Cycloadditions of 1-aza-2-azoniaallene cations to isothiocyanates

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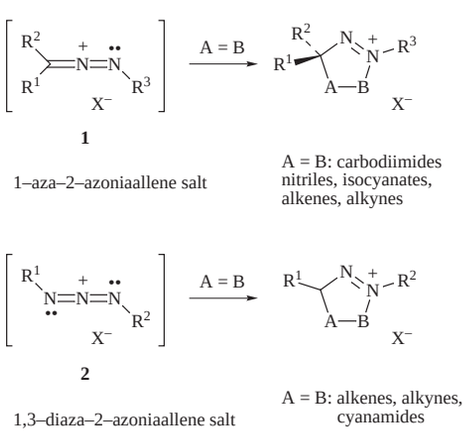
Isothiocyanates react as S-nucleophiles with 1-aza-2-azoniaallene salts **1** to give different types of 1,3,4-thiadiazolium salts (**9**, **11**, **12**) and 1,2,4-triazolium salts (**10**). Which product is formed, depends on the one hand on the ability of a substituent of the heteroallene salt **1** to undergo a [1,2] shift as a positively charged migrant (generalized Wagner–Meerwein rearrangement) or to act as a cationic leaving group, and on the other hand on Dimroth rearrangement of the initially formed thiadiazolium salt **8** to triazolium salts. The structures of the thiadiazolium salt **9c** and the triazolium salt **10d** were confirmed by X-ray structural analyses.

Introduction

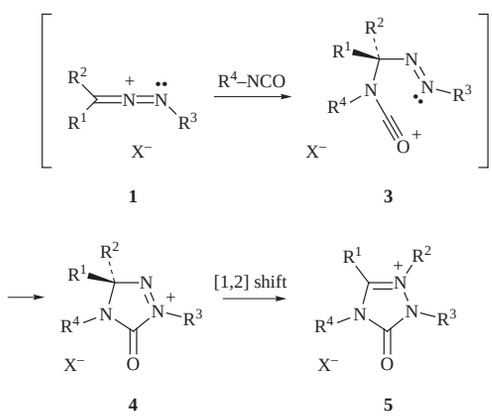
While 1,3-dipolar cycloadditions of neutral 1,3-dipoles are widely used in preparative organic chemistry,[1] reports on cycloadditions of cationic four-electron-three-center components to multiple bonds are scarce. Interesting inorganic examples of such "1,3-dipolar cycloadditions with reverse electron demand" have been reported for certain sulfur–nitrogen compounds.[2–5] For instance, the ion $S{=}N^+{=}S$ behaves as a 1,3-dipole undergoing cycloadditions to alkynes, alkenes and nitriles. In contrast, the economically important nitronium ion $O{=}N^+{=}O$ acts as a strong electrophile effecting, for example, aromatic nitration.

Recently, we reported preparations of azoniaallene salts as reactive intermediates, among others of 1-aza-2-azoniaallene salts **1** and of 1,3-diaza-2-azoniaallene salts **2**. These salts react as four-electron-three-center components in cycloadditions with many types of multiple bonds (Scheme 1).[6–8]



Scheme 1 Cycloadditions of 2-azoniaallene cations.

Cations **1** and **2** undergo cycloadditions to electron-rich alkenes with complete retention of configuration of the alkene.[7–9] This led us to assume that additions of cations **1** and **2** to alkenes and alkynes are concerted reactions, a view which is supported by semi-empirical AM1 calculations. However, cycloadditions of cations **1** and **2** to the triple bond of nitriles are most likely two-step processes with nitrilium ions as intermediates.[10] Likewise, according to AM1 calculations, cycloadditions of heteroallenes **1** to carbodiimides[11] and isocyanates[12] (Scheme 2) should proceed in two steps.



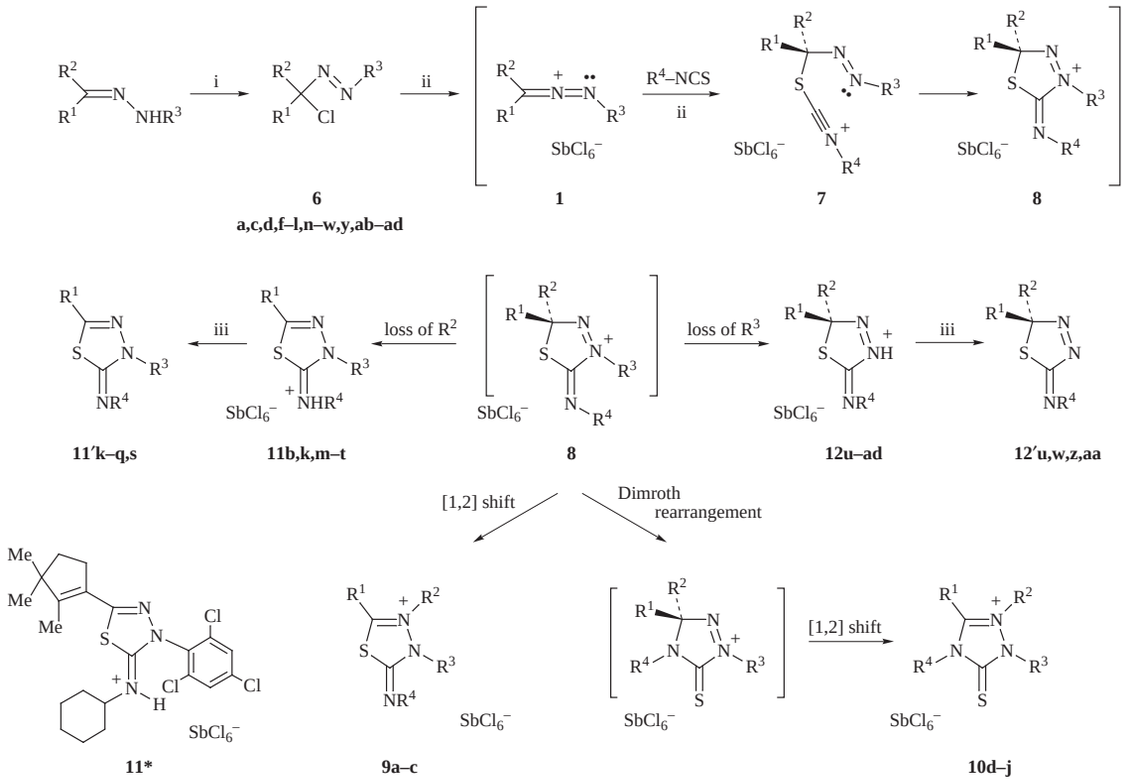
Scheme 2 Cycloadditions of isocyanates to 1-aza-2-azoniaallene salts **1**.[12]

Not all types of multiple bonds react with 2-azoniaallenes **1**, **2**. For example, no reactions could be induced between sulfinylamines R–N=S=O and cations **1**, **2**. No products could be isolated from reactions of compounds **1**, **2** with carbonyl compounds (aldehydes, ketones, carboxamides). Azomethines add as N-nucleophiles to the carbon atom of the $C{=}N^+{=}N$ unit of cations **1** with formation of rather sensitive iminium salts.[13]

Recently, we reported syntheses of 2,5- and 2,3-dihydro-2-(glucosylimino)-1,3,4-thiadiazoles formed by reaction of a glucosyl isothiocyanate with certain salts **1**.[14] Furthermore, 2,3-dihydro-2-(iminoalkyl)-1,3,4-thiadiazolium salts were produced by cycloadditions of a 1-aza-2-azoniaallene salt derived from camphor with isothiocyanates.[15] However, it soon turned out that reactions of heteroallenes **1** with isothiocyanates can lead to different products depending on the substitution pattern of cation **1**. Here we report the results of a more systematic investigation of reactions of cations **1** with isothiocyanates R–NCS.

Results and discussion

1-Aza-2-azoniaallene salts **1** were prepared as reactive intermediates by treating (1-chloroalkyl)azo compounds **6**[16] at low temperature (−60 °C, CH_2Cl_2) with antimony pentachloride (Scheme 3).[8] In the presence of an isothiocyanate a colour change between −60 °C and +23 °C of the orange suspension of the heteroallene **1** indicated a reaction. In all cases a single product was isolated in good yield and purity. No limitations



	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
a	Pr^i	Pr^i	2,4,6-$Cl_3C_6H_2$	Ph	**p**	Pr	H	2,4,6-$Cl_3C_6H_2$	Ph
b	Pr^i	Pr^i	2,4,6-$Cl_3C_6H_2$	Me	**q**	Pr^i	H	2,4,6-$Cl_3C_6H_2$	C_6H_{11}
c	Me	Pr^i	2,4,6-$Cl_3C_6H_2$	Ph	**r**	Me	Pr^i	COOEt	Ph
d	Me	Me	2,4,6-$Cl_3C_6H_2$	Pr^i	**s**	Et	Pr^i	COOEt	Ph
e	Me	Me	2,4,6-$Cl_3C_6H_2$	Ph	**t**	Pr^i	Pr^i	COOEt	Ph
f	$(CH_2)_4$		2,4,6-$Cl_3C_6H_2$	Me	**u**	Me	Me	COPh	Pr^i
g	$(CH_2)_5$		2,4,6-$Cl_3C_6H_2$	Me	**v**	Me	Me	COOEt	Pr^i
h	Me	Et	2,4,6-$Cl_3C_6H_2$	Me	**w**	Me	Et	COOEt	Ph
i	Me	Ph	2,4,6-$Cl_3C_6H_2$	Me	**x**	Me	Et	COOEt	Me
j	Ph	Et	2,4,6-$Cl_3C_6H_2$	Me	**y**	Me	Me	Bu^t	Pr^i
k	Me	Bn	2,4,6-$Cl_3C_6H_2$	Me	**z**	Me	Me	Bu^t	Ph
l	Pr^i	Pr^i	4-$NO_2C_6H_4$	Me	**aa**	Me	Me	Bu^t	allyl
m	Pr^i	Pr^i	4-$NO_2C_6H_4$	Bu^t	**ab**	Me	Et	Bu^t	Ph
n	Me	H	2,4,6-$Cl_3C_6H_2$	C_6H_{11}	**ac**	Et	Pr^i	Bu^t	Me
o	Et	H	Bu^t	Ph	**ad**	R^1–C–R^2 = 2-adamantyl		Bu^t	Pr^i

Scheme 3 *Reagents and conditions* (yields after recrystallization): i, $SbCl_5$, −60 °C, CH_2Cl_2; ii, CH_2Cl_2, −60 to 23 °C, 130 min; iii, NaOH–H_2O; **9a** 82%, **9b** 76%, **9c** 86%, **10d** 66%, **10e** 50%, **10f** 55%, **10g** 47%, **10h** 65%, **10i** 44%, **10j** 87%, **11b** 50%, **11k** 56%, **11′k** 57%, **11l** 80%, **11′l** 66%, **11m** 63%, **11′m** 66%, **11n** 66%, **11′n** 87%, **11o** 39%, **11′o** 66%, **11p** 74%, **11′p** 86% (picrate), **11q** 49%, **11′q** 77% (picrate), **11r** 41%, **11s** 36%, **11′s** 72%, **11t** 36%, **12u** 59%, **12′u** 89%, **12v** (≡ **12u**) 56%, **12w** 42%, **12′w** 58%, **12x** 48%, **12y** (≡ **12u**) 79%, **12z** 55%, **12′z** 96%, **12aa** 89%, **12′aa** 85%, **12ab** (≡ **12w**) 57%, **12ac** 54%, **12ad** 71%.

could be found for the reaction of 1-aza-2-azoniaallene salts **1** with isothiocyanates.

Concerted cycloadditions to isothiocyanates are known to occur both on the C=S and the C=N bonds in a competitive manner.[17] However, according to AM1 calculations, cycloadditions of heteroallenes **1** to isothiocyanates seem to be *two-step* reactions with nitrilium ions **7** as intermediates (Schemes 2, 3). While isocyanates act as N-nucleophiles towards heteroallenes **1** furnishing 1,2,4-triazolium salts **4** or **5** *via* acylium intermediates **3**,[12] isothiocyanates react as S-nucleophiles affording 1,3,4-thiadiazolium salts **9, 11, 12** or 1,2,4-triazolium salts **10**.

Thus, when the 1-aza-2-azoniaallene salt **1a** was treated with phenyl isothiocyanate the moderately stable thiadiazolium salt **9a** was isolated in 82% yield (after recrystallization). Correspondingly, heterocycles **9b**,**c** were obtained. Thiadiazolium salts of this type seem to be unreported in the literature.

Assignments in favour of the thiadiazolium structure **9** and against an isomeric triazolium constitution **10** are based *inter alia* on the IR spectra (KBr, CH_2Cl_2), which are characterized by a very strong, somewhat broad band between 1615 and 1670 cm^{-1} assigned to the stretching vibration of the exocyclic C=N double bond. That this absorption for exocyclic C=N is greatly enhanced has been discussed by West and Warkentin for a 2-imino-1,3,4-thiadiazole.[18,19] In the ^{13}C NMR spectra (CD_3CN) the signals for C=N were found between 168 and 180 ppm (C2) and between 140 and 150 ppm (C5).

