 (s, 3H); 7.21 (d, 2H); 7.70 (d, 2H)	21.49, 29.73, 35.61, 45.48, 64.91, 127.89, 129.55, 130.27, 131.20 (*C*=S), 132.05, 134.03, 136.32, 137.57, 144.75	1150 1330	940	569 (M^+-CSN), (472 (M^+ - $C_6H_7SO_2$), 446, 434, 402, 323, 279, 247, 212, 193, 177, 139, 135, 107, 91
5b	C_6Cl_5	4-$CH_3C_6H_4$	*t*-octyl	0.88 (s, 9H); 1.35 (s, 6H); 1.53 (s, 2H); 2.39 (s, 3H); 7.19 (d, 2H); 7.70 (d, 2H)	21.50, 31.40, 31.79, 32.25, 57.35, 67.87, 127.87, 129.54, 129.92, 131.11 (*C*=S), 132.05, 133.98, 136.10, 137.53, 144.77	1154 1340	932	605 (M^+), 590, 534, 561, 323, 246, 247, 212, 155, 139, 112, 91, 57
5c	4-ClC_6H_4	4-$CH_3C_6H_4$	*t*-butyl	1.22 (s, 9H); 2.39 (s, 3H); 7.00 (m, 2H); 7.05 (d, 2H); 7.29 (d, 2H); 7.87 (d, 2H)	21.41, 31.65, 64.09, 128.19, 128.75, 129.94, 130.89, 131.40 (*C*=S), 133.53, 137.36, 137.50, 144.61	1152 1328	958	413 (M^+), 398, 384, 330, 298, 275, 212, 187, 155, 139, 123, 91, 57
5d	C_6Cl_5	4-$CH_3C_6H_4$	*t*-amyl	0.70 (t, 3H); 1.23 (s, 6H); 1.45 (q, 2H); 2.39 (s, 3H); 7.21 (d, 2H); 7.70 (d, 2H);	8.34, 21.50, 29.13, 37.18, 66.53, 127.98, 129.61, 129.78, 131.70 (*C*=S), 132.02, 132.47, 136.07, 137.40, 144.48	1153 1340	939	563 (M^+), 533, 492, 434, 323, 247, 155, 139
5e	C_6Cl_5	4-ClC_6H_4	*t*-octyl	0.87 (s,9H); 1.34 (s,6H); 1.52 (s, 2H); 7.42 (d, 2H); 7.80 (d, 2H)	31.40, 31.83, 32,20, 57.34, 68.27, 129.37, 129.76, 130.80, 132.26, 133.85, 134.32, 136.01, 138.98 (*C*=S), 140.41	1156 1336	930	625 (M^+), 568, 554, 424, 420, 370, 302, 286, 232, 175, 143, 111, 57
5f	C_6Cl_5	4-$CH_3C_6H_4$	*t*-butyl	1.29 (s,9H); 2.39 (s, 3H); 7.21 (d, 2H); 7.71 (d, 2H)	21.54, 31.76, 63.95, 128.03 (*C*=S), 129.52, 129.63, 129.78, 131.52, 132.06, 136.25, 137.47, 144.88	1155 1337	930	549 (M^+), 534, 434, 402, 394, 323, 263, 212, 155, 139, 115, 57
(E)-**5g**[48]	C_6Cl_5	1-adamantyl	1-adamantyl	1.68 (m, 18H); 2.05 (s, 9H); 2.16 (s, 3H)	28.38, 29.74, 35.42, 35.56, 35.60, 45.45, 64.94, 125.90 (*C*=S), 131.66, 132.18, 134.07, 136.40	1139 1335	943	671 (M^+), 62), 597, 536, 428398, 334, 263, 247, 135

