1,2,4-Triazolium Salts from the Reaction of 1-Aza-2-azoniaallene Salts with Nitriles

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Aryl- and alkylhydrazones **1** of alkyl ketones and propanal are transformed to 1-chloroalkylazo compounds **2** with *tert*-butyl hypochlorite. Compounds **2** react with antimony(V) chloride or aluminum(III) chloride to give 1-aza-2-azoniaallene salts **3** as reactive intermediates, which are intercepted as 3*H*-1,2,4-triazolium salts **5** with nitriles. In most cases these salts rearrange spontaneously to form the corresponding 1*H*-triazolium salts **6**. Benzophenone arylhydrazone **1x** reacts with *tert*-butyl hypochlorite and antimony(V) chloride to furnish the 1-aryl-3-phenylindazolium salt **7**. An X-ray diffraction analysis of a 1*H*-1,2,4-triazolium salt [6,7,8,9-tetrahydro-2-methyl-3-(2,4,6-trichlorophenyl)-5*H*-[1,2,4]triazolo-[5,1-*a*]azepinium hexachloroantimonate (**6n**)] is reported.

In an attempt to synthesize the first stable 1-aza-2-azoniaallene salt **3**,[1-5] we oxidized hydrazones **1** with *tert*-butyl hypochlorite to obtain the geminal chloro azo compounds **2**. This method, which was introduced by Moon,[6] seems to be generally applicable to hydrazones of ketones, in contrast to chlorination with chlorine, which sometimes leads to mixtures of compounds. For instance, partial chlorination of the aromatic nucleus is observed for arylhydrazones. Many aldehyde hydrazones give mixtures of compounds when treated with *tert*-butyl hypochlorite. However, propanal hydrazone **1m** can be chlorinated to **2m**, a compound which has been described by Moon et al., although without reporting physical data.[7] The authors assign structure **2m'** to their product. Our assignment of the azo constitution **2m** is based on the NMR spectra ($CDCl_3$). In the ^1H NMR spectrum a double doublet at $\delta = 5.87$ for one proton coupled with $J = 5.5$ and 6.1 Hz to the signals around $\delta = 2.36$ of the diastereotopic CH_2 protons is assigned to H–C–Cl. In the ^{13}C NMR spectrum the resonance for C–Cl is found at $\delta = 88.9$ (Table 2).

On treatment of **2a** with aluminum(III) chloride ($AlCl_3$) in dichloromethane a deep yellow solution is formed, which shows a strong a broad IR absorption at $\nu = 1899\,cm^{-1}$. This band is tentatively assigned to the antisymmetric valence vibration of a cumulene **3b**. Similar broad bands were observed for other 2-azoniaallene salts.[8-10] Experiments are in progress to isolate a cumulene **3**.

With antimony(V) chloride ($SbCl_5$) in dichloromethane compounds **2** form orange precipitates, which easily dissolve in CD_3CN. However, the NMR spectra of these solutions show only signals for triazolium salts **6** with a CD_3 substituent in 5-position. We then found that triazolium salts **6** are generally produced almost quantitatively if one adds to a cold (−60 °C) mixture of **2** and a Lewis acid ($AlCl_3$ or $SbCl_5$) in dichloromethane a nitrile and warms up to room temperature. The reaction seems to work well with all kinds of nitriles, e. g. with alkyl and aryl substituted nitriles, sterically hindered nitriles like pivalonitrile, cyanamides and thiocyanates. Aryl- and alkylhydrazones of aliphatic ketones and of certain aldehydes, **1m**, can be used.

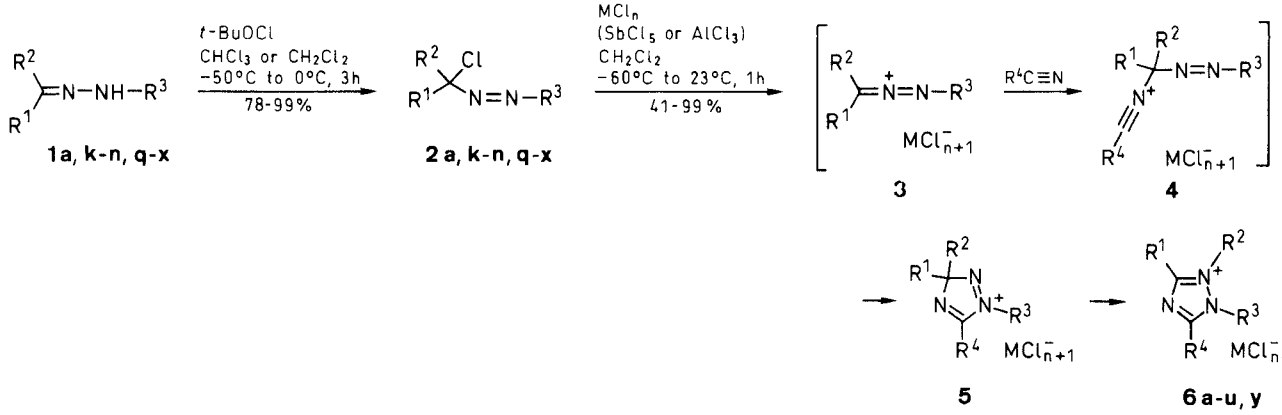
However, hydrazones of *aryl* ketones give indazolium salts.[11-15] Thus, from **2x** the indazolium salt **7** is obtained, in our opinion by an intramolecular *nucleophilic* aromatic substitution mechanism.[11] To rationalize the formation of compounds **6** (Scheme 1) the formation of an intermediate cation **3** is assumed, which reacts with the nitrile to give a nitrilium salt **4**. Obviously, nitrilium salts with an azo group in α-position to the nitrilium nitrogen atom cyclize spontaneously to furnish triazolium salts **5**.

