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CYCLOADDITION REACTIONS OF SULFONYLISOTHIOCYANATES WITH β,β-DISUBSTITUTED ENAMINES[a]

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Abstract—Sulfonylisothiocyanates **1** and β,β-dimethylenamines **2** react to yield the dipoles **3**. In nonpolar solvents an equilibrium exists between **3** and the thietanes **4**. The free activation enthalpy for the ring closure **3** → **4** was obtained from the temperature dependent NMR spectra in liquid sulfur dioxide. Protonation of **3** with perchloric acid leads to the salts **8** which, as indicated by $\Delta G^{\neq}$-values obtained from NMR spectra, are also capable of ring closure.

In contrast to sulfonylisocyanates 2 + 2-cycloaddition reactions of sulfonylisothiocyanates have received only slight consideration. In 1971 Gompper and Wetzel described stable dipoles formed from benzenesulfonylisothiocyanate with cyclic keto-enamines or ketene-S,N-acetals.[2] Several papers on cycloaddition reactions of sulfonylisothiocyanates with C=N double bonds have been published in the last few years.[3-5]

Since it is known that arylisothiocyanates react with enamines derived from isobutyraldehyde to give an equilibrium system of 1:1- and 2:1-cycloadducts,[6-8] it was of interest to us to determine which course the reaction would take if the dipole intermediate is stabilised by the sulfonyl group.

When sulfonylisothiocyanates **1** are reacted with β,β-disubstituted enamines **2** crystalline 1:1-adducts are formed (Table 1).

The spectroscopic data (IR: $>C=\overset{\oplus}{N}<$ 1630–1690 cm^{-1}; bands at about *ca* 1400 cm^{-1} which can be assigned to the SO_2–N=C–$S^{\ominus}$ group) are consistent with the dipolar structure **3**. The alternative structures, imidothietane **4** and β-thiolactame **5**, could be ruled out since they would not show a band in the region 1630–1690 cm^{-1}.

Further support for the dipolar structure in the solid state is given by the $^{14}_{7}N$-ESCA spectrum of **3k**. The spectrum shows two maxima as expected for two differently charged N atoms. The peak at 400·2 eV can be assigned to a positive nitrogen indicating the presence of an immonium cation. The peak at 396·3 eV is due to a N atom, which is only slightly negative. The position of this peak shows that the negative charge of the dipole is probably concentrated at the S atom of the thioamide anion.[9]

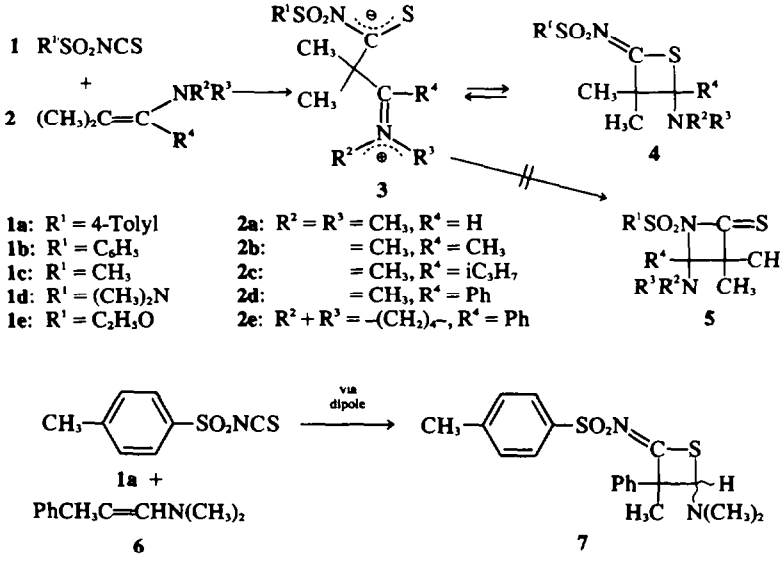
When tosylisothiocyanate **1a** is reacted with the diastereomeric enamine **6** (E/Z ratio 65%/35%) the crystalline cycloadduct **7** is formed.

The product could be identified by a strong IR-absorption at 1590 cm^{-1}, which can be assigned to the exocyclic C=N

[a] Cycloaddition reactions of heterocumulenes II. For the first part of this series see Ref. 1.