5h	C_6Cl_5	4-ClC_6H_4	*t*-butyl	1.05 (s, 9H); 7.51 (d, 2H); 8.00 (d, 2H)	30.12, 54.85, 128.58, 128.86, 129.26, 132.36 (*C*=S), 132.51, 133.70, 137.38, 141.64, 141.80	1160 1340	945	569 (M^+), 512, 469, 479, 274, 232, 175, 159, 111, 58
(E)-**5i**[48]	C_6Cl_5	C_6H_5	*t*-butyl	1.23 (s, 9H); 7.51 (m, 3H); 7.90 (d, 2H)	31.65, 63.88, 128.07, 129.11, 129.72, 131.67 (*C*=S), 132.04, 133.55, 134.11, 136.15, 140.34	1155 1335	937	535 (M^+), 520, 420, 323, 279, 247, 198, 141, 125, 109, 57
5j	C_6H_5	1-adamantyl	1-ada-mantyl	1.61 (m, 18H); 2.09 (m, 12H); 7.20 (m, 3H); 7.36 (m, 2H)	28.26, 29.67, 35.43, 35.59, 35.91, 45.23, 63.48, 65.03, 127.19 (*C*=S), 128.77, 129.46, 131.31, 133.12	1118 1300	937	501 (M^+), 379, 330, 153, 135, 109, 77
5k	C_6H_5	4-$CH_3C_6H_4$	*t*-amyl	0.56 (t, 3H); 1.19 (s, 6H); 1.41 (q, 2H); 2.41 (s, 3H); 7.05 (m, 5H); 7.30 (d, 2H); 7.91 (d, 2H)	8.35, 21.56, 29.21, 37.29, 66.53, 127.15, 128.01, 128.53, 129.31, 129.73, 132.06, 137.38, 137.74 (*C*=S), 144.20	1153 1312	945	393 (M^+), 364, 296, 264, 212, 167, 155, 153, 121, 109, 91, 77
5l	C_6H_5	4-$CH_3C_6H_4$	1-ada-mantyl	1.60 (m, 12H); 2.08 (s, 3H); 2.40 (s, 3H); 7.05 (m, 5H); 7.29 (d, 2H); 7.89 (d, 2H)	21.40, 29.57, 35.51, 45.15, 64.57, 127.23, 128.07, 128.56, 129.40, 129.57, 131.88, 136.79, 137.64 (*C*=S), 144.26	1150 1320	948	457 (M^+), 264, 212, 155, 153, 139, 135, 109
(E)-**5m**[48]	4-$O_2NC_6H_4$	4-$CH_3C_6H_4$	*t*-butyl	1.25 (s, 9H); 2.39 (s, 3H); 7.06 (d, 2H); 7.30 (d, 2H); 7.87 (d, 2H); 7.96 (d, 2H)	21.40, 31.64, 64.87, 123.72, 127.75, 128.08, 130. 09, 134.02, 137.25, 141.87 (*C*=S), 144.94, 146.31	1150 1350	940	424 (M^+), 409, 366, 309, 308, 246, 198, 180, 155, 139
5n	C_6H_5	4-$CH_3C_6H_4$	*t*-octyl	0.78 (s, 3H); 1.26 (s, 6H); 1.50 (s, 2H); 2.39 (s, 3H); 7.02 (m, 5H); 7.28 (d, 2H); 7.88 (d, 2H)	21.41, 31.25, 31.69, 32.20, 57.25, 67.88, 127.18, 128.18, 128.69, 128,96, 129.25, 129.88, 133.00, 137.74 (*C*=S), 144.34	1145 1344	945	435 (M^+), 420, 364, 280, 208, 155, 153, 139, 135, 112, 91, 77, 57
5o	2,4,5-$Cl_3C_6H_2$	4-$CH_3C_6H_4$	*t*-butyl	1.27 (s, 9H); 2.40 (s, 3H); 7.33 (d, 2H); 7.57 (s, H); 7.59 (s, H); 7.87 (d, 2H)	21.43, 31.61, 64.78, 128.07, 128.73 (*C*=S), 130.18, 130.63, 131.12, 131.24, 131.43, 132.79, 134.95, 137.23, 145.01	1151 1337	945	481 (M^+), 424, 378, 445, 268, 255, 226, 212, 213, 211, 155, 139, 123
5p	4-$O_2NC_6H_4$	4-$CH_3C_6H_4$	*t*-amyl	0.56 (t, 3H); 1.20 (s, 6H); 1.41 (q, 2H); 2.39 (s, 3H); 7.05 (d, 2H); 7.30 (d, 2H); 7.87 (d, 2H); 7.94 (d, 2H)	8.16, 21.43, 29.18, 37.24, 67.56, 123.78, 127.56, 128.10, 130.12, 134.34, 137.32, 142.03 (*C*=S), 144.94, 146.33	1160 1352	956	438 (M^+), 409, 408, 293, 212, 198, 180, 168, 155, 134, 123, 122