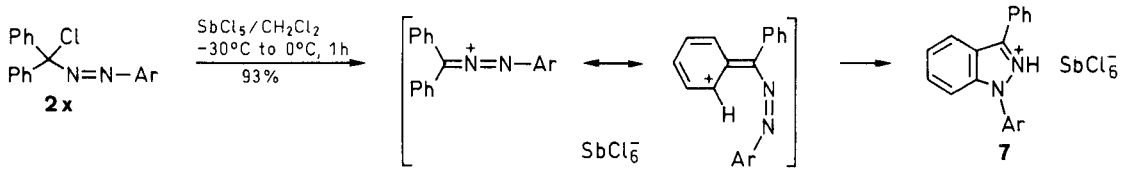
1,3,3-Trisubstituted 3*H*-1,2,4-triazolium salts **5** tend to rearrange to 1,2,3-trisubstituted 1*H*-1,2,4-triazolium salts **6**. While we were not able to observe an intermediate **5** during the preparation of the 1-(2,4,6-trichlorophenyl) substituted salts **6**, treatment of the 1-(4-chlorophenyl) substituted compound **2u** with $SbCl_5$ afforded a 4:1 mixture of **5u** and **6u**. The rearrangement **5u** → **6u** can be completed on heating the mixture in boiling acetonitrile for one hour. If the *N*-*tert*-butyl substituted azo compound **2v** is treated with $SbCl_5$, a stable salt **5v** is isolated. A solution of **5v** in CD_3CN turns dark at room temperature within a few days. The ^1H NMR spectrum of this dark solution shows some rearranged product **6v** besides unrearranged **5v**. In boiling acetonitrile **5v** decomposes quickly without rearranging to **6v**. On the other hand, the *N*-*tert*-butyl substituted azo compound **2w** eliminates isobutene already at −40 °C when treated with $SbCl_5$. The isopropyl group migrates to furnish **6y**, from which the triazole **9** is obtained with base.

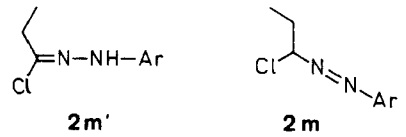
These observations show that an electron-withdrawing substituent on N1 accelerates the rearrangement **5** → **6**. Independently, a *tert*-butyl substituent on N1 is eliminated as isobutene. If the elimination is faster than the rearrangement, as in the case **5v**, a 3*H*-1,2,4-triazole **8** is formed, which polymerizes. 3*H*-1,2,4-Triazoles of type **8** seem to be unreported in the literature. However, in the case **5w**, the migration of the isopropyl group is faster than the elimination of isobutene; **5w** rearranges to **6w**, which looses isobutene to give **6y**.

If R^1 and R^2 are part of a cyclus, the sequence **5** → **6** constitutes a ring enlargement reaction reminiscent of a Beckmann rearrangement.[16] From **6m** the free base **10** is obtained with aqueous sodium hydroxide.

Our findings are related to results of Schildknecht and Hatzmann, who showed that the addition of cyanic acid

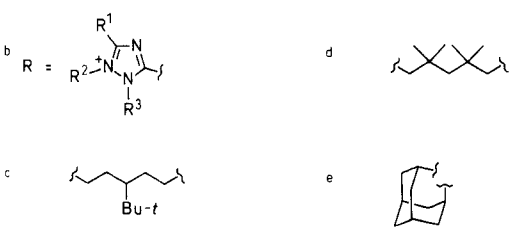






1–6	R^1	R^2	R^3	R^4
a[a]	Me	Me	2,4,6-$Cl_3C_6H_2$	Me
b	Me	Me	2,4,6-$Cl_3C_6H_2$	Me
c	Me	Me	2,4,6-$Cl_3C_6H_2$	Et
d	Me	Me	2,4,6-$Cl_3C_6H_2$	*i*-Pr
e	Me	Me	2,4,6-$Cl_3C_6H_2$	*t*-Bu
f	Me	Me	2,4,6-$Cl_3C_6H_2$	Ph
g	Me	Me	2,4,6-$Cl_3C_6H_2$	CH_2CN
h	Me	Me	2,4,6-$Cl_3C_6H_2$	CH_2R^b
i	Me	Me	2,4,6-$Cl_3C_6H_2$	Me_2N
j	Me	Me	2,4,6-$Cl_3C_6H_2$	MeS
k	Me	Et	2,4,6-$Cl_3C_6H_2$	Me
l	Me	*i*-Pr	2,4,6-$Cl_3C_6H_2$	Me
m	Et	H	2,4,6-$Cl_3C_6H_2$	Me
n	$(CH_2)_5$		2,4,6-$Cl_3C_6H_2$	Me
o	$(CH_2)_5$		2,4,6-$Cl_3C_6H_2$	Et
p	$(CH_2)_5$		2,4,6-$Cl_3C_6H_2$	Ph
q	[c]		2,4,6-$Cl_3C_6H_2$	Me
r	[d]		2,4,6-$Cl_3C_6H_2$	Me
s	$(CH_2)_{11}$		2,4,6-$Cl_3C_6H_2$	Me
t	[e]		2,4,6-$Cl_3C_6H_2$	Me
u	Me	Me	4-ClC_6H_4	Me
v	Me	Me	*t*-Bu	Me
w	Me	*i*-Pr	*t*-Bu	Me
x	Ph	Ph	2,4,6-$Cl_3C_6H_2$	–
y	Me	*i*-Pr	H	Me

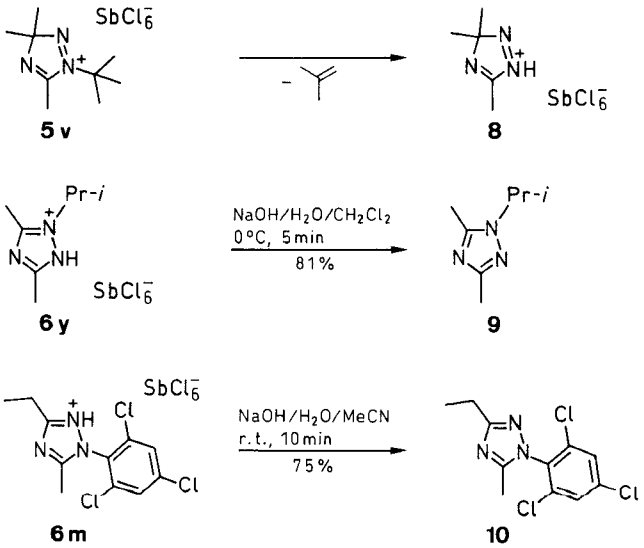
[a] $MCl_{n+1}^- = SbCl_6^-$ for **a**, **d**–**y**, $AlCl_4^-$ for **b**, **c**.