L'abbé and co-workers pointed out that a phenylimino structure is substantiated by a low-field resonance of the aromatic *ipso*-C atom (**9a**,**c** around 150 ppm) and high-field absorptions for the *ortho*- and *para*-C atoms (**9a**,**c** around 121 and 127 ppm).[20]

The constitution of the salt **9c** was additionally confirmed by X-ray structural analysis (Fig. 1, Table 1). It should be noted that the bonds N3–C13 and C12–S are *cis* orientated with respect to each other (dihedral angles S–C12–N3–C13: −6.6°;

Table 1 Selected bond lengths (pm), bond angles and torsional angles (°) for **9c**[21]

Atoms	Exp.	Atoms	Exp.
C1–N1	130.6(5)	C3–N1–C1	128.8(3)
N1–N2	140.9(4)	C6–N2–N1	119.2(3)
N2–C12	141.3(4)	N3–C12–N2	121.8(3)
C12–S	179.9(4)	C12–N3–C13	122.0(3)
S–C1	172.7(4)	C1–N1–N2–C12	2.4(4)
C1–C2	151.2(6)	N1–N2–C12–S	−0.9(4)
N1–C3	152.7(5)	N2–C12–S–C1	−0.5(3)
N2–C6	144.0(4)	C12–S–C1–N1	1.9(3)
C12–N3	125.8(5)	S–C1–N1–N2	−2.8(4)
C1–N1–N2	113.5(3)	S–C12–N3–C13	−6.6(6)
N1–N2–C12	113.9(3)	C12–N3–C13–C14	141.8(4)
N2–C12–S	107.6(3)	N2–C12–N3–C13	175.1(3)
C12–S–C1	90.5(2)	N1–N2–C6–C7	−72.6(4)
S–C1–N1	114.6(3)	C1–N1–C3–C4	67.8(5)
C2–C1–N1	125.4(4)	C2–C1–N1–N3	1.7(7)

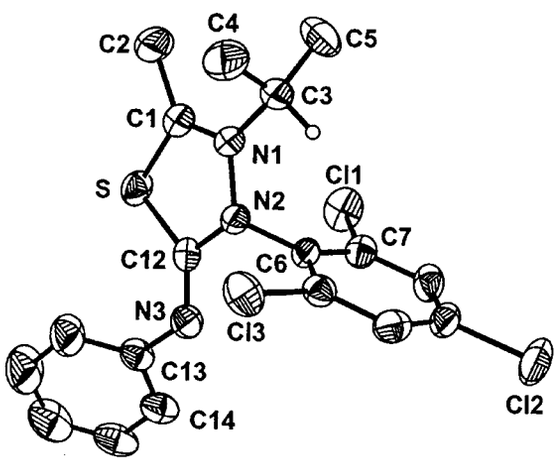


Fig. 1 ORTEP Plot for the cation **9c**.

N2–C12–N3–C13: 175.1°; C12–N3–C13–C14: 141.8°) (*cf.* structure **12′z**).

A rationale for the formation of heterocycles **9** is depicted in Scheme 3. Obviously, the initially formed cycloadducts **8** are unstable rearranging to the thiadiazolium salts **9** by a [1,2] shift of substituent R^2. Such shifts play an important role in the chemistry of azolium salts.[8,22–25] Mechanistically, these shifts can be regarded as generalized Wagner–Meerwein rearrangements.[22] In the transition state the migrant carries a positive partial charge. If there is a choice, the group forming the more stable carbenium ion migrates preferentially. Thus, in **8c** the isopropyl group migrates in preference to the methyl group.

Under the conditions described for the formation of thiadiazoles **9**, the 1-aza-2-azoniaallene **1d** reacted with isopropyl isothiocyanate to afford the triazolium salt **10d** in 66% yield. Similarly, the salts **10e–j** were obtained (Scheme 3). The ring enlargement reactions leading to the bicyclic compounds **10f,g** are worth mentioning. Triazolium salts of type **10** seem to be unreported in the literature.

In place of a strong, broad band between 1615 and 1670 cm^{-1} observed for salts **9**, compounds **10** show a moderately strong and sharp IR absorption (KBr or nujol) between 1590 and 1615 cm^{-1} assigned to the endocyclic C=N double bond, and two strong bands around 1565 and 1555 cm^{-1}. In the ^{13}C NMR spectra (CD_3CN) the signals for C=N and C=S appear at 155–160 ppm and 167–169 ppm. For neutral 4,5-dihydro-1,2,4-triazole-5-thiones chemical shifts for C=N between 145 and 160 ppm and for C=S between 161 and 169 ppm have been reported.[26–30] The four ^{13}C signals for the N-phenyl group of **10e** fall in the range of 128.8 to 133.0 ppm. The absence of phenyl signals around 150 and 121 ppm is further evidence against an isomeric structure **9e**.

Table 2 Selected bond lengths (pm), bond angles and torsional angles (°) for **10d**[21]

Atoms	Exp.	Atoms	Exp.
C1–N2	136.4(5)	N1–C2–C20	123.6(1)
N2–N1	138.5(5)	C1–N3–C31	121.0(4)
N1–C2	131.8(5)	C1–N2–N1–C2	1.0(5)
C2–N3	134.9(6)	N2–N1–C2–N3	0.0(4)
N3–C1	140.2(5)	N1–C2–N3–C1	−0.9(4)
C1–S	163.1(5)	C2–N3–C1–N2	1.5(4)
C1–N2–N1	109.9(3)	N3–C1–N2–N1	−1.5(4)
N2–N1–C2	108.1(3)	N1–N2–C1–S	179.0(3)
N1–C2–N3	108.2(4)	C31–N3–C1–S	−2.1(6)
C2–N3–C1	110.4(3)	C32–C31–N3–C1	−95.0(5)
N3–C1–N2	103.4(4)	C1–N2–N1–C11	179.9(4)
N3–C1–S	129.6(3)	C1–N3–C2–C20	179.2(4)
N2–C1–S	127.0(3)	C2–N1–N2–C21	175.6(4)
C2–N1–C11	130.4(4)	N1–N2–C21–C22	−76.1(6)

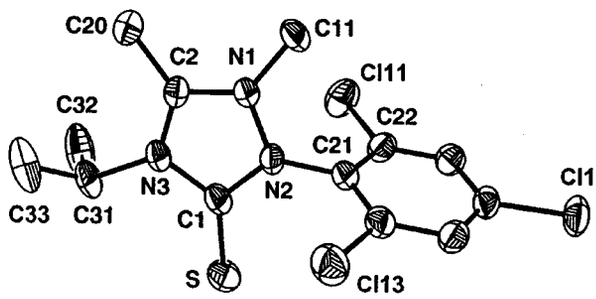


Fig. 2 ORTEP Plot for the cation **10d**.

The constitution of compound **10d** was additionally established by X-ray structural analysis (Fig. 2, Table 2).

The triazoles **10** must have been formed by Dimroth rearrangement of intermediates **8**. We never observed a Dimroth rearrangement **9**→**10**. If the [1,2] shift of R^2 of the thiadiazolium ion **8** is faster than Dimroth rearrangement, the final product is a salt **9**. *Vice versa*, if Dimroth rearrangement of the intermediate **8** is faster than a [1,2] shift of R^2, one ends up with a triazole **10**. Thus, with the good migrant isopropyl (**8a–c**) thiadiazoles **9** are produced, while with the slower migrant ethyl (**8h**) the triazolium salt **10h** is formed. The substitution patterns of compounds **9**, **10** show that an isopropyl group migrates in preference to a methyl (**9c**), the ethyl or phenyl groups. An ethyl group is a better migrant than a methyl group (**10h**), the phenyl group migrates faster than methyl (**10i**) but not as fast as ethyl (**10j**). A phenonium ion mechanism might be operative in cases of phenyl migration.

It is well known from other azolium rearrangements that substituents forming especially stable carbenium ions can escape from the heterocycle instead of migrating intramolecularly to another ring position.[8,10,14,23,31–35] When the heteroallene **1k** with R^2 = benzyl was treated with methyl isothiocyanate, instead of a thiadiazolium salt **9**, the salt **11k** without a benzyl substituent was isolated (Scheme 3). Most likely, traces of water intercepting a free benzyl cation as benzyl alcohol are responsible for this result. Recently, we reported a similar reaction leading to salt **11*** (Scheme 3), the structure of which, including the site of protonation, was secured by X-ray structural analysis.[15] From a heteroallene **1** with R^2 = *tert*-butyl and a glucosyl isothiocyanate a thiadiazolium salt **11** was formed with concomitant loss of isobutene.[14]

The isopropyl group seems to be a borderline case of a group, which either migrates to afford a salt **9** or is eliminated as propene to furnish a salt **11**. Thus, under apparently identical conditions in three experiments compound **9b** containing two isopropyl groups was obtained from the reaction of heteroallene **1a** with methyl isothiocyanate, while in three other experiments the salt **11b** with only one isopropyl substituent was

isolated. Under conditions where heteroallene **1a** reacted with methyl isothiocyanate to give the diisopropyl compound **9b**, the more electron deficient allene **1l** reacted to afford the monoisopropyl compound **11l**. Similarly, from salt **1l** and *tert*-butyl isothiocyanate the heterocycle **11m** was obtained.

The heteroallenes **1** with R^2 = H are worth mentioning. The difficulties associated with the syntheses of such compounds have been discussed elsewhere.[31] When the heteroallene **1n** was treated with cyclohexyl isothiocyanate, the thiadiazolium salt **11n** was isolated (66%). Correspondingly, from allenes **1o–q** the heterocycles **11o–q** were prepared. Not unexpectedly, a proton is a better migrant than an alkyl cation. The site of protonation of compounds **11** suggests that for R^2 = H the transformation **8**→**11** is an intermolecular process.

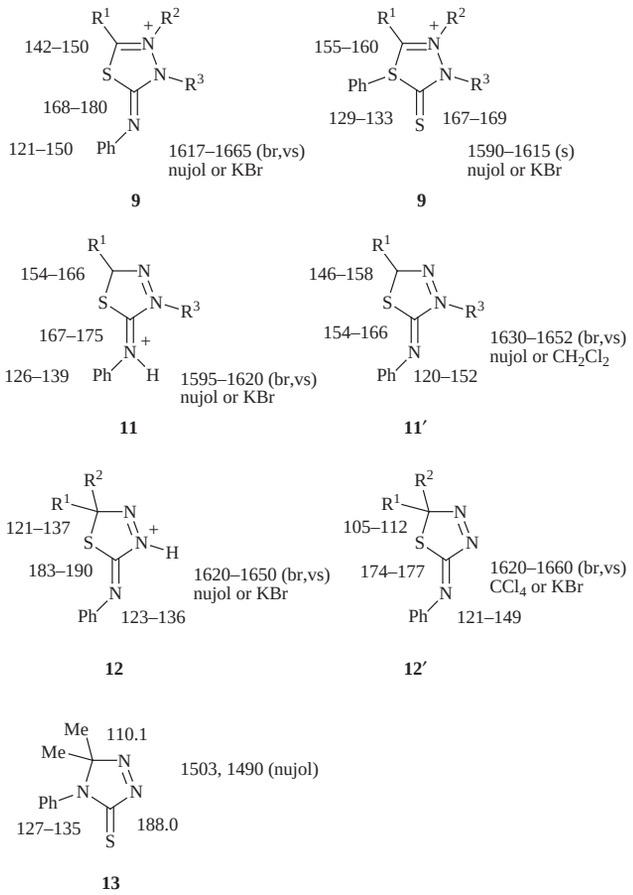
Only thiadiazolium salts (**11r–t**) were obtained from reactions of isothiocyanates with heteroallenes **1** with R^2 = isopropyl and R^3 = COOEt. On treatment with aqueous sodium hydroxide the thiadiazoles **11′k–q**,**s** were obtained from their salts. The bases **11′p**,**q** were characterized as their picrates.

Similar to compounds **9**, salts **11** are characterized by a strong, broad IR band between 1595 and 1620 cm^{-1} and other strong bands between 1540 and 1600 cm^{-1} (Nujol mull or KBr). In the ^1H NMR spectra (CD_3CN) ^3J couplings with the iminoalkyl substituent and NH indicate protonation of the exocyclic imino nitrogen atom. In the ^{13}C NMR spectra two resonances for C=N were found at 154–166 ppm and 167–175 ppm. Other than for salts **9**, no unusual shifts for the exocyclic phenyliminium groups (**11o**,**p**,**r–t**) were observed. The IR and ^{13}C NMR characteristics of the salts **11** and their bases **11′** have been put together in Scheme 4.

While heteroallenes **1** with a good leaving group R^2 such as benzyl, hydrogen, *tert*-butyl,[15] or occasionally also isopropyl, react with isothiocyanates to furnish 2,3-dihydro-2-imino-1,3,4-thiadiazolium salts **11**, cations **1** with a good leaving group R^3 afford 2,5-dihydro-2-imino-1,3,4-thiadiazolium salts **12** (Scheme 3). Obviously, a leaving group R^3 is a good one if its elimination from intermediate **8** is faster than Dimroth rearrangement **8**→**10.** Thus, when the benzoyl compound **6u** was treated with antimony pentachloride and isopropyl isothiocyanate the moderately stable iminium salt **12u** was obtained (59%). Alternatively, this salt was prepared from the carboxylate **6v** and isopropyl isothiocyanate (**12u**≡**12v**, 56%). Correspondingly, the thiadiazolium salts **12w**,**x** were obtained (Scheme 3). Again, the presence of traces of moisture in the reaction mixtures is likely to be responsible for these results.

Easily accessible are heteroallenes **1** with R^3 = *tert*-butyl.[8] Thus, when the (1-chloroalkyl)azo compound **6y** was treated with antimony pentachloride and isopropyl isothiocyanate the salt **12y** (≡**12u**) was obtained in 79% yield. Neutralization with aqueous sodium hydroxide afforded the imine **12′u** (89%). Correspondingly, the salts **12z–ad** were prepared. Interestingly, for none of the cations **12** was a [1,2] shift of R^2 (*e.g.* **12ac** with R^2 = isopropyl) observed.