Table 1. Dipoles (3) from sulfonylisothiocyantes 1 and enamines 2

3	R^1	R^2	R^3	R^4	yield	IR: $>C=\overset{\oplus}{N}<$ (N = Nujol) (KBr)
3a	4-Tolyl	CH_3	CH_3	H	53	1685 (N)
3b	4-Tolyl	CH_3	CH_3	CH_3	87	1645 (N)
3c	4-Tolyl	CH_3	CH_3	iC_3H_7	40	1640 (N)
3d	4-Tolyl	CH_3	CH_3	C_6H_5	95	1650 (N)
3e	4-Tolyl	$-(CH_2)_4-$		C_6H_5	49	1630 (KBr)
3f	C_6H_5	CH_3	CH_3	CH_3	85	1640 (N)
3g	CH_3	CH_3	CH_3	iC_3H_7	50	1646 (KBr)
3h	CH_3	CH_3	CH_3	CH_3	55	1640 (KBr)
3i	CH_3	CH_3	CH_3	H	64	1680 (N)
3k	C_6H_5	CH_3	CH_3	H	66	1690 (N)
3l	$(CH_3)_2N$	CH_3	CH_3	iC_3H_7	41	1640 (N)
3m	$(CH_3)_2N$	CH_3	CH_3	H	32	1685 (N)
3n	C_2H_5O	CH_3	CH_3	H	60	1685 (N)



double bond. The formation of the cycloadduct 7 instead of the corresponding dipole 3 can be explained by a steric effect. The phenyl residue, which when freely rotating is bulkier than the corresponding Me group, forces the intermediate dipole to ring close.

Information about the structure of the adducts from 1 and 2 in *solution* could be obtained from the ^{1}H-NMR- and soln IR-spectra. The NMR chemical shift of the dipoles **3a**, **i**, **k**, **m**, and **n** (R^4 = H) show a marked dependence on the solvent polarity. The chemical shifts of the C-H-(R^4 = H) and the $N(CH_3)_2$-signals ($R^2 = R^3 = CH_3$) in three solvents are listed in Table 2.

Table 2. Shift dependence of **3a** on solvent polarity in ppm; s = singlet, m = multiplet

	$CDCl_3$ (37°)	CD_3CN (37°)	liq. SO_2 (−20°)
δ_{C-H}	4·87 s	5·94 s	8·04 m
$\delta_{N(CH_3)_2}$	2·41 s	2·68 s	3·53 s

An inspection of Table 2 reveals a change in the chemical structure of **3a** in solvents of considerably different polarities. Interestingly the tertiary proton R^4 = H in liquid SO_2 (C-H δ = 8·04) shows an allylic ^4J long range coupling to the $N(CH_3)_2$-signal, an effect which has already been observed for dipoles of tosylisocyanates and enamines.[1] This coupling is only consistent with the dipolar structure **3a**. In the relatively nonpolar solvent, $CDCl_3$, the same proton is found more than 3 ppm upfield as a singlet (C-H δ = 4·87). This and the parallel upfield shift of the $N(CH_3)_2$-signal is a strong indication of ring closure to the corresponding thietane ring **4a** in nonpolar solvents. In CD_3CN—a solvent which has an intermediate polarity between $CDCl_3$ and SO_2—only one set of NMR-signals is observed with an intermediate chemical shift for the (R^4 = H) hydrogen, although both forms **3a** and **4a** are to be expected. This fact implies that the rate of conversion between ring and dipole is fast compared to the NMR-time scale.

Further support for the assumption of a rapid equilibrium between **3a** and **4a** are the solution IR-spectra. In $CHCl_3$ there is a strong absorption at 1600 cm^{-1}, which can be assigned to an exocyclic N-sulfonyl C=N double bond, strong evidence for the existence of **4a**. On changing the solvent to CH_3CN this absorption diminishes and a new bond appears at 1690 cm^{-1}, belonging to the immonium group of the dipole **3a**.

From the NMR-spectroscopic results it is impossible to decide whether the cycloaddition to 7 is stereoselective or not, since it was shown above that there is a rapid interchange between 4-membered ring and dipole. The one set of signals found for 7 in $CDCl_3$ indicates either a rapid equilibrium between the two diasteromeric forms or an accumulation of the thermodynamically more stable diastereomer.

The chemical shifts in CD_3CN and $CDCl_3$ of the dipoles **3** with R^4 other than H (**3b–h** and **3l**) are in agreement with those found for the dipoles formed from tosylisocyanate and enamines.[1] A change to the ionizing solvent, liquid sulfur dioxide, causes no downfield shifts, which would be expected if there were a variation in the equilibrium to the dipolar form. Thus it can be concluded that in all three solvents the compounds **3b–h** and **3l** exist in the dipolar form **3**.