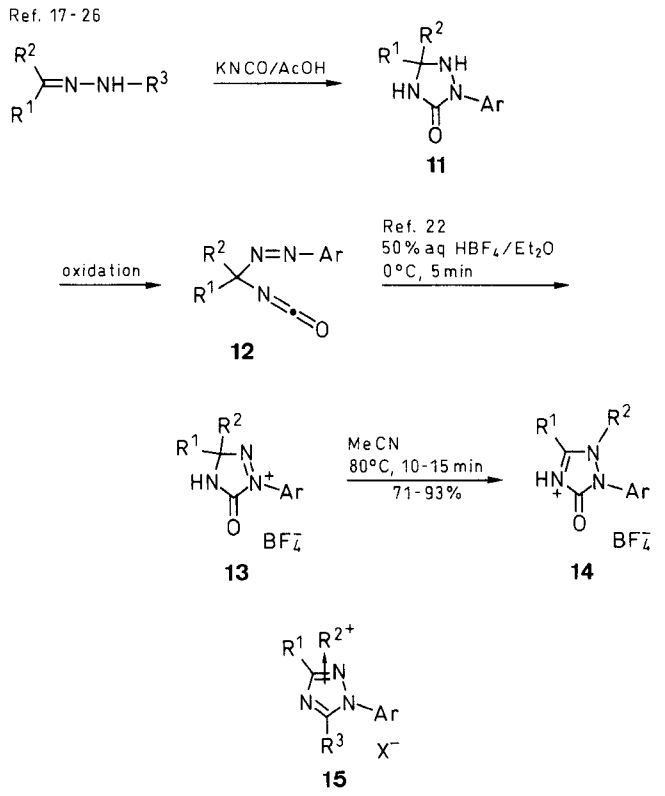


Scheme 1

to hydrazones[17,18] gives triazolones **11**, which can be oxidized to geminal azo isocyanates **12**.[19,20] Heating the isocyanates **12** to 140–170 °C affords triazolones **14**.[21] A ring expansion using this reaction has been described.[22] Recently, Gstach et al. found that the rearrangement of azo isocyanates **12** to triazolones **14** is dramatically accelerated by acids (Scheme 2). The reaction is assumed to proceed via intermediates **13** corresponding to our products **5**.[22–25] The reaction has systematically been applied for ring expansion reactions.[24] Intermediates **13** have been isolated and seem to be thermally more stable than our salts **5**.[26] An X-ray structural analysis of a compound **13** (Ar = Ph, $R^1 = R^2 = Me$) has been published.[22]

For the transformation **5** → **6** a Wagner–Meerwein 1,2-shift with a three-center transition state or a [1,5]-sigmatropic rearrangement can be discussed. However, a rearrangement via a π-complex **15** of a cation R^{2+} and an aromatic triazole cannot be excluded.[27,28]





Scheme 2

It has already been noted by Schildknecht and Gstach that in the related rearrangement **13** → **14** with $R^1 \neq R^2$ the substituent giving the more stable cation migrates. This is also true for the transformation **5** → **6**. In all cases studied so far one of the C3-substituents of **5** migrates exclusively and migration occurs in most cases[25] to N2 (and not to N4). A proton, **5m**, an ethyl group, **5k**, or an isopropyl substituent, **5l, w**, migrate in preference to a methyl group. The dramatical effect of small amounts of acids on the velocity of the rearrangement of compounds **13**[22-25] together with the preferred migratory tendency of the group, which forms the more stable carbenium ion, leads us to favor a transition state or reactive intermediate **15** for the rearrangement.

Only a few 1,2,4-triazolium salts with the substitution pattern of compounds **6** have been reported.[29-32]

The NMR and IR spectra of the new compounds are collected in Table 2. We found it difficult to decide whether in compounds **6** the substituent R^2 is located on N2 or on N4. Therefore, an X-ray diffraction analysis of **6n** was carried out confirming substitution at N2. The structure was solved using the programs SHELXS-86[33] and SHELX-76[34] by the Patterson method with subsequent difference-Fourier synthesis. The hydrogen atoms were fixed in calculated positions (d(C–H) = 96 pm). The anisotropic refinement led to agreement factors $R_1 = 0.075$ and $R_2 = 0.079$. A molecular plot[35] for the cation of **6n** is shown in the figure. Selected bond lengths, bond angles and torsional angles are presented in Table 1.

The triazolium ring of **6n** is planar. The ring shows a long N1-N2 distance of 139(1) pm characteristic for a single bond, while the other four bond distances in the ring are almost equal (133 to 136 pm. For a N=N$^+$ double bond in a 1,2,4-triazolium salt 124.3(5) pm and for C–N single bonds values of about 148 pm have been reported.[22,37,38] The positive charge of the **6n** is almost equally distributed between N1 and N2, and all C–N bonds of the triazole ring show considerable double-bond character. Compounds **6** can be regarded as aza cyanines closed on their molecular ends to a ring. The plane of the bulky aryl substituent on N1 is perpendicular to the plane of the triazolium ring [C_2–N_1–C_9–C_{10} = −93(1)°].