The salts **12** all show a very strong and broad IR band between 1620 and 1650 cm^{-1} and a sharp strong band between 1530 and 1555 cm^{-1} (nujol, KBr) (Scheme 4). The bases **12′** show a broad, strong C=N vibration between 1620 and 1660 cm^{-1} (CCl_4 or KBr). The ^{13}C resonances for the sp^3 hybridized ring carbon atoms C5 were found at unusually low field (**12** 121–137 ppm, **12′** 105–112 ppm) as were the signals for SC=N (**12** 183–190 ppm, **12′** 174–177 ppm). Similar observations for 2,5-dihydro-1,3,4-thiadiazoles have been reported by Heimgartner and co-workers.[36] In contrast to compounds **11**, for the salts **12** a $^3J_{HNCH}$ coupling was not observed. Hence in contrast to thiadiazolium salts **11**, the site of protonation of compounds **12** is unlikely to be the exocyclic imino nitrogen atom. The ^{13}C NMR resonances for the phenyl *ipso*-carbon atoms of salts **12w,z** (about 136 ppm) were not found to be shifted to unusually low fields as observed for the salts **9a,c** (around 150 ppm). However, shifts around 149 ppm were found for the bases

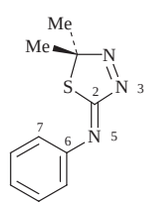


Scheme 4 Some ^{13}C NMR (ppm in CD_3CN or $CDCl_3$) and IR characteristics of the new heterocycles prepared.

12′w,z. These findings suggest N3 to be the site of protonation of salts **12**. Because of amidinium resonance, the double bond character of the exocyclic C=N bond of salts **12** should be less pronounced than in the amidines **12′**.

Compound **12z** was prepared by Landquist by oxidation of acetone 4-phenylthiosemicarbazone with manganese dioxide.[37] Under slightly different conditions Landquist obtained the isomeric triazole **13**. For reasons of comparison the spectroscopic data for compound **13** are included in Scheme 4.[18,38]

The crystallographic structure of the thiadiazole **12′z** has



12′z

been reported.[39,40] An X-ray crystallographic analysis of our product **12′z** confirmed the identity with Landquist's compound. Our crystallographic data will not be repeated here, since they are in good agreement with the literature data.

Similar to the stereochemistry observed for salts **9c** and **11***,[15] the N5–C6 and the C2–S bonds of compound **12′z** are *cis* orientated with respect to each other (dihedral angles S–C2–N5–C6: −2.0(2)°; N3–C2–N5–C6: −178.1(1)°; C2–N5–C6–C7: +145.1(2)°). This is in contrast to what one would expect for stereoelectronic reasons. Nucleophilic additions to the nitrilium triple bond of intermediates **7** are known to proceed stereoelectronically controlled in such a way that in the product the

nitrilium substituent R^4 and N-nucleophile are *cis* orientated with respect to each other.[41,42] It is tempting to speculate that under the reaction conditions the primarily formed *cis* products undergo fast isomerization to the thermodynamically more stable *trans* products **9c**,**11***,**12′z**.[43] Actually, all compounds **9**, **11**, **12** were isolated as single geometrical isomers.

Experimental

Solvents were dried by standard methods. Cycloadditions were carried out with exclusion of moisture. IR spectra were recorded on a Perkin-Elmer FTIR 1600 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-250 and WM-250 spectrometers; internal reference $SiMe_4$; 295 K; δ-scale; *J*-values are given in Hz.

X-Ray structural analysis of 9c[21]

Crystal data. $[C_{18}H_{17}Cl_3N_3S]^+[SbCl_6]^-$, $M = 748.2$, monoclinic, space group $P2_1/n$ (No. 14), $a = 811(1)$, $b = 2650(1)$, $c = 1345.0(6)$ pm, $\beta = 101.4(1)°$, $T = 248$ K, $V = 2835(4) \times 10^6$ pm^3, $Z = 4$, $F(000) = 1464$, $D_c = 1.753$ g cm^{-3}, μ(Mo-Kα) = 19.09 cm^{-1}, $\lambda = 71.073$ pm.

Data collection. Intensity data were collected on a Siemens P4 diffractometer using Mo-Kα radiation from a graphite monochromator in the θ-range of 2.18–27.00° (Wyckoff scan). The orange crystal used had dimensions 0.3 × 0.3 × 0.5 mm. Three reference reflections were measured every 97 reflections. The reference reflections showed no significant variation in intensities throughout data collection. Lorentz and polarization corrections were applied to the data and equivalent reflections were merged to give 5218 unique reflections with $I/\sigma(I) > 2$ (R_{int} = 0.0253 for all 6194 reflections).

Structure solution and refinement.[44] The structure was solved by direct methods in *Pn* and refined in $P2_1/n$. All atoms including all hydrogen atoms were located by difference-Fourier synthesis. The hydrogen atoms were refined with fixed isotropic *U*. A semi-empirical absorption correction was applied by using psi-scan data. The final cycles of full-matrix least-squares refinement converged against $R = 0.0380$ and $wR(F) = 0.0904$ for 357 parameters and 5218 reflections with weights of $1/[\sigma^2(F) + 0.034000P^2 + 5.660400P]$ where $P = (F_o^2 + 2F_c^2)/3$. In the final difference-Fourier map there were residual peaks in the range −0.79 to +0.87 × 10^{-6} e pm^{-3}.

X-Ray structural analysis of 10d[21]

Crystal data. $[C_{13}H_{15}Cl_3N_3S]^+[SbCl_6]^-$, $M = 686.1$, monoclinic, space group $P2_1/n$ (No. 14), $a = 956.6(3)$, $b = 1878.6(7)$, $c = 1414.7(5)$ pm, $\beta = 105.2(1)°$, $T = 243$ K, $V = 2453(2) \times 10^6$ pm^3, $Z = 4$, $F(000) = 1336$, $D_c = 1.858$ g cm^{-3}, μ(Mo-Kα) = 22.11 cm^{-1}, $\lambda = 71.073$ pm.

Data collection. Intensity data were collected on a Siemens R3m/V diffractometer using Mo-Kα radiation from a graphite monochromator in the θ-range of 2.0–27.0° (Wyckoff scan). The yellow crystal used had dimensions 0.35 × 0.35 × 0.40 mm. Three reference reflections were measured every 97 reflections. The reference reflections showed no significant variation in intensities throughout data collection. Lorentz and polarization corrections were applied to the data and equivalent reflections were merged to give 4289 unique reflections with $I/\sigma(I) > 4$ (R_{int} = 0.046 for all 5349 reflections).

Structure solution and refinement.[45] The structure was solved by the Patterson method. All non-hydrogen atoms were located by difference-Fourier synthesis. For the hydrogen atoms the riding model with d(C–H) = 0.95 pm and fixed isotropic *U* was applied. A semi-empirical absorption correction was applied by using psi-scan data. The final cycles of full-matrix least-squares refinement converged against $R = 0.0368$ and $wR(F) = 0.0395$ for 244 parameters and 4289 reflections with weights of $1/[\sigma^2(F) + 0.00001F^2]$. In the final difference-Fourier map there were residual peaks in the range −0.85 to +0.98 × 10^{-6} e pm^{-3}.

Preparation of the hydrazones: general procedure

A solution of the ketone (100 to 120 mmol) and the hydrazine (100 mmol) in EtOH (100 ml) containing AcOH (1 ml) was boiled under reflux for 6 to 12 h. Evaporation of the solvent and crystallization of the residue at −15 °C from EtOH afforded the pure hydrazone. Alternatively, the crude hydrazone was dissolved in pentane. The solution was left at −15 °C for 12 h. Filtration with added decolorizing charcoal and evaporation of the solvent furnished the pure hydrazone.

The following new hydrazones were obtained.

2,4-Dimethylpentan-3-one (2,4,6-trichlorophenyl)hydrazone. The title compound was isolated (24.66 g, 80%) as a brownish oil (Found: C, 50.89; H, 5.55, N, 9.18. $C_{13}H_{17}Cl_3N_2$ (MW = 307.7) requires C, 50.75; H, 5.57; N, 9.11%); ν_{max}(neat)/cm^{-1} 1559, 1468; δ_H(250 MHz; $CDCl_3$) 1.12 (d, *J* 6.8, 6 H), 1.23 (d, *J* 7.0, 6 H) (CH_3), 2.62 (septet, *J* 6.8), 3.04 (septet, *J* 7.0) (CH), 7.13 (br, NH), 7.25 (aryl); δ_C(62.9 MHz; $CDCl_3$) 18.8, 21.7 (CH_3), 27.9, 31.3 (CH), 125.9, 126.4, 128.6, 139.4 (aryl), 164.1 (C=N).

1-Phenylpropanone (2,4,6-trichlorophenyl)hydrazone. The title compound was isolated (20.64 g, 63%) as a moderately stable crystalline powder; mp 63–64 °C (decomp.) (Found: C, 54.87; H, 4.10; N, 8.63. $C_{15}H_{13}Cl_3N_2$ (MW = 327.6) requires C, 54.99; H, 4.00; N, 8.55%); ν_{max}(CH_2Cl_2)/cm^{-1} 1687, 3355; δ_H(250 MHz; $CDCl_3$) *ca.* 5:1 mixture of the geometrical isomers; main isomer 1.29 (t, *J* 7.7, CH_3), 2.77 (q, *J* 7.7, CH_2), 7.49 (br, NH), 7.21–7.78 (several m, aryl); minor isomer 1.12 (t, *J* 7.5, CH_3), 2.57 (q, *J* 7.5, CH_2); δ_C(62.9 MHz; $CDCl_3$) main isomer 10.1 (CH_3), 19.3 (CH_2), 151.7 (C=N); minor isomer 11.1 (CH_3), 31.4 (CH_2), 153.6 (C=N).

2,4-Dimethylpentan-3-one (4-nitrophenyl)hydrazone. The title compound was isolated (21.19 g, 85%) as an orange powder; mp 113–115 °C (Found: C, 62.61; H, 7.69; N, 16.90. $C_{13}H_{19}N_3O_2$ (MW = 249.3) requires C, 62.63; H, 7.68; N, 16.85%); ν_{max}(CCl_4)/cm^{-1} 3375, 1601; δ_H(250 MHz; $CDCl_3$) 1.18 (d, *J* 6.7), 1.20 (d, *J* 6.9) (CH_3), 2.69 (septet, *J* 6.7), 2.95 (septet, *J* 6.9) (CH), 7.07 (m, 2 H), 8.13 (m, 2 H) (aryl), 7.92 (br, NH); δ_C(62.9 MHz; $CDCl_3$) 19.0, 22.1 (CH_3), 27.6, 30.9 (CH), 111.6, 126.1, 139.5, 151.0, 162.2 (aryl, C=).

Ethyl 3-methyl-2-butylidenecarbazate. The title compound was isolated (15.36 g, 89%) as a semi-solid resin, which decomposed during the next few days (Found: C, 55.87; H, 9.27; N, 16.24. $C_8H_{16}N_2O_2$ (MW = 172.2) requires C, 55.79; H, 9.36; N, 16.26%); ν_{max}(CH_2Cl_2)/cm^{-1} 3387, 1741, 1710; δ_H(250 MHz; $CDCl_3$) *ca.* 20:1 mixture of the geometric isomers; main component 1.08 (d, *J* 6.9, 6 H), 1.30 (t, *J* 6.9), 1.83 (CH_3), 2.64 (septet, *J* 6.9, CH), 4.25 (q, *J* 7.0, CH_2), 8.60 (br, NH); δ_C(62.9 MHz; $CDCl_3$) main component 12.0, 14.6, 19.8 (2 C) (CH_3), 36.9, 61.6 (br) (CH, CH_2), 155.0 (br), 174.4 (C=).

Ethyl 2-methyl-3-pentylidenecarbazate. The title compound was isolated (11.36 g, 61%) as prisms; mp 56–58 °C (Found: C, 57.80; H, 9.67; N, 15.26. $C_9H_{18}N_2O_2$ (MW = 186.3) requires C, 58.03; H, 9.74; N, 15.04%); ν_{max}(CCl_4)/cm^{-1} 3395, 1760, 1716, 1701; δ_H(250 MHz; $CDCl_3$) main isomer 1.11 (t, *J* 7.7, 3 H), 1.11 (d, *J* 7.0, 6 H), 1.32 (t, *J* 7.2, 3 H) (CH_3), 2.22 (q, *J* 7.7), 4.27 (q, *J* 7.2, coupled to 1.32) (CH_2), 2.66 (septet, *J* 7.0, CH), 7.82 (br, NH); δ_C(62.9 MHz; $CDCl_3$) main isomer 10.1, 14.6,

19.4, 20.0 (2 C), 36.2, 61.7 (br) (CH_3, CH_2, CH), 154.3 (br), 161.7 (C=).

Ethyl 2,4-dimethyl-3-pentylidenecarbazate. The title compound was isolated (16.42 g, 82%) as a powder; mp 71–73 °C (Found: C, 59.63; H, 10.17; N, 14.01. $C_{10}H_{20}N_2O_2$ (MW = 200.3) requires C, 59.97; H, 10.06; N, 13.99%); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3386, 1741, 1709; δ_H(250 MHz; $CDCl_3$) 1.14 (d, *J* 6.8, 6 H), 1.16 (d, *J* 7.0, 6 H), 1.31 (t, *J* 7.1) (CH_3), 2.64 (septet, *J* 6.8), 2.84 (septet, *J* 7.0) (CH), 4.25 (q, *J* 7.1, CH_2), 8.05 (br, NH); δ_C(62.9 MHz; $CDCl_3$) 14.6, 18.9 (2 C), 21.5 (2 C) (CH_3), 27.7, 31.5 (CH), 61.5 (br, CH_2), 154.5 (br), 164.5 (C=).