TABLE 4b (*Continued*)

Cpd.	R^1	R^2	R^3	^1H NMR ($CDCl_3$) δ (ppm)	^{13}C NMR ($CDCl_3$) δ (ppm)	IR (KBr) (cm^{-1}) ν_{SO_2}	$\nu_{S=N}$	MS (70 eV) *m/z*
5q	4-$CH_3C_6H_4$	C_6H_5	*t*-butyl	1.22 (s, 9H); 2.20 (s, 3H); 6.89 (s, 4H); 7.56 (m, 3H); 8.00 ; (d, 2H)	20.99, 31.79, 63.91, 128.05, 129.11, 129.26, 130.58, 132.26 (*C*=S), 133.19, 137.73, 138.29, 140.42	1155 1322	948	379 (M^+), 364, 264, 238, 232, 222, 212, 181, 167, 155, 149, 141, 135, 123, 121, 115, 91, 77
5r	$(CH_3)_2CH$	4-ClC_6H_4	*t*-amyl	0.87 (t, 3H); 1.02 (d, 6H); 1.39 (s, 6H); 1.70 (q, 2H); 3.86 (septet, H); 7.50 (d, 2H); 7.92 (d, 2H)	8.70, 21.94, 29.38, 36.83, 37.48, 66.35, 128.81 (*C*=S), 129.10, 129.54, 138.67, 139.61	1161 1335	942	379 (M^+), 350, 321, 318, 245, 221, 159, 111, 43
5s	C_6Cl_5	1-adamantyl	*t*-butyl	1.31 (s, 9H); 1.74 (s, 6H); 2.08 (s, 6H); 2.22 (s, 3H)	28.50, 31.90, 35.51, 35.67, 64.04, 64.65, 125.95 (*C*=S), 131.12, 132.02, 133.90, 136.09	1135 1335	944	561 (M^+ -S), 550, 536, 478, 458, 323, 282, 247, 212, 135, 57
(E)-**5t**[8,9]	C_6H_5	4-$CH_3C_6H_4$	t-butyl	1.20 (s, 9H); 2.4 (s, 3H); 7.08 (s, 5H); 7.33 (d, 2H); 7.93 (d, 2H);	21.38, 31.58, 63.75, 127.41, 128.17, 128.64, 129.85, 129.88, 132.21, 137.56, 138.08 (*C*=S), 144.44	1140 1300	950	379 (M^+), 350, 321, 318, 245, 221, 159, 111, 43

described by the resonance forms **A**, **D**, and **E**.[19] Careful inspection of the crude reaction



products obtained from **4** and *t*-alkylamines failed to provide evidence of geometrical isomers of the isolated **5**. The assignment of the *E*- or *Z*-structure to the isolated **5** must await the results of X-ray crystallographic structure determinations of selected **5**. Detailed spectroscopic studies of **3** and **5** as well as extended investigations of the reactions of **3** and **5** will be presented elsewhere.