In liq. SO_2 the dipoles **3** show temperature dependent signals for the dialkylamino group. From the measured coalescence temperatures T_c the free activation enthalpies $\Delta G^{\neq}$ for the exchange of the two groups were obtained (Table 3). Krebs and Breckwoldt have found a rotational barrier $\Delta G^{\neq} > 25$ kcal for immonium salts.[10] The $\Delta G^{\neq}$ value of 10–13 kcal differs considerably from a pure rotational mechanism of exchange for the alkylamino group in the dipole **3**. Since there is a rapid interchange

Table 3. NMR-characteristics of the dipoles 3

	$\delta_{C(CH_3)_2}$	$\delta_{N(CH_3)_2}$	δ_{C-H}	solvent	$\Delta\nu$ [Hz]	T_c [°C]	$\Delta G^{\neq}$ (liq. SO_2) [kcal/mol]	
3a	1·38	2·68	5·94	CD_3CN	—	—		<10[b]
3b	1·35	3·40, 3·68	—	liq. SO_2	15	−10		13·5
3c	1·53	3·12	—	CD_3CN	17	−40		11·8
3d	1·40	3·30	—	CD_3CN	14	−10		13·5
3e	1·46	—	—	CD_3CN	—	—		—[a]
3f	1·37	3·40, 3·65	—	liq. SO_2	14	−10		13·5
3g	1·66	3·40	—	liq. SO_2	16	−33		12·2
3h	1·58	3·46	—	CD_3CN	8	−10		13·8
3i	1·40	2·50	4·96	$CDCl_3$	—	—		—[a]
3k	1·37	2·43	4·83	$CDCl_3$	—	—		<10[b]
3l	1·60	3·46	—	CD_3CN	15	−37		12·1
3m	1·43	2·75	5·08	CD_3CN	—	—		—[a]
3n	1·48	2·60	5·16	$CDCl_3$	—	—		—[a]
7	$-CH_3$ 1·70	2·20	5·08	$CDCl_3$	—	—		—[a]

[a] not measured; [b] broadening at −60°.

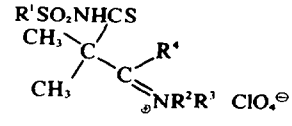
between dipole and the corresponding cycloadduct, it can be assumed that the measured $\Delta G^{\neq}$ values indicate the activation barrier between the dipole **3** and the cycloadduct **4** in which rotation around the C–NR_2 single-bond is essentially unhindered. Any comparison of the $\Delta G^{\neq}$ values must be made with great care, because strong entropy effects can be expected. However, it is likely that mainly steric effects stemming from the group R^4 are responsible for the height of the activation barrier. Thus it seems consistent that **3a** and **3k** (R^4 = H) have $\Delta G^{\neq}$ values less than 10 kcal, whereas the $\Delta G^{\neq}$ value of **3c**, **3g** and **3l** (R^4 = i-C_3H_7) are found around 12 kcal. The unexpected high activation barrier of 13·5 kcal and more for the dipoles **3b**, **3f** and **3h** (R^4 = Me) are most likely caused by a stronger solvation at the immonium cation. With R^4 = i-C_3H_7 this effect is negligible due to the larger steric hindrance for the solvent. For R^4 = H the solvation effect is overcompensated by attraction of the negative part of the dipole so that the $\Delta G^{\neq}$ value here is the lowest. The considerably lower activation barrier to ring closure for the sulfonylisothiocyanate dipoles **3** in CD_3CN ($\Delta G^{\neq}$ < 9 kcal, since **3** shows sharp N-alkyl peaks until −70° with no indication of exchange broadening) compared with those for the sulfonylisocyanate dipoles (13–18 kcal in CD_3CN)[1] can be explained by the stronger nucleophilicity of the thioamide anion versus the amide anion which favors ring closure.

The dipoles **3** were protonated with a mixture of perchloric acid and acetanhydride. The IR and NMR characteristics of the obtained salts **8** are listed in Table 4. The spectroscopic data of **8** are consistent with the structure of immonium perchlorates.