Acetone benzoylhydrazone. The title compound was isolated (12.91 g, 73%) as powder; mp 136–138 °C (Found: C, 68.18; H, 6.72; N, 16.10. $C_{10}H_{12}N_2O$ (MW = 176.2) requires C, 68.16; H, 6.86; N, 15.90%); $\nu_{max}(CCl_4)$/cm^{-1} 1656; δ_H(250 MHz; $CDCl_3$) 1.97 (br), 2.09 (br) (CH_3), 7.32–7.79 (several m, phenyl), 8.97 (br, NH); δ_C(62.9 MHz; $CDCl_3$) 16.8 (br), 25.5 (br) (CH_3), 127.3 (br), 128.6 (br), 131.7, 133.7 (phenyl), 156.6 (br), 164.2 (br)(C=).

Ethyl 2-butylidenecarbazate. The title compound was isolated (10.44 g, 66%) as prisms (from pentane); mp 33–35 °C (Found: C, 52.75; H, 8.97; N, 17.55. $C_7H_{14}N_2O_2$ (MW = 158.2) requires C, 53.14; H, 8.92; N, 17.71%); $\nu_{max}(CCl_4)$/cm^{-1} 3394, 1760, 1701; δ_H(250 MHz; $CDCl_3$) *ca*. 4:1 mixture of the geometrical isomers; main isomer 1.10 (t, *J* 7.6), 1.31 (br, t, *J* 7.1), 1.87 (CH_3), 2.33 (q, *J* 7.6), 4.26 (br, q, *J* 7.1) (CH_2), 8.26 (br, NH); δ_C(62.9 MHz; $CDCl_3$) main isomer 11.1, 14.5, 14.6, 32.2, 61.7 (br) (CH_3, CH_2, CH), 154.8 (br), 155.2 (C=).

Butan-2-one *tert*-butylhydrazone. The title compound was prepared from butan-2-one (10.82 g, 150 mmol) and *tert*-butylhydrazinium chloride (12.46 g, 100 mmol) instead of the free hydrazine; yield 10.19 g (57%) of the hydrochloride of the *title hydrazone*; mp 122–124 °C (decomp.) (Found: C, 53.19; H, 10.60; N, 15.93. $C_8H_{19}ClN_2$ (MW = 178.7) requires C, 53.77; H, 10.72; N, 15.68%); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1654, 1564; δ_H(250 MHz; $CDCl_3$) 1.11 (t, *J* 7.3), 1.53 (9 H), 2.42 (q, *J* 7.3), 2.46 (CH_3), 10.78 (br, NH_2); δ_C(62.9 MHz; $CDCl_3$) 9.8, 20.7, 24.9 (3 C), 33.1, 60.3 (CH_3, CH_2, C), 179.5 (C=N). A mixture of the hydrochloride (8.94 g, 50 mmol) and Na_2CO_3 (7.95 g, 75 mmol) in H_2O (100 ml) was stirred for 10 min. Repeated extraction with pentane and usual work-up afforded the *title hydrazone* as a volatile oil (5.05 g, 71%); $C_8H_{18}N_2$ (MW = 142.2); δ_H(250 MHz; $CDCl_3$) main isomer 1.06 (t, *J* 7.3), 1.18 (9 H), 1.69 (CH_3), 2.22 (q, *J* 7.3, CH_2), 4.03 (br, NH_2); δ_C(62.9 MHz; $CDCl_3$) main isomer 11.1, 13.8, 28.6 (3 C), 32.3, 53.2 (CH_3, CH_2, C), 148.1 (C=N).

2-Methylpentan-3-one *tert*-butylhydrazone. The title compound was isolated (5.96 g, 35%) as a moderately stable impure pale yellow oil; bp 67–69 °C/15 Torr; $C_{10}H_{22}N_2$ (MW = 170.3); δ_H(250 MHz; $CDCl_3$) main isomer 1.06 (t, *J* 7.3), 1.07 (d, *J* 6.8, 6 H), 1.17 (9 H) (CH_3), 2.13 (q, *J* 7.3, CH_2), 2.44 (septet, *J* 6.8, CH), 4.37 (br, NH); δ_C(62.9 MHz; $CDCl_3$) main isomer 10.0, 19.8, 20.5, 28.4 (3 C), 35.5, 53.3 (CH_3, CH_2, CH, C), 154.9 (C=N).

Tricyclo[3.3.1.1^{3,7}]decanone *tert*-butylhydrazone. The title compound was prepared from adamantanone (15.02 g, 100 mmol) and *tert*-butylhydrazinium chloride (12.46 g, 100 mmol) instead of the free hydrazine. The hydrochloride of the *title hydrazone* was obtained as a powder (19.39 g, 76%); mp 209–211 °C (decomp.) (Found: C, 65.32; H, 9.73; N, 11.03. $C_{14}H_{25}ClN_2$ (MW = 256.8) requires C, 65.48; H, 9.81; N, 10.91%); ν_{max}(Nujol)/cm^{-1} 1633; δ_H(250 MHz; CD_3SOCD_3; 313 K) 1.37 (9 H, CH_3), 1.76–2.09 (several m, 12 H, CH_2), 2.61 (br, 1 H), 3.28 (br, 1 H) (CH), 11.19 (br, NH); δ_C(62.9 MHz; CD_3SOCD_3; 313 K) 24.3, 26.7, 34.0, 35.5, 37.8, 38.5, 38.7, 57.9 (CH_3, CH_2, CH, C), 185.2 (C=N). The *title hydrazone* was prepared from its hydrochloride in the manner described for butan-2-one *tert*-butylhydrazone and was isolated as an oil (8.38 g, 76%); $C_{14}H_{24}N_2$ (MW = 220.4); ν_{max} (CH_2Cl_2)/cm^{-1} 3352, 1732, 1722; δ_H(250 MHz; $CDCl_3$) 1.18 (9 H, CH_3), 1.73–1.99 (several m, 12 H, CH_2, CH), 2.55 (br, 1 H), 3.00 (br, 1 H) (CH), 4.23 (br, NH); δ_C(62.9 MHz; $CDCl_3$) 28.1, 28.4 (3 C), 29.2, 36.6, 37.5, 39.2, 39.9, 53.0 (CH_3, CH_2, CH, C), 157.7 (C=N).

Preparation of the (1-chloroalkyl)azo compounds: general procedure

The reactions were carried out with exclusion of light. A solution of *tert*-butyl hypochlorite[46] (1.30 g, 12 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a cold (−50 °C) solution of the hydrazone (10 mmol) in CH_2Cl_2 (20 ml). After stirring at −50 °C for 1 h and then at 0 °C for 2 to 10 h, and finally at 23 °C for 0 to 3 h, the solvent was removed under reduced pressure. In most cases the moderately stable orange oily residue **6** was used without further purification.

The following new 1-chloroazo compounds were obtained.

1-[(1-Chloro-1-isopropyl-2-methylpropyl)azo]-2,4,6-trichlorobenzene 6a. The title compound was isolated (3.08 g, 90%) as an orange oil; $C_{13}H_{16}Cl_4N_2$ (MW = 342.1); δ_H(250 MHz; $CDCl_3$) 1.09 (d, *J* 6.7, 6 H), 1.13 (d, *J* 6.7, 6 H) (CH_3), 2.83 (septet, *J* 6.7, 2 CH), 7.41 (aryl); δ_C(62.9 MHz; $CDCl_3$) 17.3, 17.6 (CH_3), 35.8 (CH), 109.8 (C), 127.8, 129.2, 134.0, 145.3 (aryl).

1-[(1-Chloro-1-phenylpropyl)azo]-2,4,6-trichlorobenzene 6j. The title compound was isolated (3.28 g, 91%) as an orange oil; $C_{15}H_{12}Cl_4N_2$ (MW = 362.1); δ_H(250 MHz; $CDCl_3$) 1.07 (t, *J* 7.3, CH_3), 2.67 (q, *J* 7.3) (CH_2), 7.37 (aryl), 7.33–7.73 (several m, phenyl); δ_C(62.9 MHz; $CDCl_3$) 9.0 (CH_3), 36.4 (CH_2), 101.4 (C), 127.2, 127.3, 128.4, 128.7, 128.9, 133.8, 139.3, 145.7 (phenyl, aryl).

1-[(1-Chloro-1-isopropyl-2-methylpropyl)azo]-4-nitrobenzene 6l. The title compound was isolated (13.90 g, 98%) as an orange crystalline powder; mp 59–61 °C (Found: C, 55.00; H, 6.27; N, 14.94. $C_{13}H_{18}ClN_3O_2$ (MW = 283.8) requires C, 55.02; H, 6.39; N, 14.81%); δ_H(250 MHz; $CDCl_3$) 1.06 (d, *J* 6.7), 1.07 (d, *J* 6.7) (CH_3), 2.87 (septet, *J* 6.7, CH), 7.86 (m, 2 H), 8.36 (m, 2 H) (aryl); δ_C(62.9 MHz; $CDCl_3$) 17.3, 17.7 (CH_3), 36.3 (CH), 108.5 (CCl), 123.5, 124.8, 148.9, 154.3 (aryl).

Ethyl (1-chloro-1,2-dimethylpropyl)diazenecarboxylate 6r. The title compound was isolated (1.80 g, 87%) as a yellow oil; $C_8H_{15}ClN_2O_2$ (MW = 206.7); $\nu_{max}(CCl_4)$/cm^{-1} 1769; δ_H(250 MHz; $CDCl_3$) 0.93 (d, *J* 6.7), 1.14 (d, *J* 6.7), 1.41 (t, *J* 7.1), 1.81 (CH_3), 2.57 (septet, *J* 6.7, CH), 4.44 (q, *J* 7.1, CH_2); δ_C(62.9 MHz; $CDCl_3$) 14.1, 17.2, 17.4, 26.4, 38.2 (CH_3, CH), 64.7 (CH_2), 101.0 (C), 161.8 (C=O).

Ethyl (1-chloro-1-ethyl-2-methylpropyl)diazenecarboxylate 6s. The title compound was isolated (1.95 g, 88%) as a yellow oil; $C_9H_{17}ClN_2O_2$ (MW = 220.7); $\nu_{max}(CCl_4)$/cm^{-1} 1769; δ_H(250 MHz; $CDCl_3$) 0.89 (t, *J* 7.3), 0.90 (d, *J* 6.8), 1.14 (d, *J* 6.8), 1.42 (t, *J* 7.1) (CH_3), 2.32 (m, 2 H), 4.45 (q, *J* 7.2, 2 H) (CH_2), 2.67 (septet, *J* 6.8, CH); δ_C(62.9 MHz; $CDCl_3$) 7.8, 14.2, 17.0, 17.3, 32.6, 37.1, 64.7 (CH_3, CH_2, CH), 104.8 (C), 161.9 (C=O).

Ethyl (1-chloro-1-isopropyl-2-methylpropyl)diazenecarboxylate 6t. The title compound was isolated (2.03 g, 87%) as a yellow oil; $C_{10}H_{19}ClN_2O_2$ (MW = 234.7); $\nu_{max}(CCl_4)$/cm^{-1} 1769; δ_H(250 MHz; $CDCl_3$) 1.03 (t, *J* 6.9, 12 H), 1.41 (t, *J* 7.1) (CH_3), 2.78 (septet, *J* 6.9, CH), 4.44 (q, *J* 7.1, CH_2); δ_C(62.9 MHz; $CDCl_3$) 14.2, 17.0 (2 C), 17.3 (2 C) (CH_3), 35.9 (2 CH), 64.6 (CH_2), 108.0 (C), 162.0 (C=O).

1-Benzoylazo-1-chloro-1-methylethane 6u. The title compound was isolated (1.82 g, 86%) as brownish oil; $C_{10}H_{11}ClN_2O$

(MW = 210.7); ν_{max} (CCl_4)/cm^{-1} 1726; δ_H(250 MHz; $CDCl_3$) 1.98 (CH_3), 7.45–7.93 (several m, phenyl); δ_C(62.9 MHz; $CDCl_3$) 29.8 (CH_3), 93.8 (CCl), 129.0, 129.6, 130.2, 134.9 (phenyl), 181.3 (C=O).

Ethyl (1-chloro-1-methylpropyl)diazenecarboxylate 6w. The title compound was isolated (1.63 g, 85%) as a yellow oil (Found: C, 43.36; H, 6.51; N, 14.50. $C_7H_{13}ClN_2O_2$ (MW = 192.6) requires C, 43.64; H, 6.80; N, 14.55%); ν_{max}(CH_2Cl_2)/cm^{-1} 1762; δ_H(250 MHz; $CDCl_3$) 0.99 (t, *J* 7.4), 1.41 (t, *J* 7.1), 1.86 (CH_3), 2.23 (m, 2 H), 4.44 (q, *J* 7.1) (CH_2); δ_C(62.9 MHz; $CDCl_3$) 8.3, 14.1, 27.9, 35.2, 64.8 (CH_3, CH_2), 97.3 (C), 161.7 (C=O).

1-[(1-Chloro-1-methylpropyl)azo]-1,1-dimethylethane 6ab. The title compound was isolated (1.01 g, 57%) as a volatile yellow oil; $C_8H_{17}ClN_2$ (MW = 176.7); ν_{max}(CCl_4)/cm^{-1} 1474, 1455; δ_H(250 MHz; $CDCl_3$) 0.94 (t, *J* 7.3), 1.24 (9 H), 1.73 (CH_3), 2.13 ($AA'X_3$ spectrum, CH_2); δ_C(62.9 MHz; $CDCl_3$) 8.4, 26.9 (3 C), 28.2 (CH_3), 35.6 (CH_2), 67.3 (C), 96.7 (CCl).