EXPERIMENTAL

The required chlorodithioformates **2c**,[3,31] **2d**,[3,27] **2e**,[3,25] **2f**,[32] **2g**,[32] **2h**,[3,27,30] **2i**,[3,33] and **2j**,[3,25] were prepared according to literature procedures as was sodium 1-adamantanesulfinate dihydrate.[46]

2-Benzothiazolyl Chlorodithioformate **2a**. A solution of sodium hydroxide (2.00 g, 0.05 mol) in 30 mL water was added dropwise over a period of 30 min to a stirred solution of 2-mercaptobenzothiazole (8.36 g, 0.05 mol) and thiophosgene (5.75 g, 0.05 mol) in 100 mL chloroform at 0–5°C. After the addition was completed, the reaction mixture was allowed to warm up to 25°C and then stirred for another 1 h. The precipitated salts were filtered off and the organic layer washed with water (3 times), dried over anhydrous calcium chloride, and evaporated *in vacuo*. The crude product was chromatographed over a column of silica gel with ether/petroleum ether 1:6 as eluent. After evaporation of the solvent crude **2a** crystallized, recrystallization from petroleum ether yielded 8.20 g (67%), m.p. 63–64°C, IR (KBr): $\nu_{C=S}$ 1138 cm^{-1}. Found: C 39.11, H 1.65, Cl 14.87, N 5.83, S 28.85%. Calc. for $C_8H_4ClNS_3$ (245.66): C 39.11, H 1.62, Cl 14.43, N 5.70, S 39.15%. The chlorodithioformate **2d**,[3,27] was prepared and purified according to the same procedure.

1,2,2-Triphenyl-1-ethenyl Chlorodithioformate **2b**. A solution of sodium hydroxide (0.80 g, 0.02 mol) in 15 mL water was added dropwise over a period of 30 min to a stirred solution of 1,2,2-triphenyl-1-ethenethiol[47] (5.76 g, 0.02 mol) and thiophosgene (2.30 g, 0.02 mol) in 50 mL chloroform at 0–5°C. After the addition was completed, the reaction mixture was allowed to warm up to 25°C and stirred for 2 h. The precipitated salts were filtered off and the organic layer washed with water (3 times), dried over anhydrous calcium chloride, and evaporated *in vacuo*. The product was recrystallized from petroleum ether to yield 5.20 g (71%) **2b**, m.p. 134–135°C, IR (KBr): $\nu_{C=S}$ 1113 cm^{-1}. Found: C 68.78, H 4.15, Cl 9.64, S 17.84%. Calc. for $C_{21}H_{15}ClS_2$ (366.78): C 68.76, H 4.09, Cl 9.66, S 17.48%.

C-Sulfonyldithioformates **3**. The two-phase mixture of the appropriate **2** (0.15 mol), the appropriate sodium sulfinate dihydrate (0.15 mol), 2 g tetrabutylammonium hydrogen sulfate, 250 mL benzene, and 250 mL water was stirred at 35–45°C (except in the case of **2h** which was stirred at room temperature, yield: 83%, lit.[7] 65%), and the progress of the reaction monitored by TLC (Merck silica gel 60, eluent ether/petroleum ether 1:6). When the reaction was completed the benzene phase was washed with water (3 times), dried over anhydrous calcium chloride, and evaporated *in vacuo*. The red oily residue was triturated with 200 mL ether/petroleum ether 1:2 (for **3e**), with 50 mL ether and cooled (**3q**), or by digestion with cold ethanol and cooled (**3m** and **3n**) whereupon the crude product slowly crystallized. The recrystallization was carried as shown in Table 2a.