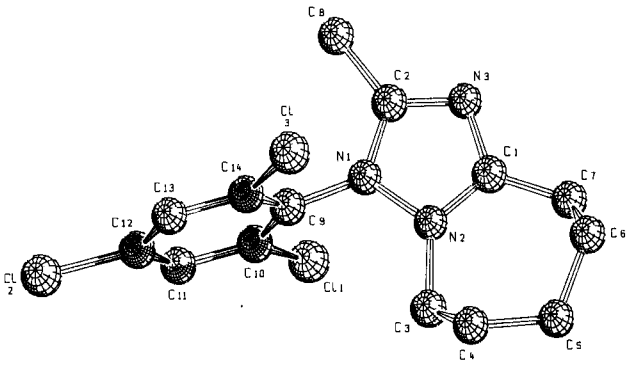


Figure. SCHAKAL plot of cation of **6n**.

Table 1. Selected Bond Lengths (pm), Bond Angles and Torsional Angles (deg) of the Cation of **6n**[36]

N1-C2	136 (1)	C7-C1	149 (1)	C6-C7-C1	114 (1)
C2-N3	133 (1)	N1-C2-N3	111 (1)	C7-C1-N2	123 (1)
N3-C1	135 (1)	C2-N3-C1	106.7 (9)	N1-C2-N3-C1	0 (1)
C1-N2	135 (1)	N3-C1-N2	111 (1)	C2-N3-C1-N2	0 (1)
N2-N1	139 (1)	C1-N2-N1	106.1 (8)	C2-N1-C9-C10	−93 (1)
N1-C9	144 (1)	N2-N1-C2	106.2 (9)	C8-C2-N1-C9	−4 (1)
C2-C8	150 (1)	N1-C9-C10	119.8 (9)	N1-N2-C3-C4	125 (1)
N2-C3	149 (1)	N1-N2-C3	123.7 (9)	N2-C3-C4-C5	71 (1)
C3-C4	150 (2)	N2-C3-C4	112 (1)	C3-C4-C5-C6	−67 (1)
C4-C5	152 (2)	C3-C4-C5	116 (1)	C4-C5-C6-C7	67 (1)
C5-C6	154 (2)	C4-C5-C6	116 (1)	C5-C6-C7-C1	−74 (1)
C6-C7	154 (1)	C5-C6-C7	114 (1)	C6-C7-C1-N2	56 (1)

All solvents are dried by standard methods. The experiments are carried out with exclusion of moisture. The melting points are uncorrected. IR spectra: IR-Mattson Polaris FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra: Bruker WM-250 and AC-250 spectrometers; internal reference TMS. X-Ray diffraction analysis: Syntex $P2_1$ diffractometer (graphite monochromator, $\lambda_{Mo-K\alpha}$ = 71.069 pm).

Preparation of the Hydrazones 1:

A mixture of the carbonyl compound (100 mmol or 110 to 120 mmol, if the carbonyl compound is volatile), the hydrazine (100 mmol), AcOH (1 mL), and EtOH (80 mL) was boiled under reflux for 5 h. The product crystallized on cooling (−20°C). The crude product was dissolved in boiling EtOH, and the solution was kept at −20°C for crystallization.

Acetone (2,4,6-Trichlorophenyl)hydrazone (**1a**):

From acetone (6.97 g, 120 mmol) and (2,4,6-trichlorophenyl)hydrazine (21.15 g, 100 mmol). From EtOH (30 mL) colorless needles (18.00 g, 72%); mp 56–58°C (Lit.[39] 58–59°C).

2-Butanone (2,4,6-Trichlorophenyl)hydrazone (**1k**):

From 2-butanone (7.93 g, 110 mmol) and (2,4,6-trichlorophenyl)hydrazine (21.15 g, 100 mmol). From EtOH (8 mL) a pale yellow powder (19.52 g, 74%); mp 36–38°C.