1-[(1-Chloro-1-ethyl-2-methylpropyl)azo]-1,1-dimethylethane 6ac. The title compound was isolated (1.69 g, 83%) as a volatile yellow oil; $C_{10}H_{21}ClN_2$ (MW = 204.7); δ_H(250 MHz; $CDCl_3$; 273 K) 0.83 (t, *J* 7.3), 0.87 (d, *J* 6.7), 1.09 (d, *J* 6.8), 1.27 (9 H) (CH_3), 2.21 (m, CH_2), 2.55 (septet, *J* 6.7, CH); δ_C(62.9 MHz; $CDCl_3$; 273 K) 7.9, 17.1, 17.3, 27.1 (3 C) (CH_3), 32.5, 37.0, 67.9 (C, CH, CH_2), 104.4 (CCl).

1-[(2-Chlorotricyclo[3.3.1.1^{3,7}]decan-2-yl)azo]-1,1-dimethylethane 6ad. The title compound was isolated (2.43 g, 95%) as a yellow oil; $C_{14}H_{23}ClN_2$ (MW = 254.8); δ_H(250 MHz; $CDCl_3$) 1.27 (9 H, CH_3), 1.76–2.46 (several m, 14 H, CH_2, CH); δ_C(62.9 MHz; $CDCl_3$) 26.7 (3 C), 27.1, 27.2, 34.6, 34.7, 38.4, 39.6, 68.0 (CH_3, CH_2, CH, C), 98.7 (CCl).

Reactions of (1-chloroalkyl)azo compounds 6 with isothiocyanates: general procedure

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a cold (−60 °C) solution of the (1-chloroalkyl)azo compound **6** (10 mmol) and the isothiocyanate (12 to 20 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at −60 °C for 1 h, then at 0 °C for 1 h and finally at +23 °C for 10 min. After dropwise addition of Et_2O (50 ml) the mixture was kept at −15 °C for 12 h. The product was isolated by filtration.

Preparation of the heterocycles 11′,12′ from their salts 11,12: general procedures

Method A. A solution of NaOH (3.20 g, 80 mmol) in H_2O (20 ml) was added to a solution of a salt **11** or **12** (10 mmol) in CH_2Cl_2 (30 ml)–MeOH (6 ml). The mixture was stirred at −10 °C for 1 h and then at 23 °C for 15 min. Separation of the organic layer and extraction of the aqueous layer with CH_2Cl_2 (2 × 30 ml) afforded after usual work-up the heterocycle **11′** or **12′**.

Method B. In the manner described for method A. However, the salt **11** or **12** (10 mmol) is dissolved in CH_2Cl_2 (60 ml)–MeCN (6 ml).

2,3-Dihydro-4,5-diisopropyl-2-phenylimino-3-(2,4,6-trichlorophenyl)-1,3,4-thiadiazol-4-ium hexachloroantimonate 9a

From azo compound **6a** (3.42 g, 10 mmol) and phenyl isothiocyanate (2.03 g, 15 mmol), *title compound* **9a** was isolated as a powder (7.05 g, 91%), which was recrystallized at −15 °C from warm MeCN (30 ml) to afford a yellow powder (6.39 g, 82%); mp 213–215 °C (decomp.) (Found: C, 31.17; H, 2.74; N, 5.42. $C_{20}H_{21}Cl_9N_3SSb$ (MW = 776.3) requires C, 30.94; H, 2.73; N, 5.41%); ν_{max}(KBr)/cm^{-1} 1661 (br, vs), 1592 (m), 1577 (m), 1564 (m); δ_H(250 MHz; CD_3CN; 273 K) 1.44 (d, *J* 6.7, 6 H), 1.62 (d, *J* 7.0, 6 H) (CH_3), 3.86 (septet, *J* 6.7), 4.61 (br m, CH), 6.90–7.49 (several m, phenyl), 7.88 (aryl); δ_C(62.9 MHz; CD_3CN; 273 K) 21.1, 22.8 (CH_3), 33.0, 63.7 (CH), 120.9, 127.3, 130.4 (br), 131.5, 131.6, 138.7, 141.0, 148.4, 149.6, 179.5 (br) (aryl, C=N).

2,3-Dihydro-4,5-diisopropyl-2-methylimino-3-(2,4,6-trichlorophenyl)-1,3,4-thiadiazol-4-ium hexachloroantimonate 9b

From azo compound **6a** (3.42 g, 10 mmol) and methyl isothiocyanate (0.88 g, 12 mmol), *title compound* **9b** was precipitated from the reaction mixture with pentane (60 ml) to afford a brownish powder (6.42 g, 89%), which was recrystallized at −15 °C from MeCN (10 ml) to furnish a colourless powder (5.46 g, 76%); mp 168–171 °C (decomp.) (Found: C, 25.02; H, 2.75; N, 5.85. $C_{15}H_{19}Cl_9N_3SSb$ (MW = 714.2) requires C, 25.22; H, 2.68; N, 5.88%); ν_{max}(KBr)/cm^{-1} 1617 (br, vs), 1555 (s); δ_H(250 MHz; CD_3CN; 273 K) 1.50 (d, *J* 6.7, 6 H), 1.59 (d, *J* 7.0, 6 H), 3.07 (CH_3), 3.86 (septet, *J* 6.7), 4.56 (br m) (CH), 7.82 (aryl); δ_C(62.9 MHz; CD_3CN; 273 K) 21.1 (br), 22.8 (br), 33.0, 43.0, 63.4 (CH_3, CH), 130.7 (br), 131.4, 138.7, 140.5, 146.0, 179.8 (br) (aryl, C=N).

2,3-Dihydro-4-isopropyl-5-methyl-2-phenylimino-3-(2,4,6-trichlorophenyl)-1,3,4-thiadiazol-4-ium hexachloroantimonate 9c

From azo compound **6c**[8] (3.14 g, 10 mmol) and phenyl isothiocyanate (2.03 g, 15 mmol), *title compound* **9c** was isolated as a yellow powder (7.08 g, 95%), which was recrystallized at −15 °C from MeCN (10 ml)–Et_2O (2 ml) to afford orange prisms (6.46 g, 86%); mp 156–157 °C (decomp.) (Found: C, 29.05; H, 2.33; N, 5.65. $C_{18}H_{17}Cl_9N_3SSb$ (MW = 748.3) requires C, 28.89; H, 2.29; N, 5.62%); ν_{max}(Nujol)/cm^{-1} 1651 (vs), 1590 (s), 1576 (m), 1566 (m); ν_{max}(CH_2Cl_2)/cm^{-1} 1665 (vs), 1592 (s), 1566 (s), 1552 (m); δ_H(250 MHz; CD_3CN; 273 K) 1.60 (d, *J* 7.0, 6 H), 2.93 (CH_3), 4.57 (septet, *J* 7.0, CH), 6.89–7.48 (several m, phenyl), 7.89 (aryl); δ_C(62.9 MHz; CD_3CN; 273 K) 19.3, 20.4 (2 C) (CH_3), 63.1 (CH), 120.8 (*o*-C phenyl), 127.2 (*p*-C phenyl), 129.9, 131.5, 131.6, 138.7, 141.0 (phenyl, aryl), 148.4, 149.6 (i-C phenyl, C=N), 168.7 (br, $C=N^+$).

4,5-Dihydro-4-isopropyl-2,3-dimethyl-5-thioxo-1-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-2-ium hexachloroantimonate 10d

Compound **10d** was prepared from azo compound **6d**[8] (2.86 g, 10 mmol) and isopropyl isothiocyanate (1.21 g, 12 mmol). Reprecipitation at −20 °C from MeCN (8 ml)–Et_2O (40 ml) afforded *title compound* **10d** as yellow needles (4.56 g, 66%) suitable for X-ray structural analysis; mp 184–186 °C (decomp.) (Found: C, 22.53; H, 2.17; N, 5.99. $C_{13}H_{15}Cl_9N_3SSb$ (MW = 686.2) requires C, 22.75; H, 2.20; N, 6.13%); ν_{max}(KBr)/cm^{-1} 1603 (m), 1566 (s), 1552 (s); δ_H(250 MHz; CD_3CN) 1.69 (d, *J* 7.0, 6 H), 2.89, 3.68 (CH_3), 5.21 (septet, *J* 7.0, CH), 7.84 (aryl); δ_C(62.9 MHz; CD_3CN) 13.4, 19.3 (2 C), 36.3 (CH_3), 54.5 (CH), 125.9 (i-C), 131.1 (*m*-C), 137.9 (*o*-C), 141.3 (*p*-C), 155.4, 167.4 (C=N, C=S).

4,5-Dihydro-2,3-dimethyl-4-phenyl-5-thioxo-1-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-2-ium hexachloroantimonate 10e

Compound **10e** was prepared from azo compound **6d**[8] (2.86 g, 10 mmol) and phenyl isothiocyanate (1.62 g, 12 mmol). Reprecipitation at −20 °C from MeCN (10 ml)–Et_2O (50 ml) afforded *title compound* **10e** as yellow needles (3.58 g, 50%); mp 185–187 °C (decomp.) (Found: C, 26.71; H, 1.86; N, 5.74. $C_{16}H_{13}Cl_9N_3SSb$ (MW = 720.1) requires C, 26.68; H, 1.82; N, 5.84%); ν_{max}(KBr)/cm^{-1} 1615 (s), 1593 (m), 1566 (s), 1554 (s); δ_H(250 MHz; CD_3CN) 2.61, 3.76 (CH_3), 7.53–7.75 (several m, phenyl), 7.90 (aryl); δ_C(62.9 MHz; CD_3CN) 13.8, 36.8 (CH_3), 126.0,

131.4, 138.2, 141.7 (aryl), 128.2, 131.7, 132.5, 133.0 (phenyl), 156.3, 168.9 (C=N, C=S).

2,3,5,6,7,8-Hexahydro-1-methyl-2-thioxo-3-(2,4,6-trichlorophenyl)-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium hexachloroantimonate 10f

From azo compound **6f**[11] (3.12, 10 mmol) and methyl isothiocyanate (0.88 g, 12 mmol), *title compound* **10f** was obtained as a brown powder (6.00 g, 88%), which was recrystallized at −20 °C from CH_2Cl_2 (30 ml)–Et_2O (7 ml) to afford pale brown needles (3.79 g, 55%); mp 192–194 °C (decomp.) (Found: C, 22.89; H, 1.91; N, 6.10. $C_{13}H_{13}Cl_9N_3SSb$ (MW = 684.2) requires C, 22.82; H, 1.92; N, 6.14%); ν_{max}(KBr)/cm^{-1} 1612 (m), 1568 (m), 1555 (s); δ_H(250 MHz; CD_3CN) 3.65 (CH_3), 2.12 (m, 4 H), 3.12 (m, 2 H), 3.81 (m, 2 H) (CH_2), 7.86 (aryl); δ_C(62.9 MHz; CD_3CN) 17.7, 21.6, 23.4, 33.1, 48.3 (CH_3, CH_2), 125.6, 131.3, 138.0, 141.6 (aryl), 156.0, 168.5 (C=N, C=S).

1,2,3,5,6,7,8,9-Octahydro-1-methyl-2-thioxo-3-(2,4,6-trichlorophenyl)[1,2,4]triazolo[1,5-*a*]azepin-4-ium hexachloroantimonate 10g

From azo compound **6g**[8] (3.26, 10 mmol) and methyl isothiocyanate (0.88 g, 12 mmol), *title compound* **10g** was obtained as a dark yellow powder (4.83 g, 69%), which was recrystallized at −20 °C from MeCN (6 ml) to afford a yellow powder (3.28 g, 47%); mp 190–192 °C (decomp.) (Found: C, 24.10; H, 2.15; N, 6.05. $C_{14}H_{15}Cl_9N_3SSb$ (MW = 698.2) requires C, 24.08; H, 2.17; N, 6.02%); ν_{max}(Nujol)/cm^{-1} 1596 (m), 1566 (s), 1556 (s); δ_H(250 MHz; CD_3CN) 3.76 (CH_3), 1.94 (m, 6 H), 3.28 (m, 2 H), 4.11 (m, 2 H) (CH_2), 7.85 (aryl); δ_C(62.9 MHz; CD_3CN) 22.8, 26.1, 26.7, 28.3, 34.3, 52.5 (CH_3, CH_2), 125.8, 131.3, 138.3, 141.7 (aryl), 160.1, 168.7 (C=N, C=S).

2–Ethyl-4,5-dihydro-3,4-dimethyl-5-thioxo-1-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-2-ium hexachloroantimonate 10h

From azo compound **6h**[8] (3.00, 10 mmol) and methyl isothiocyanate (0.88 g, 12 mmol), *title compound* **10h** was obtained as a yellow powder (5.86 g, 87%), which was recrystallized at −20 °C from MeCN (10 ml) to afford a yellow powder (4.34 g, 65%); mp 198–200 °C (decomp.) (Found: C, 21.46; H, 1.98; N, 6.22. $C_{12}H_{13}Cl_9N_3SSb$ (MW = 672.2) requires C, 21.44; H, 1.95; N, 6.25%); ν_{max}(Nujol)/cm^{-1} 1600 (m), 1568 (m), 1557 (s); δ_H(250 MHz; CD_3CN) 1.29 (t, *J* 7.3), 2.81, 3.71 (CH_3), 4.16 (q, *J* 7.3, CH_2), 7.86 (aryl); δ_C(62.9 MHz; CD_3CN) 12.9, 14.3, 34.1 (CH_3), 46.3 (CH_2), 126.1, 131.5, 137.9, 141.6 (aryl), 155.7, 168.6 (C=N, C=S).