Table 4. Protonation products **8** from **3** and perchloric acid

Dipoles		IR (KBr): >C=$\overset{\oplus}{N}$<	IR (KBr): NH	NMR (CD_3CN): $\delta_{C(CH_3)_2}$	NMR (CD_3CN): $\delta_{N(CH_3)_2}$	$\Delta\nu$ [Hz]	T_c [°C]	$\Delta G^{\neq}$ (CD_3CN) [kcal/mol]
3a	8a	1690	3100	1·53	3·10	—	—	<10[b]
3b	8b	1645	3040	1·60	3·4 (broad.)	15	−10	13·5
3c	8c	1640	3110	1·66	3·33	27	−47	11·3
3d	8d	1640	3100	1·53	3·27	—	—	—[a]
3e	8e	1630	3100	1·52	3·6(m)	7	−15	13·6
3f	8f	1650	3130	1·63	3·4 (broad.)	16	20	15·1
3g	8g	1645	3200	1·70	3·56	16	−46	11·6
3h	8h	1640	3200	1·70	3·5 (broad.)	8	27	15·8
3m	8m	1605	2700	1·60	2·81	—	—	—[a]

[a] not measured; [b] broadening at −60°.



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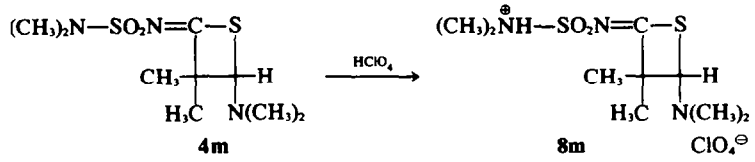
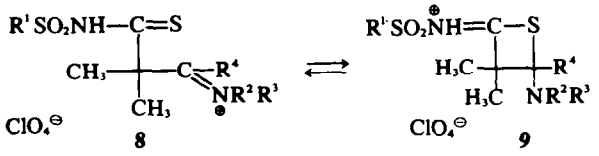
For the product obtained from **4m** and perchloric acid the structure **8m**



4m **8m**

is proposed, since the IR-absorptions at 2700 and 1605 cm^{-1} (ammonium and exocyclic N-sulfonylimino group) and the NMR data (C–H $\delta = 5{\cdot}4$; CD_3CN) are not consistent with the immonium structure.

In the NMR spectra of **8a–h** (CD_3CN) the N-alkyl peaks are temperature dependent. As for the unprotonated species **3** the $\Delta G^{\neq}$ values obtained for the protonated dipoles (Table 4) are much too low to be the barrier to internal rotation around the immonium $>C=\overset{\oplus}{N}<$ bond Therefore we suggest a ring closure mechanism to **9** as being responsible for exchange.



8 **9**

The role of the perchlorate anion in this process should be negligible because of its nonpolarizability.

In comparison to the dipoles **3** the intermediate ring closure of **8** implies that even without the formal negative charge the nucleophilicity of the thioamide sulfur is strong enough to attract the positive immonium cation. Thus the $\Delta G^{\neq}$ values obtained for the protonated products **8** represent an analogous activation barrier to ring closure to that already found for the dipoles **3**. Again the obtained $\Delta G^{\neq}$ values indicate a steric influence of R^4 on the ring closure, although here also strong entropy effects are to be expected.

EXPERIMENTAL

M.ps obtained on a Leitz heating microscope are uncorrected. IR spectra were recorded on a Perkin-Elmer model 257 in KBr or as a Nujol-suspension, soln spectra on a model 421. The 60 MHz ^{1}H-NMR spectra were recorded on the Varian models T 60, A 60 and NV 14. TMS served as the internal standard.

The sulfonylisothiocyanates were obtained by the methods of Hartke or Ried.[11,12]

Compounds **2a** and **2f** were prepared by the method of Brannock and Burpitt,[13] and compounds **2c. d, e** were obtained by the method of White and Weingarten.[14]

1-Dimethylamino-1-methylisobutene-(1) (**2b**). To a soln of MeMgI (0·12 mole) in 50 ml abs ether 14·4 g (0·11 mole) 1 - dimethylamino - 1 - chloro - isobutene - (1)[15,16] was added dropwise at −10°. After completion the mixture was stirred 1 hr at room temp and decanted from the liquid Mg salt. The salt was washed twice with abs ether and the ethereal phase was distilled yielding 6 g **2b** (48%) b.p. 60 (70 mm); IR: C=C–N 1680 cm^{-1}. NMR: $\delta = 1{\cdot}53$ (s, $C(CH_3)_2$), $\delta = 1{\cdot}66$ ($-CH_3$, s, broadened by homoallylic coupling with $C(CH_3)_2$, $J < 1$ Hz), $\delta = 2{\cdot}23$ (s, $N(CH_3)_2$).