α-Chloromethanesulfenyl Chlorides **4**. *Method A*: Chlorine gas was passed through a stirred solution or suspension of the appropriate **3** (20 mmol) in 200 mL carbon tetrachloride at room temperature until the color disappeared (2–15 min). Excess chlorine was removed by passing through a stream of nitrogen. The solvent was evaporated under reduced pressure and the oily residue triturated with 40 mL ether/

petroleum ether 1:4 whereupon it slowly crystallized. The recrystallization was carried out as shown in Table 3a. *Method B*: To a stirred solution of the appropriate **3** (10.4 mmol) in 50 mL carbon tetrachloride was added, at room temperature, the stoichiometric amount of chlorine (0.75 g, 10.4 mmol), dissolved in carbon tetrachloride. After 15 min the color disappeared. The solvent was evaporated under reduced pressure, and the residue worked up as above.

C-Sulfonyldithioformate Thiocarbonyl S-Imides **5**. A stirred solution of the appropriate **4** (3 mmol) in 30 mL chloroform was treated with the appropriate *t*-alkylamine (10 mmol) at room temperature. After the addition was completed, the reaction mixture was stirred for another 15 min, the precipitated salts filtered off, and the chloroform phase washed with water (5 times), dried over anhydrous calcium chloride, and evaporated *in vacuo*. The residue was triturated with 40 mL petroleum ether with cooling whereupon the crude product slowly crystallized. The recrystallization was carried as shown in Table 4a.

(E)-S-Pentachlorophenyl C-(1-adamantylsulfonyl)-dithioformate S-[(N-1-adamantyl)-imide] (E)-**5g**.[48] 1-Adamantaneamine (1.51 g, 10 mmol), dissolved in 30 mL chloroform, was added at room temperature portionwise to a stirred solution of **4b** (1.78 g, 3 mmol), dissolved in 50 mL of the same solvent, and the reaction mixture stirred for another 15 min. The precipitated salts were filtered off, and the orange filtrate evaporated *in vacuo*. The solid residue was dissolved in 50 mL ether, filtered, the ethereal phase concentrated *in vacuo*, and the crude product chromatographed on a column of silica gel with ether/petroleum ether 1:5 as eluent. After evaporation of the solvent and recrystallization from ether **5g** was obtained as fine orange needles. Compounds **5e**, **5h**, and **5s** were prepared and purified like **5g**.

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REFERENCES AND NOTES

1. Permanent address: Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt.
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3. U. Kraatz, *Houben-Weyl*, **E4**, 414 (1983).
4. H. E. Simmons, D. C. Blomstrom and R. D. Vest, *J. Amer. Chem. Soc.*, **84**, 4756 (1962).
5. D. W. Grisley, Jr., *J. Org. Chem.*, **26**, 2544 (1961).
6. A. Senning, *Sulfur Lett.*, **12**, 235 (1991).
7. I. El-Sayed, M. F. Abdel-Megeed, S. M. Yassin and A. Senning, *Sulfur Lett.*, **15**, 1 (1992).
8. C. O. Haagensen, *Acta Cryst., Sect. B*, **B34**, 3143 (1978).
9. S. Holm, J. A. Boerma, N. H. Nilsson and A. Senning, *Chem. Ber.*, **109**, 1069 (1976).
10. I. Crossland, *Acta Chem. Scand.*, **B31**, 890 (1977).
11. a) S. Tamagaki and S. Oae, *Tetrahedron Lett.*, 1159 (1972); b) S. Tamagaki, K. Sakaki and S. Oae, *Bull. Chem. Soc. Jpn.*, **46**, 2608 (1973); c) eidem, *ibid.*, **47**, 3084 (1974); d) eidem, *Heterocycles*, **2**, 39 (1974).
12. A. Tangerman and B. Zwanenburg, *Tetrahedron Lett.*, 259 (1977).
13. P. A. T. W. Porskamp and B. Zwanenburg, *J. Org. Chem.*, **48**, 4582 (1983).
14. T. Saito, A. Koide, Y. Kikuchi, and S. Motoki, *Phosphorus Sulfur*, **17**, 153 (1983).
15. A. Koide, T. Saito and S. Motoki, *Synthesis*, 486 (1981).
16. a) G. J. Wentrup and F. Boberg, *Justus Liebigs Ann. Chem.*, 387 (1978); b) F. Boberg, U. Puttins and G. J. Wentrup, *Justus Liebigs Ann. Chem.*, 689 (1979).
17. a) F. Boberg, A. Paetz, B. Bruchmann and A. Garming, *Phosphorus Sulfur*, **33**, 99 (1987).
18. F. Boberg, A. Otten, U. Kirchner and A. Stahnke, XVth International Symposium on the Organic Chemistry of Sulfur, Caen, France, 1992; Abstracts of Papers, p. 183.
19. A. Otten, Ph.D. Thesis, TU Clausthal, 1992.
20. F. Arndt, E. Milde and G. Eckert, *Ber.*, **56**, 1976 (1923).
21. P. Klason, *Ber.*, **20**, 2376 (1887).
22. J. v. Braun, *Ber.*, **35**, 3377 (1902).
23. H. Rivier and P. Richard, *Helv. Chim. Acta*, **8**, 499 (1925).
24. K. A. Jensen, *J. Prakt. Chem.*, **148**, 101 (1937).