4,5-Dihydro-3,4-dimethyl-2-phenyl-5-thioxo-1-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-2-ium hexachloroantimonate 10i

Compound **10i** was prepared from azo compound **6i**[10] (3.48 g, 10 mmol) and methyl isothiocyanate (7.31 g, 100 mmol). Addition of Et_2O to the reaction mixture and keeping the temperature at −15 °C for 3 h afforded *title compound* **10i** as a brown powder (6.09 g, 85%), which was recrystallized at −15 °C from MeCN (6 ml) to furnish a yellow powder (3.17 g, 44%); mp 203–205 °C (decomp.) (Found: C, 26.61; H, 1.83; N, 5.72. $C_{16}H_{13}Cl_9N_3SSb$ (MW = 720.2) requires C, 26.68; H, 1.82; N, 5.83%); ν_{max}(KBr)/cm^{-1} 1591 (m), 1564 (s), 1554 (s); δ_H(250 MHz; CD_3CN) 2.68, 3.84 (CH_3), 7.65 (m, 7 H, aryl, phenyl); δ_C(62.9 MHz; CD_3CN) 13.8, 34.4 (CH_3), 126.3, 128.8, 129.0, 130.9, 132.0, 135.2, 137.9, 141.3 (aryl, phenyl), 157.4, 168.1 (C=N, C=S). When less than a tenfold excess of methyl isothiocyanate over **6i** was used, 3-methyl-1-(2,4,6–trichlorophenyl)-1*H*-indazolium hexachloroantimonate was formed as a side product.[10]

2-Ethyl-4,5-dihydro-4-methyl-3-phenyl-5-thioxo-1-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-2-ium hexachloroantimonate 10j

From azo compound **6j** (3.62 g, 10 mmol) and methyl isothiocyanate (1.46 g, 20 mmol), *title compound* **10j** was isolated as a yellow powder (6.84 g, 93%), which was recrystallized at −15 °C from MeCN (6 ml)–CH_2Cl_2 (4 ml) to furnish yellow prisms (6.42 g, 87%); mp 211–213 °C (decomp.) (Found: C, 27.89; H, 2.11; N, 5.76. $C_{17}H_{15}Cl_9N_3SSb$ (MW = 734.2) requires C, 27.81; H, 2.06; N, 5.72%); ν_{max}(Nujol)/cm^{-1} 1603 (m), 1565 (s), 1556 (s); δ_H(250 MHz; CD_3CN; 283 K) 1.21 (t, *J* 7.2), 3.62 (CH_3), 4.10 (q, *J* 7.2, CH_2), 7.80–7.94 (m, phenyl), 7.92 (aryl); δ_C(62.9 MHz; CD_3CN; 283 K) 14.9, 35.4 (CH_3), 47.5 (CH_2), 118.7, 126.4, 130.9, 131.3, 131.5, 135.9, 137.8, 141.6 (phenyl, aryl), 154.8, 169.1 (C=N, C=S).

***N*-[2,3-Dihydro-5-isopropyl-3-(2,4,6-trichlorophenyl)-1,3,4-thiadiazol-2-ylidene]methylammonium hexachloroantimonate 11b**

From azo compound **6a** (3.42 g, 10 mmol) and methyl isothiocyanate (0.88 g, 12 mmol), *title compound* **11b** was isolated as a yellow powder (4.51 g, 67%), which was recrystallized from CH_2Cl_2 (30 ml)–pentane (5 ml) to afford yellow prisms (3.33 g, 50%); mp 221–223 °C (decomp.) (Found: C, 21.23; H, 2.01; N, 6.15. $C_{12}H_{13}Cl_9N_3SSb$ (MW = 672.2) requires C, 21.44; H, 1.95; N, 6.25%); ν_{max}(Nujol)/cm^{-1} 3298, 1614 (br, vs), 1555 (vs); δ_H(250 MHz; CD_3CN) 1.41 (d, *J* 6.8, 6 H), 3.16 (d, *J* 4.7) (CH_3), 3.37 (septet, *J* 6.8, CH), 7.84 (aryl), 8.34 (br, coupled to 3.16, NH); δ_C(62.9 MHz; CD_3CN) 21.8 (2 C), 32.4, 37.1 (CH_3, CH), 129.4, 131.2, 136.5, 140.6 (aryl), 166.2 (C=N), 171.4 (SC=N).

***N*-[2,3-Dihydro-5-methyl-3-(2,4,6-trichlorophenyl)-1,3,4-thiadiazol-2-ylidene]methylammonium hexachloroantimonate 11k**

From azo compound **6k**[12] (3.28 g, 10 mmol) and methyl isothiocyanate (0.88 g, 12 mmol), *title compound* **11k** was isolated as a yellow powder (4.70 g, 73%), which was recrystallized at −15° C from MeCN (7 ml) to afford a pale yellow powder (3.61 g, 56%); mp 214–216 °C (decomp.) (Found: C, 18.78; H, 1.53; N, 6.28. $C_{10}H_9Cl_9N_3SSb$ (MW = 644.1) requires C, 18.64; H, 1.41; N, 6.52%); ν_{max}(Nujol)/cm^{-1} 3298, 1621 (br, vs), 1556 (vs); δ_H(250 MHz; CD_3CN) 2.68, 3.14 (d, *J* 4.9) (CH_3), 7.85 (aryl), 8.13 (br, coupled to 3.14, NH); δ_C(62.9 MHz; CD_3CN) 17.3, 37.0 (CH_3), 129.4, 131.3, 136.5, 140.7 (aryl), 156.5 (C=N), 171.8 (SC=N).

2,3-Dihydro-5-methyl-2-methylimino-3-(2,4,6-trichlorophenyl)-1,3,4-thiadiazole 11′k

Compound **11′k** was prepared from salt **11k** (6.44 g, 10 mmol) (method A). Crystallization at −15 °C from $CHCl_3$ (6 ml) afforded *title compound* **11′k** as an orange powder (1.74 g, 57%); mp 123–125 °C (Found: C, 39.12; H, 2.80; N, 13.52. $C_{10}H_8Cl_3N_3S$ (MW = 308.6) requires C, 38.91; H, 2.61; N, 13.61%); ν_{max}(Nujol)/cm^{-1} 1652 (br, vs), 1570 (m), 1552 (m); δ_H(250 MHz; $CDCl_3$) 2.44, 3.03 (CH_3), 7.44 (aryl); δ_C(62.9 MHz; $CDCl_3$) 18.0, 44.2 (CH_3), 128.9, 133.5, 135.9, 136.5 (aryl), 145.9 (C=N), 156.7 (SC=N).

2,3-Dihydro-5-isopropyl-2-methylimino-3-(4-nitrophenyl)-1,3,4-thiadiazole 11′l

Compound **11l** was prepared from azo compound **6l** (2.84 g, 10 mmol) and methyl isothiocyanate (0.88 g, 12 mmol). The reaction mixture was stirred at 23 °C for 3 h. The impure orange hexachloroantimonate **11l** (4.91 g, 80%) was transformed into *title compound* **11′l** (method B). Crystallization at −15 °C from hot EtOH (40 ml) afforded pale brown needles (1.82 g, 66%); mp 114–116 °C (Found: C, 51.52; H, 5.09; N, 19.69. $C_{12}H_{14}N_4O_2S$ (MW = 278.3) requires C, 51.78; H, 5.07; N, 20.13%); ν_{max}(KBr)/cm^{-1} 1636 (br, vs), 1593 (vs); δ_H(250 MHz; $CDCl_3$) 1.36 (d, *J* 6.9, 6 H), 3.17 (CH_3), 3.07 (septet, *J* 6.9, CH), 8.21 (m, 2 H), 8.33 (m, 2 H) (aryl); δ_C(62.9 MHz; $CDCl_3$) 21.3 (2 C), 32.2 (CH_3), 44.5 (CH), 119.5, 124.4, 143.3, 145.7, 155.6, 157.0 (aryl, C=N).

N-[2,3-Dihydro-5-isopropyl-3-(4-nitrophenyl)-1,3,4-thiadiazol-ylidene]-*tert*-butylammonium hexachloroantimonate 11m

From azo compound **6l** (2.84 g, 10 mmol) and *tert*-butyl isothiocyanate (1.38 g, 12 mmol), *title compound* **11m** was obtained as a brown powder (5.77 g, 88%), which was recrystallized at −15 °C from MeCN (10 ml)–Et_2O (30 ml) to afford a pale brown powder (4.15 g, 63%); mp 225–229 °C (decomp.) (Found: C, 27.59; H, 3.29; N, 8.62. $C_{15}H_{21}Cl_6N_4O_2SSb$ (MW = 655.9) requires C, 27.47; H, 3.23; N, 8.54%); ν_{max}(KBr)/cm^{-1} 3356, 1614 (s), 1588 (vs); δ_H(250 MHz; CD_3CN) 1.41 (d, *J* 6.9, 6 H), 1.48 (9 H) (CH_3), 3.35 (septet, *J* 6.9, CH), 7.87 (m, 2 H), 8.46 (m, 2 H) (aryl), 7.52 (br, NH); δ_C(62.9 MHz; CD_3CN) 21.9 (2 C), 27.6 (3 C) (CH_3), 31.9, 59.0 (C, CH), 127.1, 129.1, 141.1, 150.3, 165.6, 166.7 (aryl, C=N).

2-*tert*-Butylimino-2,3-dihydro-5-isopropyl-3-(4-nitrophenyl)-1,3,4-thiadiazole 11′m

Compound **11′m** was prepared from salt **11m** (6.56 g, 10 mmol) (method A). After crystallization at −15 °C from hot EtOH (10 ml) *title compound* **11′m** was obtained as an orange crystalline powder (2.10 g, 66%); mp 84–85 °C (Found: C, 56.25; H, 6.28; N, 17.48. $C_{15}H_{20}N_4O_2S$ (MW = 320.4) requires C, 56.23; H, 6.29; N, 17.49%); ν_{max}(CCl_4)/cm^{-1} 1632 (br, vs), 1592 (vs); δ_H(250 MHz; $CDCl_3$) 1.34 (9 H), 1.35 (d, *J* 6.9, 6 H) (CH_3), 3.03 (septet, *J* 6.9, CH), 8.20 (m, 2 H), 8.40 (m, 2 H) (aryl); δ_C(62.9 MHz; $CDCl_3$) 21.3 (2 C), 27.9 (3 C) (CH_3), 32.1, 54.8 (C, CH), 119.9, 124.2, 143.0, 145.8, 146.3, 156.8 (aryl, C=N).

N-[2,3-Dihydro-5-methyl-3-(1,2,4-trichlorophenyl)-1,3,4-thiadiazol-2-ylidene]cyclohexylammonium hexachloroantimonate 11n

From azo compound **6n**[31] (2.72 g, 10 mmol) and cyclohexyl isothiocyanate (1.70 g, 12 mmol), *title compound* **11n** was isolated as a brown powder (5.76 g, 81%), which was dissolved in CH_2Cl_2 (25 ml). Addition of pentane (35 ml) and crystallization at −15 °C afforded fine yellow prisms (4.72 g, 66%); mp 222–226 °C (decomp.) (Found: C, 25.36; H, 2.45; N, 5.86. $C_{15}H_{17}Cl_9N_3SSb$ (MW = 712.2) requires C, 25.30; H, 2.41; N, 5.90%); ν_{max}(KBr)/cm^{-1} 3287, 1606 (vs), 1557 (vs); δ_H(250 MHz; CD_3CN) 2.68 (CH_3), 1.12–2.07 (several m, 10 H, CH_2), 3.33 (br m, CH), 7.83 (aryl), 8.05 (br d, *J* 7.6, coupled to 3.33, NH); δ_C(62.9 MHz; CD_3CN) 17.3, 25.2, 25.3, 32.2, 64.3 (CH_3, CH_2, CH), 129.6, 131.2, 136.4, 140.5 (aryl), 156.4, 169.5 (C=N).

2-Cyclohexylimino-2,3-dihydro-5-methyl-3-(1,2,4-trichlorophenyl)-1,3,4-thiadiazole 11′n

Compound **11′n** was prepared from **11n** (7.12 g, 10 mmol) (method B). Crystallization at −15 °C from hot EtOH (5 ml) afforded *title compound* **11′n** as prisms (3.26 g, 87%); mp 65–67 °C (Found: C, 47.77; H, 4.23; N, 11.24. $C_{15}H_{16}Cl_3N_3S$ (MW = 376.7) requires C, 47.82; H, 4.28; N, 11.16%); ν_{max}(CCl_4)/cm^{-1} 1645 (br, vs); δ_H(250 MHz; $CDCl_3$) 2.38 (CH_3), 1.18–1.74 (several m, 10 H, CH_2), 2.56 (br, CH), 7.41 (aryl); δ_C(62.9 MHz; $CDCl_3$) 17.9, 24.9, 25.7, 33.3, 68.6 (CH_3, CH_2, CH), 128.8, 134.1, 135.4, 136.6, 145.5 (br), 151.9 (br) (aryl, C=N).

N-[3-*tert*-Butyl-5-ethyl-2,3-dihydro-1,3,4-thiadiazol-2-ylidene]-phenylammonium hexachloroantimonate 11o

From azo compound **6o**[31] (1.63 g, 10 mmol) and phenyl isothiocyanate (1.62 g, 12 mmol), *title compound* **11o** was obtained as a grey powder (3.64 g, 61%), which was crystallized at −15 °C from MeCN (35 ml)–Et_2O (35 ml) to afford a pale yellow powder (2.33 g, 39%); mp 141–144 °C (decomp.) (Found: C, 28.29; H, 3,34; N, 6.96. $C_{14}H_{20}Cl_6N_3SSb$ (MW = 596.9) requires C, 28.17; H, 3.38; N, 7.04%); ν_{max}(KBr)/cm^{-1} 3392, 1595 (s), 1574 (s), 1538 (vs); δ_H(250 MHz; CD_3CN) 1.26 (t, *J* 7.5), 1.79 (9 H) (CH_3), 2.84 (q, *J* 7.5, CH_2), 7.47–7.62 (m, phenyl), 8.76 (br, NH); δ_C(62.9 MHz; CD_3CN) 12.9, 24.8, 28.5 (3 C), 67.9 (CH_3, CH_2, C), 126.7, 131.0, 131.7, 140.4 (phenyl), 158.6, 170.6 (C=N).