Table 2. Selected NMR and IR Data for the New Compounds Prepared

Product	Molecular Formula[a]	^{1}H NMR (CD_3CN/TMS)[b] δ, J (Hz)	^{13}C NMR (CD_3CN/TMS)[b] δ	IR (KBr) ν (cm^{-1})
1a	$C_9H_9Cl_3N_2$ (251.5)	1.97, 2.02 (CH_3), 6.74 (NH), 7.28 (aryl)[c]	16.0, 25.0 (CH_3), 127.3, 127.8, 128.6, 139.2 (aryl), 151.2 (C=N)[c]	1378, 1455, 1470,[d] 1547, 1636, 1725, 3342[e]
1k	$C_{10}H_{11}Cl_3N_2$ (265.6)	main component: 1.10 (t, J = 7.5), 1.92 (CH_3), 2.30 (q, J = 7.5, CH_2), 6.82 (NH), 7.26 (aryl); minor component: 1.18 (t, J = 7.7), 1.98 (CH_3), 2.37 (q, J = 7.7, CH_2), 6.86 (NH), 7.26 (aryl)[c,f]	main component: 10.9, 14.5 (CH_3), 31.9 (CH_2), 154.4 (C=N); minor component: 9.5, 22.2, 23.0 (CH_3, CH_2), 155.9 (C=N)[c,f]	1378, 1455, 1540, 1563,[d] 1632, 1725, 3346[e]
1l	$C_{11}H_{13}Cl_3N_2$ (279.6)	1.11 (d, J = 6.9, 6H), 1.89 (CH_3), 2.54 (sept, J = 6.9), 6.84 (NH), 7.27 (aryl)[c,g]	12.5, 19.9 (2C) (CH_3), 36.9 (CH), 126.4, 127.0, 128.7, 139.2 (aryl), 157.3 (C=N)[c,g]	1378, 1455, 1490,[d] 1551, 3346[e]
1m	$C_9H_9Cl_3N_2$ (251.5)	main component: 1.10 (t, J = 7.5, CH_3), ≈ 2.28 (m, CH_2), 7.22 (t, J = 5.1, CH), 7.14 (NH), 7.28 (aryl); minor component: 1.21 (t, J = 7.6, CH_3), ≈ 2.28 (m, CH_2), 6.73 (m, CH), 7.14 (NH), 7.29 (aryl)[c,h]	main component: 10.9 (CH_3), 25.5 (CH_2), 147.8 (C=N); minor component: 10.4 (CH_3), 19.7 (CH_2), 148.0 (C=N)[c,h]	1382, 1447, 1482, 1540, 1571, 3292[e]
1n	$C_{12}H_{13}Cl_3N_2$ (291.6)	1.71 (m, 6H), 2.33 (m, 2H), 2.46 (m, 2H) (CH_2), 6.84 (NH), 7.28 (aryl)[c]	25.6, 25.7, 26.0, 27.0, 35.1 (CH_2), 127.3, 127.6, 128.6, 139.4 (aryl), 158.7 (C=N)[c]	1378, 1456,[d] 1466, 1540, 3346[e]
1q	$C_{16}H_{21}Cl_3N_2$ (347.7)	0.90 (CH_3), 7.26 (NH), 7.29 (aryl)[c]	25.8, 26.3, 27.5 (3C), 32.6, 34.7, 47.4 (CH_3, CH_2, CH, C), 127.3, 127.7, 128.6, 139.5 (aryl), 158.6 (C=N)[c]	1370, 1470, 1544, 1567, 3350[e]
1r	$C_{16}H_{21}Cl_3N_2$ (347.7)	1.02 (6H), 1.08 (6H) (CH_3), 1.43, 2.10, 2.22 (CH_2), 6.85 (NH), 7.29 (aryl)[c]	30.9, 31.2 (CH_3), 34.6, 35.1, 39.1, 47.7, 52.6 (CH_2, C), 127.4, 127.6, 128.6, 139.6 (aryl), 157.6 (C=N)[c]	1374, 1466, 1559, 3350[e]
1s	$C_{18}H_{25}Cl_3N_2$ (375.8)	1.33 (m, 14H), 1.69 (m, 4H), 2.34 (m, 4H) (CH_2), 7.11 (NH), 7.26 (aryl)[c]	22.7, 23.0, 23.4, 23.5, 24.1, 25.1, 25.6, 26.0, 27.9, 32.5 (CH_2), 126.2, 126.7, 128.7, 139.4 (aryl), 156.0 (C=N)[c]	1378, 1466, 1551, 3350[e]
1t	$C_{16}H_{17}Cl_3N_2$ (343.7)	1.88–2.03 (12H), 2.64 (1H), 3.33 (1H), 6.77 (NH), 7.29 (aryl)[c]	27.8 (2C), 30.7 (1C), 36.4 (1C), 37.5 (2C), 39.0 (2C), 39.3 (1C) (CH_2, CH), 127.5, 127.6, 128.6, 139.8 (aryl), 166.3 (C=N)[c]	1378, 1466, 1544, 3346[e]
1u	$C_9H_{11}ClN_2$ (182.7)	1.80, 2.00 (CH_3), 6.79 (NH)[c]	15.5, 25.2 (CH_3), 113.9, 123.7, 128.8, 144.3, 144.7 (aryl, C=N)[c]	1497, 1555, 1598, 3369[e]
1v	$C_7H_{16}N_2$ (128.2)	1.17 (9H), 1.71, 1.92 (CH_3), 4.15 (NH)[c]	15.2, 25.4, 28.6 (3C) (CH_3), 53.0 (C), 143.9 (C=N)[c]	1362, 1389,[d] 1439, 1474,[d] 1551, 1586[d,e]
1w	$C_9H_{20}N_2$ (156.3)	1.05 (d, J = 6.8), 1.17 (9H), 1.65 (CH_3), 2.43 (sept, J = 6.8, CH), 4.28 (NH)[c,g]	11.8, 20.1, 28.5 (3C), 37.0, 53.3 (CH_3, CH, C), 150.9 (C=N)[c,g]	1466, 1540, 1717[e]
1x	$C_{19}H_{13}Cl_3N_2$ (375.7)		125.5, 126.6, 126.7, 128.2, 128.7, 128.8, 129.4, 129.7, 132.4, 137.2, 137.7, 148.5[c]	1485, 1540,[d] 1559, 1578,[d] 3322[e]
2a	$C_9H_8Cl_4N_2$ (286.0)	2.02 (CH_3), 7.39 (aryl)[c,i]	30.1 (CH_3), 94.0 (CCl), 126.6, 128.6, 133.3, 145.2 (aryl)[c,i]	1382, 1424, 1578, 1725[e]
2k	$C_{10}H_{10}Cl_4N_2$ (300.0)	1.09 (t, J = 7.4), 1.95 (CH_3), 2.32 (m, CH_2), 7.37 (aryl)[c]	8.7, 28.4, 35.5 (CH_3, CH_2), 98.2 (CCl), 126.8, 128.8, 133.5, 145.8 (aryl)[c]	1378, 1424, 1440,[d] 1578, 1725[e]
2l	$C_{11}H_{12}Cl_4N_2$ (314.0)	1.07 (d, J = 6.7), 1.21 (d, J = 6.8), 1.91 (CH_3), 2.67 (sept, J = 6.7, CH), 7.38 (aryl)[c]	17.6, 17.7, 27.1 (CH_3), 38.3 (CH), 102.1 (CCl), 126.6, 128.7, 133.3, 145.7 (aryl)[c,i]	1378, 1420, 1430,[d] 1460,[d] 1547, 1578, 1725[e]
2m	$C_9H_8Cl_4N_2$ (286.0)	1.18 (t, J = 7.3) (CH_3), 2.36 (m, CH_2), 5.87 (dd, J = 5.5 and 6.4, CH), 7.38 (aryl)[c]	9.6 (CH_3), 29.8 (CH_2), 88.9 (CCl), 126.8, 128.8, 133.7, 145.3 (aryl)[c]	1382, 1424, 1459, 1540, 1578, 1725[e]
2n	$C_{12}H_{12}Cl_4N_2$ (326.1)	7.38 (aryl)[c]	22.3, 24.8, 37.9 (CH_2), 98.3 (CCl), 126.8, 128.8, 133.4, 146.0 (aryl)[c]	1382, 1424, 1447, 1578, 1725[e]
2q	$C_{16}H_{20}Cl_4N_2$ (382.2)	main component: 0.86 (CH_3), 7.38 (aryl); minor component: 0.94 (CH_3), 7.37 (aryl)[c,j]	22.8, 25.0, 27.6, 32.4, 37.6, 40.8, 46.9 (minor c.), 47.0 (main c.) (CH_3, CH_2, CH, C), 94.9 (main c.), 98.7 (minor c.) (CCl), 126.7, 128.7, 133.2, 145.8 (aryl, minor c.), 126.8, 128.8, 133.4, 145.9 (aryl, main c.)[c,j]	1370, 1380,[d] 1424, 1443, 1474, 1540, 1582, 1725[e]
2r	$C_{16}H_{20}Cl_4N_2$ (382.2)	1.05 (6H), 1.17 (6H) (CH_3), 1.45 (2H), 2.18 (q, J = 14.2) (CH_2), 7.38 (aryl)[c]	31.3, 32.8, 33.0, 50.8, 51.3 (CH_3, CH_2, C), 98.5 (CCl), 126.2, 128.6, 133.0, 146.1 (aryl)[c]	1374, 1428, 1459, 1482, 1528, 1578, 1725[e]
2s	$C_{18}H_{24}Cl_4N_2$ (410.2)	1.43 (14H), 1.71 (m, 4H), 2.11 (m, 2H), 2.40 (m, 2H) (CH_2), 7.38 (aryl)[c]	20.9, 22.4, 22.8, 25.8, 26.3, 36.4 (CH_2), 101.4 (CCl), 126.8, 128.8, 133.4, 146.1 (aryl)[c]	1378, 1416,[d] 1443, 1470, 1578, 1725[e]
2t	$C_{16}H_{16}Cl_4N_2$ (378.1)	7.40 (aryl)[c]	27.2, 27.3, 34.8, 38.4, 39.8 (CH_2, CH), 101.7 (CCl), 127.0, 128.9, 133.5, 146.5 (aryl)[c]	1382, 1416, 1455, 1544, 1571, 1725[e]
2u	$C_9H_{10}Cl_2N_2$ (217.1)	1.93 (CH_3)[c]	30.3 (CH_3), 92.8 (CCl), 124.2, 129.3, 137.4, 149.3 (aryl)[c]	1366, 1405, 1478, 1517, 1590, 1655, 1729, 1779, 1910[e]
2v	$C_7H_{15}ClN_2$ (162.7)	1.23 (9H), 1.77 (6H) (CH_3)[c]	26.7 (3C), 30.0 (2C) (CH_3), 66.9 (C), 92.4 (CCl)[c]	1366, 1455, 1551, 1721[e]