25. H. C. Godt and R. E. Wann, *J. Org. Chem.*, **26,** 4047 (1961).
26. D. M. McKinnon and A. Queen, *Can. J. Chem.*, **50,** 1401 (1972).
27. J. Goerdeler and H. Hohage, *Chem. Ber.*, **106,** 1487 (1973).
28. P. Beak and J. W. Worley, *J. Amer. Chem. Soc.*, **94,** 597 (1972).
29. N. H. Nilsson, *J. Chem. Soc., Perkin Trans.* 1, 1308 (1974).
30. B. Sturm and G. Gattow, *Z. Anorg. Allg. Chem.*, **508,** 136 (1984).
31. M. H. River, *Bull. Soc. Chim. Fr. [4]*, **1,** 733 (1907).
32. H. C. Hansen, B. Jensen and A. Senning, *Sulfur Lett.*, **3,** 61 (1985).
33. H. Viola and R. Mayer, *Z. Chem.*, **19,** 289 (1979).
34. L. Benatiu and P. C. Montevecchi, *J. Org. Chem.*, **41,** 2639 (1976).
35. N. H. Nilsson and A. Senning, *Chem. Ber.*, **107,** 2345 (1974).
36. N. H. Nilsson, C. Jacobsen and A. Senning, *Chem. Commun.*, 658 (1970).
37. J. A. Boerma, N. H. Nilsson and A. Senning, *Tetrahedron*, **30,** 2735 (1974).
38. N. H. Nilsson, C. Jacobsen and A. Senning, *Chem. Commun.*, 314 (1971).
39. A. Senning, H. C. Hansen and S. J. i Skorini, *Phosphorus Sulfur*, **5**, 359 (1979).
40. S. Holm and A. Senning, *Tetrahedron Lett.*, 2389 (1973).
41. K. R. Gassen, *Houben-Weyl*, **E14a/3,** 159 (1992).
42. S. Motoki and T. Saito, *Sulfur Rep.*, **4,** 33 (1984).
43. B. Zwanenburg and B. G. Lenz, *Houben-Weyl*, **E11,** 943 (1985).
44. a) B. Zwanenburg and B. G. Lenz, *Houben-Weyl*, **E11,** 913 (1985). b) B. Zwanenburg, *Recl. Trav. Chim Pays-Bas*, **101,** 1, 1982.
45. I. El-Sayed, M. F. Abdel-Megeed, S. M. Yassin and A. Senning, unpublished observations.
46. I. El-Sayed, M. F. Abdel-Megeed, S. M. Yassin and A. Senning, *Sulfur Lett.*, **15,** 209 (1993).
47. C. F. Koelsch and G. Ullyot, *J. Amer. Chem. Soc.*, **55,** 3883 (1933).
48. F. Krebs Larsen and R. Grønbæk Hazell, single-crystal X-ray structure determination to be published elsewhere.