3-*tert*-Butyl-5-ethyl-2,3-dihydro-2-phenylimino-1,3,4-thiadiazole 11′o

From salt **11o** (5.97 g, 10 mmol) (method B), *title compound* **11′o** was obtained as fine orange prisms (1.73 g, 66%); mp 62–64 °C (Found: C, 64.63; H, 7.38; N, 16.20. $C_{14}H_{19}N_3S$ (MW = 261.4) requires C, 64.33; H, 7.33; N, 16.08%); ν_{max}(CCl_4)/cm^{-1} 1614 (br, vs), 1587 (vs); δ_H(250 MHz; $CDCl_3$) 1.17 (t, *J* 7.6), 1.67 (9 H) (CH_3), 2.58 (q, *J* 7.6, CH_2), 7.00– 7.34 (several m, phenyl); δ_C(62.9 MHz; $CDCl_3$) 12.5, 25.2, 28.1 (3 C), 61.2 (CH_3, CH_2, C), 121.0, 122.9, 129.4, 146.0 (phenyl), 153.3, 156.5 (C=N).

N-[2,3-Dihydro-5-propyl-3-(2,4,6-trichlorophenyl)-1,3,4-thiadiazol-2-ylidene]phenylammonium hexachloroantimonate 11p

From azo compound **6p**[31] (3.00 g, 10 mmol) and phenyl isothiocyanate (1.62 g, 12 mmol), *title compound* **11p** was obtained as a pale brown powder (5.88 g, 80%), which was crystallized at −15 °C from CH_2Cl_2 (25 ml)–pentane (25 ml) to afford yellow prisms (5.41 g, 74%); mp 140–142 °C (decomp.) (Found: C, 27.83; H, 2.08; N, 5.66. $C_{17}H_{15}Cl_9N_3SSb$ (MW = 734.2) requires C, 27.81; H, 2.06; N, 5.72%); ν_{max}(KBr)/cm^{-1} 3251, 1604 (vs), 1581 (vs), 1544 (vs); δ_H(250 MHz; CD_3CN) 1.01 (t, *J* 7.4, CH_3), 1.80 (m), 2.99 (t, *J* 7.3) (CH_2), 7.44–7.64 (m, phenyl), 7.90 (aryl), 9.85 (br, NH); δ_C(62.9 MHz; CD_3CN) 13.3, 22.4, 33.0 (CH_3, CH_2), 124.5, 129.6, 131.0, 131.4, 131.8, 136.3, 138.1, 140.8 (phenyl, aryl), 161.2, 171.2 (C=N).

N-[2,3-Dihydro-5-propyl-3-(2,4,6-trichlorophenyl)-1,3,4-thiadiazol-2-ylidene]phenylammonium picrate 11*p

Compound **11′p** was prepared from salt **11p** (7.34 g, 10 mmol) (method A). The oily base was dissolved in a saturated solution of picric acid (*ca*. 3.44 g, 15 mmol) in EtOH. Crystallization at −15 °C afforded *title compound* **11*p** as a yellow powder (5.37 g, 86%); mp 138–140 °C (decomp.) (Found: C, 43.96; H, 2.68; N, 13.27. $C_{23}H_{17}Cl_3N_6O_7S$ (MW = 627.8) requires C, 44.00; H, 2.73; N, 13.39%); ν_{max}(CH_2Cl_2)/cm^{-1} 1631 (br, vs), 1590 (s), 1552 (s); δ_H(250 MHz; $CDCl_3$) 1.04 (t, *J* 7.4, CH_3), 1.78 (m), 2.82 (t, *J* 7.3) (CH_2), 7.23–7.42 (m, phenyl), 8.91 (aryl), 12.08 (br, NH); δ_C(62.9 MHz; $CDCl_3$) 13.2, 21.5, 32.9 (CH_3, CH_2), 122.7 (br), 126.2, 127.4 (br), 129.1, 130.1, 130.9, 132.3, 135.9, 137.8, 139.5, 144.3 (br), 154.7 (br), 157.6, 163.8 (br) (phenyl, aryl, C=N).

N-[2,3-Dihydro-5-isopropyl-3-(2,4,6-trichlorophenyl)-1,3,4-thiadiazol-2-ylidene]cyclohexylammonium hexachloroantimonate 11q

From azo compound **6q**[31] (3.00 g, 10 mmol) and cyclohexyl isothiocyanate (1.70 g, 12 mmol), *title compound* **11q** was obtained as a pale orange powder (5.12 g, 69%), which was dissolved in CH_2Cl_2 (25 ml)–MeCN (0.5 ml). Addition of pentane (30 ml) and crystallization at −15 °C afforded a powder (3.65 g, 49%); mp 172–179 °C (decomp.) (Found: C, 27.54; H, 2.90; N, 5.76. $C_{17}H_{21}Cl_9N_3SSb$ (MW = 740.3) requires C, 27.58; H, 2.86; N, 5.68%); ν_{max}(KBr)/cm^{-1} 3286, 1602 (br, vs), 1550 (vs); δ_H(250 MHz; CD_3CN) 1.40 (d, *J* 6.8, CH_3), 1.19–2.07 (several m, 10 H, CH_2), 3.34 (br m), 3.36 (septet, *J* 6.8) (CH), 7.83 (aryl), 8.07 (br d, *J* 7.9, coupled to 3.34, NH); δ_C(62.9 MHz; CD_3CN) 21.8, 25.3, 32.2, 32.3, 64.5 (CH_3, CH_2, CH), 129.7, 131.2, 136.4, 140.5 (aryl), 166.2, 169.2 (C=N).

N-[2,3-Dihydro-5-isopropyl-3-(2,4,6-trichlorophenyl)-1,3,4-thiadiazol-2-ylidene]cyclohexylammonium picrate 11*q

Compound **11′q** was prepared from salt **11q** (7.40 g, 10 mmol) (method A). The oily base was transformed into the picrate in the manner described for **11p**. *Title compound* **11q** was obtained

as yellow prisms (4.88 g, 77%); mp 193–195 °C (decomp.) (Found: C, 43.84; H, 3.77; N, 12.86. $C_{23}H_{23}Cl_3N_6O_7S$ (MW = 633.9) requires C, 43.58; H, 3.66; N, 13.26%); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1631 (vs), 1620 (vs), 1563 (vs); δ_H(250 MHz; $CDCl_3$) 1.45 (d, *J* 6.8, CH_3), 1.13–2.11 (several m, 10 H, CH_2), 3.16 (m, 1 H), 3.28 (septet, *J* 6.8, 1 H) (CH), 7.26 (2 H), 8.80 (2 H) (aryl), 11.14 (br, NH); δ_C(62.9 MHz; $CDCl_3$) 21.6, 24.5, 25.0, 31.1, 31.6, 65.6 (CH_3, CH_2, CH), 126.2, 127.9, 129.1, 129.2, 135.8, 138.6, 141.0, 160.2, 162.0, 166.2 (aryl, C=N).

N-[3-Ethoxycarbonyl-2,3-dihydro-5-methyl-1,3,4-thiadiazol-2-ylidene]phenylammonium hexachloroantimonate 11r

From azo compound **6r** (2.07 g, 10 mmol) and phenyl isothiocyanate (2.03 g, 15 mmol), *title compound* **11r** was isolated as an orange powder (3.64 g, 61%), which was recrystallized at −15 °C from MeCN (10 ml) to afford pale yellow prisms (2.43 g, 41%); mp 168–170 °C (decomp.) (Found: C, 24.28; H, 2.40; N, 7.20. $C_{12}H_{14}Cl_6N_3O_2SSb$ (MW = 598.8) requires C, 24.06; H, 2.36; N, 7.02%); ν_{max}(Nujol)/cm^{-1} 3276, 1751 (vs), 1617 (vs), 1567 (s); δ_H(250 MHz; CD_3CN) 1.47 (t, *J* 7.1, CH_3), 4.66 (q, *J* 7.1, CH_2), 7.49–7.65 (several m, phenyl), 11.09 (br, NH); δ_C(62.9 MHz; CD_3CN) 14.3, 17.0 (CH_3), 69.0 (CH_2), 125.6, 131.7, 131.8, 138.9, 150.2, 154.2, 174.7 (phenyl, C=).

N-[3-Ethoxycarbonyl-5-ethyl-2,3-dihydro-1,3,4-thiadiazol-2-ylidene]phenylammonium hexachloroantimonate 11s

From azo compound **6s** (2.21 g, 10 mmol) and phenyl isothiocyanate (2.03 g, 15 mmol), *title compound* **11s** was isolated as a pale yellow powder (3.25 g, 53%), which was recrystallized at −15 °C from MeCN (10 ml) to afford a powder (2.21 g, 36%); mp 158–160 °C (decomp.) (Found: C, 25.74; H, 2.66; N, 6.89. $C_{13}H_{16}Cl_6N_3O_2SSb$ (MW = 612.8) requires C, 25.48; H, 7.63; N, 6.86%); ν_{max}(Nujol)/cm^{-1} 3278, 1748 (vs), 1614 (s), 1592 (m), 1562 (s); δ_H(250 MHz; CD_3CN) 1.29 (t, *J* 7.5), 1.47 (t, *J* 7.1) (CH_3), 2.93 (q, *J* 7.9), 4.67 (q, *J* 7.1) (CH_2), 7.48–7.65 (several m, phenyl), 11.11 (br, NH); δ_C(62.9 MHz; CD_3CN) 12.7, 14.3 (CH_3), 25.1, 69.1 (CH_2), 125.8, 131.8, 131.9, 139.1, 150.4, 159.7, 174.7 (phenyl, C=).

Ethyl 5-ethyl-2,3-dihydro-2-phenylimino-1,3,4-thiadiazole-3-carboxylate 11′s

From salt **11s** (6.13 g, 10 mmol) (method B), *title compound* **11′s** was isolated as an oil (2.44 g, 88%), which crystallized at −15 °C from Et_2O (100 ml) to afford a powder (2.00 g, 72%); mp 92–93 °C (Found: C, 56.34; H, 5.49; N, 15.19. $C_{13}H_{15}N_3O_2S$ (MW = 277.3) requires C, 56.30; H, 5.45; N, 15.15%); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1757 (vs), 1637 (br, vs), 1592 (s); δ_H(250 MHz; $CDCl_3$) 1.22 (t, *J* 7.6), 1.45 (t, *J* 7.2) (CH_3), 2.70 (q, *J* 7.6), 4.50 (q, *J* 7.1) (CH_2), 7.00–7.39 (several m, phenyl); δ_C(62.9 MHz; $CDCl_3$) 12.3, 14.4 (CH_3), 25.5, 64.1 (CH_2), 120.2, 124.7, 129.6, 149.6, 152.4, 153.6, 154.0 (phenyl, C=).

N-[3-Ethoxycarbonyl-2,3-dihydro-5-isopropyl-1,3,4-thiadiazol-2-ylidene]phenylammonium hexachloroantimonate 11t

From azo compound **6t** (2.35 g, 10 mmol) and phenyl isothiocyanate (2.03 g, 15 mmol), *title compound* **11t** was isolated as a yellow powder (3.19 g, 51%), which was recrystallized at −15 °C from MeCN (5 ml)–Et_2O (5 ml) to afford a yellow powder (2.27 g, 36%); mp 185–187 °C (decomp.) (Found: C, 26.79; H, 2.84; N, 6.56. $C_{14}H_{18}Cl_6N_3O_2SSb$ (MW = 626.8) requires C, 26.82; H, 2.89; N, 6.70%); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3236, 1761 (vs), 1611 (vs), 1591 (s), 1560 (s); δ_H(250 MHz; CD_3CN) 1.33 (d, *J* 6.9, 6 H), 1.48 (t, *J* 7.0) (CH_3), 3.27 (septet, *J* 6.9), 4.67 (q, *J* 7.0) (CH_2), 7.50–7.69 (several m, phenyl), 9.46 (br, NH); δ_C(62.9 MHz; CD_3CN) 14.3, 21.7 (2 C) (CH_3), 32.1, 69.0 (CH_2), 125.7, 131.7, 131.8, 139.0, 150.3, 164.0, 174.4 (phenyl, C=).

2,5-Dihydro-2-(isopropylimino)-5,5-dimethyl-1,3,4-thiadiazol-3-ium hexachloroantimonate 12u (≡ 12v, 12y)

(a) From azo compound **6u** (2.11 g, 10 mmol) and isopropyl isothiocyanate (2.02 g, 20 mmol), *title compound* **12u** was obtained as a brown powder (3.38 g, 67%), which was recrystallized at −15 °C from MeCN (6 ml)–Et_2O (2 ml) to afford an ochreous powder (2.98 g, 59%); mp 154–156 °C (decomp.) (Found: C, 16.77; H, 2.78; N, 8.13. $C_7H_{14}Cl_6N_3SSb$ (MW = 506.7) requires C, 16.59; H, 2.78; N, 8.29%); ν_{max}(Nujol)/cm^{-1} 3213, 1636 (br, vs), 1546 (s); δ_H(250 MHz; CD_3CN) 1.51 (d, *J* 6.5, 6 H), 2.05 (6 H) (CH_3), 3.98 (septet, *J* 6.5, CH), 11.66 (br, NH); δ_C(62.9 MHz; CD_3CN) 20.4 (2 C), 26.0 (2 C) (CH_3), 58.3 (CH), 121.7 (C5), 187.9 (br, C=N).