General procedure for the preparation of the dipoles **3**. To 0·01 mol of **2** in 20 ml dry ether at −10° the equiv amount of **1** dissolved in ether was added dropwise. A ppt immediately appeared which was filtered off with exclusion of moisture and recrystallized from acetonitril/ether (dry). In the same way the following dipoles were prepared:

Compound	m.p.	Calc: Found:	C	H	O	N	S
1-N,N-Dimethylimmonium-isobutane-2-N′-(4-toluene-sulfonyl)-thiocarboxamidate (**3a**)	96–99	$C_{14}H_{20}O_2N_2S_2$ (312·46)	53·82 53·30	6·45 6·56	10·24	8·97 9·06	20·52 20·63
2-N,N-Dimethylimmonium-3-methylbutane-3-N′-(4-toluene-sulfonyl)-thiocarboxamidate (**3b**)	133–135	$C_{15}H_{22}O_2N_2S_2$ (326·48)	55·18 54·63	6·79 6·78	9·80	8·58 8·67	19·64 19·55
3-N,N-Dimethylimmonium-2,4-dimethylpentane-4-N′-(4-toluenesulfonyl)-thio-carboxamidate (**3c**)	108–110	$C_{17}H_{26}O_2N_2S_2$ (354·54)	57·59 57·10	7·39 7·27	9·03	7·90 7·83	18·09 18·97
1-N,N-Dimethylimmonium-1-phenylisobutane-2-N′-(4-toluenesulfonyl)-thio-carboxamidate (**3d**)	94–98	$C_{20}H_{24}O_2N_2S_2$ (388·55)	61·82 61·24	6·23 6·27	8·24	7·21 7·70	16·50 15·10

Compound	m.p.	Calc: Found:	C	H	O	N	S
1-Tetramethyleneimmonium-1-phenylisobutane-2-N'-(4-toluenesulfonyl)-thiocarboxamidate (**3e**)	161–163	$C_{22}H_{26}O_2N_2S_2$ (414·59)	63·74 63·63	6·32 6·27	7·72	6·76 6·72	15·47 15·70
2-N,N-Dimethylimmonium-3-methylbutane-3-N'-benzenesulfonyl-thiocarboxamidate (**3f**)	92–96	$C_{14}H_{20}O_2N_2S_2$ (312·46)	53·82 53·30	6·45 6·65	10·24	8·97 8·81	20·52 20·14
3-N,N-Dimethylimmonium-2,4-dimethylpentane-4-N'-methanesulfonyl-thiocarboxamidate (**3g**)	134–135	$C_{11}H_{22}O_2N_2S_2$ (278·44)	47·50 47·20	7·96 7·82	11·49	10·06 9·98	23·03 23·06
2-N,N-Dimethylimmonium-3-methylbutane-3-N'-methanesulfonyl-thiocarboxamidate (**3h**)	95–100(d)	$C_9H_{18}O_2N_2S_2$ (250·38)	43·17 42·56	7·25 7·60	12·78	11·19 11·04	25·61 24·54
1-N,N-Dimethylimmonium-isobutane-2-N'-methanesulfonyl-thiocarboxamidate (**3i**)	90–95(d)	$C_8H_{16}O_2N_2S_2$ (204·29)	40·65 40·02	6·82 6·97	13·54	11·85 11·96	27·13 27·27
1-N,N-Dimethylimmonium-isobutane-2-N'-benzensulfonyl-thiocarboxamidate (**3k**)	105–107	$C_{13}H_{18}O_2N_2S_2$ (293·43)	52·32 52·28	6·08 6·12	10·32	9·39 9·27	21·49 21·36
3-N,N-Dimethylimmonium-2,4-dimethylpentane-4-N',N'',N''-dimethylaminosulfonyl-thiocarboxamidate (**3l**)	127(d)	$C_{12}H_{25}O_2N_3S_2$ (307·48)	46·88 46·06	8·20 8·19	10·41	13·67 13·57	20·86 21·12
1-N,N-Dimethylimmoniumisobutane-2-N',N'',N'-dimethylamino-sulfonyl-thiocarboxamidate (**3m**)	97–100(d)	$C_6H_{19}O_2N_3S_2$ (265·40)	40·73 40·66	7·22 7·68	12·06	15·83 15·86	24·16 23·83
1-N,N-Dimethylimmoniumiso-butane-2-N'-ethoxysulfonyl-thiocarboxamidate (**3n**)	65–75(d)	$C_9H_{18}O_3N_2S_2$ (266·38)	40·58 39·69	6·81 7·19	18·02	10·02 10·08	24·07 23·57
N-(4-toluenesulfonyl)-2-imino-3-methyl-3-phenyl-4-dimethylaminothietane (**6**)	80–85(d)	$C_{19}H_{22}O_2N_2S_2$ (374·53)	60·93 60·81	5·92 6·02	8·54	7·48 6·88	17·12 15·60