Table 2. (continued)

Product	Molecular Formula[a]	^{1}H NMR (CD_3CN/TMS)[b] δ, J (Hz)	^{13}C NMR (CD_3CN/TMS)[b] δ	IR (KBr) ν (cm^{-1})
2w	$C_9H_{19}ClN_2$ (190.7)	0.93 (d, J = 6.7), 1.09 (d, J = 6.7), 1.25 (9H), 1.68 (CH_3), 2.45 (sept, J = 6.7, CH)[c]	17.4, 17.5, 26.5, 26.9 (3C), 38.5, 67.4, (CH_3, CH, C), 100.4 (CCl)[c]	1366, 1466, 1547, 1563, 1717[e]
2x	$C_{19}H_{12}Cl_4N_2$ (410.1)		100.7 (CCl), 127.2, 128.3, 128.5, 128.8, 128.9, 133.8, 140.4, 145.7 (aryl)[c]	1382, 1416, 1447, 1493[e]
5v	$C_9H_{18}Cl_6N_3Sb$ (502.7)	1.82 (6H), 1.87 (9H), 2.94 (3H) (CH_3)	17.5, 21.1 (2C), 28.2 (3C) (CH_3), 78.6, 114.5 (C), 161.0 (C=N)[k]	1378, 1405, 1439, 1455, 1517, 1686
6a	$C_{11}H_{11}Cl_9N_3Sb$ (626.1)	2.47, 2.70, 3.69 (CH_3), 7.95 (aryl)[i]	13.1, 14.2, 35.3 (CH_3), 124.3, 131.6, 136.8, 142.2 (aryl), 160.9, 161.9 (C=N)[k]	1393, 1451, 1517, 1551
6b	$C_{11}H_{11}AlCl_7N_3$ (460.4)	2.47, 2.72, 3.72 (CH_3), 7.92 (aryl)	13.1, 14.2, 35.3 (CH_3), 124.3, 131.6, 136.9, 142.3 (aryl), 161.0, 162.0 (C=N)	1389, 1455, 1490, 1517, 1559, 1644
6c	$C_{12}H_{13}AlCl_7N_3$ (474.4)	1.30 (t, J = 7.6), 2.73, 3.71 (CH_3), 2.70 (q, J = 7.6, CH_2), 7.92 (aryl)	10.9, 14.2, 20.8, 35.1 (CH_3, CH_2), 124.2, 131.5, 136.8, 142.2 (aryl), 161.9, 164.9 (C=N)[i]	1385, 1459, 1486, 1509, 1560,[d] 1567, 1644
6d	$C_{13}H_{15}Cl_9N_3Sb$ (654.1)	1.33 (d, J = 7.1), 2.76, 3.72 (CH_3), 2.85 (sept, J = 7.1, CH), 7.90 (aryl)[l]	14.1, 20.8, 27.7, 34.9 (CH_3, CH), 124.0, 131.4, 136.6, 142.3 (aryl), 161.8, 168.4 (C=N)[l]	1385, 1443, 1462, 1497,[d] 1551
6e	$C_{14}H_{17}Cl_9N_3Sb$ (668.1)	1.32 (3CH_3), 2.73, 3.62 (CH_3), 7.92 (aryl)	14.3, 28.8 (3C), 34.8, 36.2 (CH_3, C), 126.6, 131.7, 137.0, 142.3 (aryl), 161.1, 169.8 (C=N)	1378, 1439, 1466, 1480,[d] 1551
6f	$C_{16}H_{13}Cl_9N_3Sb$ (688.1)	2.84, 3.82 (CH_3), 7.92 (2H, aryl)	14.5, 35.3 (CH_3), 123.6, 126.0, 129.3, 130.9, 132.0, 135.1, 136.8, 142.5 (aryl), 159.9, 162.4 (C=N)	1378, 1447, 1478, 1540,[d] 1551, 1601
6g	$C_{12}H_{10}Cl_9N_4Sb$ (651.1)	2.79, 3.78 (CH_3), 4.17 (CH_2), 7.95 (CH_2)	14.5 (CH_3), 18.4 (CH_2), 35.9 (NCH_3), 112.7 (CN), 123.4, 131.9, 137.1, 143.2 (aryl), 154.6, 163.1 (C=N)	1385, 1439, 1486, 1517, 1551
6h	$C_{21}H_{18}Cl_{18}N_6Sb_2$ (1236.1)	2.75, 3.78 (CH_3), 4.39 (CH_2), 7.94 (aryl)	14.6 (CH_3), 25.7 (CH_2), 36.0 (NCH_3), 123.4, 131.9, 137.2, 143.1 (aryl), 155.5, 162.9 (C=N)	1385, 1447, 1482, 1513,[d] 1555
6i	$C_{12}H_{14}Cl_9N_4Sb$ (655.1)	2.51, 2.97 (6H), 3.40 (CH_3), 7.86 (aryl)[i]	14.0, 33.7, 39.9 (2C) (CH_3), 126.9, 131.3, 138.0, 141.1 (aryl), 159.8, 162.1 (C=N)[i]	1385, 1424, 1463, 1497, 1551, 1644
6j	$C_{11}H_{11}Cl_9N_3SSb$ (658.1)	2.74, 2.82, 3.73 (CH_3), 7.89 (aryl)[m]	14.3, 15.4, 35.4 (CH_3), 123.9, 131.7, 137.2, 142.8 (aryl), 162.2, 165.5 (C=N)[m]	1378, 1400,[d] 1470, 1551
6k	$C_{12}H_{13}Cl_9N_3Sb$ (640.1)	1.31 (t, J = 7.3), 2.47, 2.77 (CH_3), 4.21 (q, J = 7.3, CH_2), 7.93 (aryl)	13.1, 14.1, 14.2 (CH_3), 44.9 (CH_2), 124.2, 131.6, 136.5, 142.2 (aryl), 160.9, 161.3 (C=N)[i]	1393, 1455, 1486, 1513, 1536, 1567