(b) From azo compound **6v**[14] (1.79 g, 10 mmol) and isopropyl isothiocyanate (2.02 g, 20 mmol), *title compound* **12u** was obtained as a brown powder (4.25 g, 84%), which was recrystallized at −15 °C from CH_2Cl_2 (8 ml) to afford a brown powder (2.81 g, 56%); mp 154–156 °C (decomp.).

(c) From azo compound **6y**[8] (1.63 g, 10 mmol) and isopropyl isothiocyanate (1.21 g, 12 mmol), *title compound* **12u** was obtained as a powder (4.00 g, 79%); mp 152–153 °C (decomp.).

2,5-Dihydro-2-(isopropylimino)-5,5-dimethyl-1,3,4-thiadiazole 12′u

From salt **12u** (5.07 g, 10 mmol) (method A), prisms of *title compound* **12′u** were isolated (1.52 g, 89%); mp 64–66 °C (Found: C, 49.21; H, 7.63; N, 24.11. $C_7H_{13}N_3S$ (MW = 171.3) requires C, 49.09; H, 7.65; N, 24.54%); $\nu_{max}(CCl_4)$/cm^{-1} 1652 (br, vs); δ_H(250 MHz; $CDCl_3$) 1.33 (d, *J* 6.3, 6 H), 1.83 (6 H) (CH_3), 3.31 (septet, *J* 6.3, CH); δ_C(62.9 MHz; $CDCl_3$) 22.5 (2 C), 28.6 (2 C) (CH_3), 60.5 (CH), 105.6 (C5), 174.3 (C=N).

5-Ethyl-2,5-dihydro-5-methyl-2-(phenylimino)-1,3,4-thiadiazol-3-ium hexachloroantimonate 12w (≡ 12ab)

(a) From azo compound **6w** (1.93 g, 10 mmol) and phenyl isothiocyanate (2.03 g, 15 mmol), *title compound* **12w** was obtained as a dark yellow powder (3.31 g, 60%), which was recrystallized at −15 °C from CH_2Cl_2 (5 ml)–Et_2O (3 ml) to afford a pale brown powder (2.34 g, 42%); mp 148–150 °C (decomp.) (Found: C, 24.04; H, 2.49; N, 7.45. $C_{11}H_{14}Cl_6N_3SSb$ (MW = 554.8) requires C, 23.81; H, 2.54; N, 7.57%); ν_{max}(Nujol)/cm^{-1} 3177, 1626 (vs), 1541 (s); δ_H(250 MHz; CD_3CN; 273 K) 0.91 (t, *J* 7.4), 2.09 (CH_3), 2.57 (m, CH_2), 7.74 (m, phenyl), 9.96 (br, NH); δ_C(62.9 MHz; CD_3CN; 273 K) 9.8, 24.4, 33.2 (CH_3, CH_2), 123.0 (C5), 128.0, 131.8, 132.7, 135.5 (phenyl), 183.7 (C=N).

(b) Compound **12w** was prepared from azo compound **6ab** (1.77 g, 10 mmol) and phenyl isothiocyanate (1.62 g, 12 mmol). However, in place of Et_2O pentane (50 ml) was added to the reaction mixture. After 12 h at −15 °C *title compound* **12w** was obtained as a dark yellow powder (3.96 g, 71%), which was recrystallized at −15 °C from MeCN (6 ml) to furnish a pale brown powder (3.15 g, 57%); 148–150 °C (decomp.).

5-Ethyl-2,5-dihydro-5-methyl-2-(phenylimino)-1,3,4-thiadiazole 12′w

From salt **12w** (5.55 g, 10 mmol) (method A), *title compound* **12′w** was isolated as a yellow powder (1.74 g, 79%), which was recrystallized at −15 °C from $CHCl_3$ (3 ml) to afford a yellow powder (1.26 g, 58%); mp 58–60 °C (decomp.) (Found: C, 60.10; H, 6.10; N, 18.31. $C_{11}H_{13}N_3S$ (MW = 219.3) requires C, 60.24; H, 5.97; N, 19.16%); ν_{max}(KBr)/cm^{-1} 1623 (br, vs), 1588 (s); δ_H(250 MHz; $CDCl_3$) 0.86 (t, *J* 7.4), 1.86 (CH_3), 2.21 (m, CH_2), 7.22–7.48 (several m, phenyl); δ_C(62.9 MHz; $CDCl_3$) 9.1, 26.6, 33.6 (CH_3, CH_2), 111.9 (C5), 121.1, 126.8, 129.4, 148.2 (phenyl), 174.3 (C=N).

5-Ethyl-2,5-dihydro-5-methyl-2-(methylimino)-1,3,4-thiadiazol-3-ium hexachloroantimonate 12x

Compound **12x** was prepared from azo compound **6w** (1.93 g, 10 mmol) and methyl isothiocyanate (1.46 g, 20 mmol) in the manner described for **12w**. *Title compound* **12x** was obtained as a yellow powder (3.56 g, 72%), which was recrystallized at −15 °C from MeCN (4 ml) to furnish a yellow powder (2.35 g, 48%); mp 118–120 °C (decomp.) (Found: C, 14.38; H, 2.45; N, 8.53. $C_6H_{12}Cl_6N_3SSb$ (MW = 492.7) requires C, 14.63; H, 2.45; N, 8.53%); ν_{max}(Nujol)/cm^{-1} 3233, 1646 (br, vs), 1544 (m); δ_H(250 MHz; CD_3CN; 273 K) 0.86 (t, *J* 7.3), 2.06, 3.55 (CH_3), 2.53 (m, CH_2), 10.08 (br, NH); δ_C(62.9 MHz; CD_3CN; 273 K) 9.6, 24.7, 33.2, 38.7 (CH_3, CH_2), 126.4 (C5), 189.7 (C=N).

2,5-Dihydro-5,5-dimethyl-2-(phenylimino)-1,3,4-thiadiazol-3-ium hexachloroantimonate 12z

From azo compound **6y**[8] (1.63 g, 10 mmol) and phenyl isothiocyanate (1.62 g, 12 mmol), *title compound* **12z** was obtained as a yellow powder (4.86 g, 90%), which was crystallized at −15 °C from warm MeCN (6 ml) to furnish pale yellow needles (2.98 g, 55%); 125–127 °C (decomp.) (Found: C, 22.26; H, 2.23; N, 7.76. $C_{10}H_{12}Cl_6N_3SSb$ (MW = 540.8) requires C, 22.21; H, 2.24; N, 7.77%); ν_{max}(KBr)/cm^{-1} 3214, 1626 (vs), 1539 (s); δ_H(250 MHz; CD_3CN) 2.09 (6 H, CH_3), 7.72 (m, phenyl), 11.46 (br, NH); δ_C(62.9 MHz; CD_3CN) 26.0 (CH_3), 122.4 (C), 122.9, 131.8, 132.5, 136.0 (phenyl), 184.1 (br, C=N).

2,5-Dihydro-5,5-dimethyl-2-(phenylimino)-1,3,4-thiadiazole 12′z[37]

From salt **12y** (5.41 g, 10 mmol) (method A), *title compound* **12′z** was obtained as a yellow powder (1.97 g, 96%). Crystallization at −15 °C from a dilute solution in cyclohexane afforded pale green needles suitable for X-ray crystallographic analysis; mp 100–102 °C (lit.,[37] 100–102 °C). $C_{10}H_{11}N_3S$ (MW = 205.3); ν_{max}(CCl_4)/cm^{-1} 1640 (br, vs), 1554 (m); δ_H(250 MHz; $CDCl_3$) 1.87 (CH_3), 7.23–8.48 (several m, phenyl); δ_C(62.9 MHz; $CDCl_3$) 28.3 (CH_3), 106.9 (C5), 121.1, 126.8, 129.4, 148.2 (phenyl), 174.3 (C=N); EI-MS *m*/*z* 177 (M − N_2, 16%), 74 ($Me_2C{=}S^+$, 100%).

2-(Allylimino)-2,5-dihydro-5,5-dimethyl-1,3,4-thiadiazol-3-ium hexachloroantimonate 12aa

From azo compound **6y**[8] (1.63 g, 10 mmol) and isopropyl isothiocyanate (1.19 g, 12 mmol), *title compound* **12aa** was obtained as a yellow powder (4.50 g, 89%); mp 116–121 °C (decomp.) (Found: C, 16.76; H, 2.43; N, 8.18. $C_7H_{12}Cl_6N_3SSb$ (MW = 504.8) requires C, 16.66; H, 2.40; N, 8.33%); ν_{max}(KBr)/cm^{-1} 3224, 1628 (br, vs), 1545 (m); δ_H(250 MHz; CD_3CN) 2.05 (6 H, CH_3), 4.41 (m, CH_2), 5.54 (m), 5.95 (m) (CH), 10.85 (br, NH); δ_C(62.9 MHz; CD_3CN) 26.0 (CH_3), 54.5 (CH_2), 122.1 (C5), 123.7, 127.5 (C=), 189.3 (C=N).

2-(Allylimino)-2,5-dihydro-5,5-dimethyl-1,3,4-thiadiazole 12′aa

From salt **12aa** (5.05 g, 10 mmol) (method A), *title compound* **12′aa** was obtained as a yellow oil (1.44 g, 85%); mp 97–99 °C (Found: C, 49.46; H, 6.65; N, 24.74. $C_7H_{11}N_3S$ (MW = 169.2) requires C, 49.68; H, 6.55; N, 24.84%); ν_{max}(CCl_4)/cm^{-1} 1652 (br, vs); δ_H(250 MHz; $CDCl_3$) 1.85 (CH_3), 4.06 (m, 2 H), 5.28 (m), 6.08 (m) (CH); δ_C(62.9 MHz; $CDCl_3$) 28.4 (CH_3), 60.8 (CH_2), 106.3 (C5), 116.9, 133.4 (C=), 176.9 (C=N).

5-Ethyl-2,5-dihydro-5-isopropyl-2-(methylimino)-1,3,4-thiadiazol-3-ium hexachloroantimonate 12ac

Compound **12ac** was prepared from azo compound **6ac** (2.05 g, 10 mmol) and methyl isothiocyanate (1.10 g, 15 mmol) in the manner described for **12w**. *Title compound* **12ac** was obtained as a yellow powder (3.28 g, 63%), which was recrystallized at −15 °C from MeCN (5 ml) to furnish a yellow powder (2.81 g, 54%); mp 63–65 °C (decomp.) (Found: C, 18.23; H, 2.93; N, 8.11. $C_8H_{16}Cl_6N_3SSb$ (MW = 520.8) requires C, 18.44; H, 3.09; N, 8.06%); ν_{max}(Nujol)/cm^{-1} 3193, 1652 (br, vs), 1552 (s); δ_H(250 MHz; CD_3CN) 0.78 (t, *J* 7.3), 0.86 (d, *J* 6.6), 1.21 (d, *J* 6.7), 3.57 (CH_3), 2.55 (m, 1 H), 2.75 (m, 1 H) (CH_2), 2.99 (septet, *J* 6.7, CH), 10.90 (br, NH); δ_C(62.9 MHz; CD_3CN) 8.8, 18.1, 20.0, 30.5, 37.6, 38.9 (CH_3, CH_2, CH), 136.6 (C5), 188.9 (C=N).

Spiro[tricyclo[3.3.1.1^{3,7}]decane-2,2′-(2′,5′-dihydro-5′-isopropylimino-1′,3′,4′-thiadiazol-4-ium)] hexachloroantimonate 12ad

From azo compound **6ad** (2.55 g, 10 mmol) and isopropyl isothiocyanate (2.02 g, 20 mmol), *title compound* **12ad** was obtained as a pale yellow powder (4.86 g, 81%), which was recrystallized at −15 °C from MeCN (9 ml)–Et_2O (5 ml) to furnish a powder (4.26 g, 71%); mp 208–210 °C (decomp.) (Found: C, 28.22; H, 3.65; N, 6.65. $C_{14}H_{22}Cl_6N_3SSb$ (MW = 598.9) requires C, 28.08; H, 3.70; N, 7.02%); ν_{max}(Nujol)/cm^{-1} 3263, 1625 (vs), 1531 (m); δ_H[250 MHz; CD_2Cl_2–CD_3CN (2:1)] 1.56 (d, *J* 6.5, 6 H), 1.91–2.77 (several m, 14 H), 4.00 (septet, *J* 6.5, CH), 8.86 (br, NH); δ_C[62.9 MHz; CD_2Cl_2–CD_3CN (2:1)] 20.6, 27.0, 27.3, 36.8, 37.6, 39.0, 41.6, 58.1 (CH_3, CH_2, CH), 136.5 (C5), 184.9 (C=N).

4,5-Dihydro-3,3-dimethyl-4-phenyl-3*H*-1,2,4-triazole-5-thione 13[37]

Compound **13** was prepared from acetone 4-phenylthiosemicarbazone (2.07 g, 10 mmol) according to the literature method.[37] Pure orange prisms of *title compound* **13** were obtained in low yield (0.27 g, 13%); mp 167–168 °C (lit.,[37] 172–174 °C); $C_{10}H_{11}N_3S$ (MW = 205.3); ν_{max}(Nujol)/cm^{-1} 1503 (s), 1490 (s); δ_H(250 MHz; $CDCl_3$) 1.64 (6 H, CH_3), 7.15–7.60 (several m, phenyl); δ_C(62.9 MHz; $CDCl_3$) 22.5 (CH_3), 110.1 (C5), 127.3, 129.7, 130.3, 134.8 (phenyl), 188.0 (C=S); EI-MS *m*/*z* 177 (M − N_2, 50%), 74 ($Me_2C{=}S^+$, 100%).

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