General procedure for protonation of the dipoles **3**. To 1 mmol dipole **3** in 5 ml dry acetonitril 0·4 ml of a 1 : 2 mixture of 60% perchloric acid and Ac_2O (mixed at −40°) was added at room temp. Subsequently ether was added and the mixture was stored in the refrigerator to give the protonation products **8**. Likewise were prepared:

Compound	yield	m.p.	Calc: Found:	C	H	O	N	S	Cl
3-N,N-Dimethylimmonium-2,2-dimethyl-N'-(4-toluenesulfonyl)-thiopropionamideperchlorate (**8a**)	42%	111–120	$C_{14}H_{21}O_6N_2S_2Cl$ (412·92)	40·72 40·95	5·13 5·65	23·25	6·78 6·52	15·53 15·66	8·59 8·74
3-N,N-Dimethylimmonium-2,2-dimethyl-N-(4-toluenesulfonyl)-thiobutyramideperchlorate (**8b**)	80%	153–156	$C_{15}H_{23}O_6N_2S_2Cl$ (426·95)	42·20 42·10	5·43 5·61	22·48	6·56 6·55	15·02 14·86	8·30 8·18
3-N,N-Dimethylimmonium-2,2,4-trimethyl-N'-(toluenesulfonyl)-thiovaleramideperchlorate (**8c**)	55%	160–162	$C_{17}H_{27}O_6N_2S_2Cl$ (455·00)	44·89 44·78	5·98 5·98	21·10	6·16 6·27	14·09 13·99	7·79 8·04
3-N,N-Dimethylamino-3-phenyl-2,2-dimethyl-N'-(4-toluenesulfonyl)-thiopropionamide-perchlorate (**8d**)	45%	135–138	$C_{20}H_{25}O_6N_2S_2Cl$ (489·02)	49·12 49·14	5·15 5·35	18·71	5·73 5·63	13·11 12·88	7·25 7·40
3-N,N-Tetramethyleneimmonium-3-phenyl-2,2-dimethyl-N'-(4-toluenesulfonyl)-thiopropion-amideperchlorate (**8e**)	90%	108–115	$C_{22}H_{27}O_6N_2S_2Cl$ (515·08)	51·30 51·48	5·28 5·41	18·64	5·44	12·45 11·55	6·88 6·45
3-N,N-Dimethylimmonium-2,2-dimethyl-N'-benzenesulfonyl-thiobutyramideperchlorate (**8f**)	43%	167–170	$C_{14}H_{21}O_6N_2S_2Cl$ (412·92)	40·72 40·73	5·13 5·14	23·25	6·78 6·69	15·53 15·63	8·59 8·51

Compound	yield	m.p.	Calc: Found:	C	H	O	N	S	Cl
3-N,N-Dimethylimmonium-2,2,4-trimethyl-N'-methanesulfonyl-thiovaleramideperchlorate (**8g**)	66%	169–174	$C_{11}H_{23}O_6N_2S_2Cl$ (378·70)	34·87 34·92	6·12 6·29	25·74	7·39 7·58	16·92 16·57	9·36 9·40
3-N,N-Dimethylimmonium-2,2-dimethyl-N'-methanesulfonyl-thiobutyramideperchlorate (**8h**)	57%	170–171(d)	$C_9H_{19}O_6N_2S_2Cl$ (350·85)	30·81 30·74	5·46 5·45	27·36	7·98 7·98	18·28 18·24	10·11 10·24
N-(N',N'-Dimethylammonium-sulfonyl)-4-imino-3,3-dimethyl-2-dimethylaminothietane-perchlorate (**8m**)	63%	48–51°	$C_9H_{20}O_6N_3S_2Cl$ (365·86)	29·55 30·81	5·51 5·51	26·24	11·49 11·24	17·53	9·69 8·88

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