6l	$C_{13}H_{15}Cl_9N_3Sb$ (654.2)	1.59 (d, J = 7.0, 6H), 2.43, 2.85 (CH_3), 4.44 (sept, J = 7.0, CH), 7.94 (aryl)	13.1, 15.7, 20.9 (2C) (CH_3), 56.2 (CH), 124.4, 131.8, 137.0, 142.4 (aryl), 160.6, 161.0 (C=N)	1378,[d] 1389, 1436,[d] 1459, 1482,[d] 1517,[d] 1532, 1559
6m	$C_{11}H_{11}Cl_9N_3Sb$ (626.1)	1.38 (t, J = 7.5), 2.64 (CH_3), 3.00 (q, J = 7.5, CH_2), 7.82 (aryl), 12.89 (NH)	11.0, 20.1 (CH_3), 129.1, 130.9, 135.2, 140.3 (aryl), 155.7, 158.9 (C=N)	1385, 1463, 1563, 1605
6n	$C_{14}H_{15}Cl_9N_3Sb$ (666.1)	1.86 (m), 3.25 (m), 4.11 (m) (CH_2), 2.45 (CH_3), 7.92 (aryl)	13.2 (CH_3), 23.8, 26.7, 28.9, 29.6, 50.6 (CH_2), 124.2, 131.7, 137.2, 142.5 (aryl), 160.9, 166.5 (C=N)	1389, 1416,[d] 1436,[d] 1455, 1486, 1513, 1536, 1563
6o	$C_{15}H_{17}Cl_9N_3Sb$ (680.2)	1.30 (t, J = 7.5, CH_3), 1.86 (m), 2.69 (q, J = 7.5), 3.28 (m), 4.11 (m) (CH_2), 7.93 (aryl)	10.9 (CH_3), 20.9, 23.8, 26.7, 29.0, 29.5, 50.4 (CH_2), 124.2, 131.7, 137.2, 142.5 (aryl), 164.8, 166.5 (C=N)	1389, 1459, 1482, 1509, 1528, 1555
6p	$C_{19}H_{17}Cl_9N_3Sb$ (728.2)	≈ 2.0 (m, 6H), 3.36 (m), 4.19 (m) (CH_2), 7.90 (2H, aryl)	23.7, 26.8, 29.1, 29.6, 50.4 (CH_2), 123.8, 125.9, 129.5, 130.9, 132.0, 135.2, 137.3, 142.7 (aryl), 159.9, 167.0 (C=N)	1420, 1451, 1478, 1528, 1563, 1601
6q	$C_{18}H_{23}Cl_9N_3Sb$ (722.2)	0.92 (3CH_3), 2.46 (CH_3), 1.49 (m, 3H), 2.24 (m, 2H), 3.07 (m, 1H), 3.45 (m, 1H), 4.10 (m, 2H) (CH, CH_2), 7.89 (aryl)[l, n]	13.1, 24.7, 27.5, 27.7, 27.9, 34.1, 49.5, 50.9 (C, CH, CH_2, CH_3), 123.7, 131.3, 131.4, 136.7, 136.9, 142.3 (aryl), 160.4, 165.6 (C=N)[l, n]	1370, 1389, 1416, 1432, 1451, 1482, 1513, 1536, 1563
6r	$C_{18}H_{23}Cl_9N_3Sb$ (722.2)	0.97 (6H), 1.09 (6H), 2.50 (CH_3), 1.75 (s), 3.20 (s), 4.00 (s) (CH_2), 7.92 (aryl)	13.6, 28.2, 30.6, 33.6, 34.8, 40.3, 55.8, 58.2 (C, CH_2, CH_3), 123.6, 131.7, 136.7, 142.4 (aryl), 161.4, 164.1 (C=N)	1393, 1409,[d] 1459, 1482,[d] 1524, 1567
6s	$C_{20}H_{27}Cl_9N_3Sb$ (750.3)	2.47 (CH_3), 3.08 (t, J = 7.4, 2H), 4.18 (t, J = 7.2, 2H) (CH_2), 7.89 (aryl)[l]	13.2 (CH_3), 24.6, 25.0, 25.2, 25.4, 25.7, 26.0, 26.1, 26.3, 26.6, 27.2, 48.8 (CH_2), 124.0, 131.6, 136.5, 142.4 (aryl), 161.3, 164.8 (C=N)[l]	1389, 1443, 1466, 1513, 1567
6t	$C_{18}H_{18}Cl_9N_3Sb$ (717.2)	2.45 (CH_3), 3.58 (m), 4.29 (m) (HCN), 7.92 (aryl)	13.2 (CH_3), 27.3, 30.6, 32.0, 33.0, 33.8, 56.5 (CH_2, CH), 124.2, 131.7, 137.1, 142.5 (aryl), 161.0, 169.5 (C=N)	1447, 1482, 1505,[d] 1532, 1567
6u	$C_{11}H_{13}Cl_7N_3Sb$ (557.2)	2.41, 2.65, 3.65 (CH_3), 7.58 (m), 7.79 (m) (aryl)	13.5, 13.6, 35.5 (CH_3), 128.6, 130.9, 132.1, 140.2 (aryl), 159.3, 159.5 (C=N)	1401, 1436, 1490, 1520, 1540[d]
6y	$C_7H_{14}Cl_6N_3Sb$ (474.7)	1.47 (d, J = 7.6), 2.47, 2.65 (CH_3), 4.69 (sept, J = 7.6, CH)	10.6, 11.5, 21.7 (2C) (CH_3), 53.5 (CH), 150.3, 152.0 (C=N)	1393, 1455, 1567, 1609
7	$C_{19}H_{12}Cl_9N_2Sb$ (709.1)		111.5, 119.1, 124.5, 124.8, 127.5, 127.6, 129.6, 130.5, 130.7, 133.6, 136.4, 136.9, 140.5, 141.9, 146.9 (aryl, C=N)[l]	1451, 1478, 1509, 1551, 1625

Table 2. (continued)

Product	Molecular Formula[a]	^{1}H NMR (CD_3CN/TMS)[b] δ, J (Hz)	^{13}C NMR (CD_3CN/TMS)[b] δ	IR (KBr) ν (cm^{-1})
9	$C_7H_{13}N_3$ (139.2)	1.46 (d, J = 6.6), 2.33, 2.40 (CH_3), 4.40 (sept, J = 6.6, CH)[c]	11.8, 13.9, 22.3 (2C) (CH_3), 49.6 (CH), 150.6, 158.9 (C=N)[c]	1331, 1378, 1420, 1451, 1509, 1555[d,e]
10	$C_{11}H_{10}Cl_3N_3$ (290.6)	1.36 (t, J = 7.6), 2.28 (CH_3), 2.80 (q, J = 7.6, CH_2), 7.52 (aryl)[c]	11.7, 12.3, 21.8 (CH_3, CH_2), 128.9, 132.0, 135.5, 136.9 (aryl), 154.3, 166.4 (C=N)[c]	1383,[d] 1393, 1463, 1513, 1578, 1725[e]

[a] Satisfactory microanalyses obtained: C ±0.40%, H ±0.44%, N ±0.33%. Deviations up to 2.22% for the volatile compounds **2v** and **9**.
[b] At 295 K.
[c] In $CDCl_3$.
[d] Shoulder.
[e] In CCl_4.
[f] Mixture of the geometrical isomers (≈ 4 : 1).
[g] Only traces of a second isomer.
[h] Mixture of isomers (≈ 3 : 1).
[i] At 273 K.
[j] Mixture of isomers (≈ 2 : 1).
[k] At 263 K.
[l] In $CD_3CN/CDCl_3$ (2 : 1).
[m] At 313 K.
[n] Because of hindered rotation around the N1-aryl bond six signals for aromatic carbon atoms are observed.

3-Methyl-2-butanone (2,4,6-Trichlorophenyl)hydrazone **(11)**:

From 3-methyl-2-butanone (9.51 g, 110 mmol) and (2,4,6-trichlorophenyl)hydrazine (21.15 g, 100 mmol). The product crystallized from the mixture on cooling (22.65 g, 81%). Recrystallization from EtOH (20 mL) affords a pale yellow powder (18.45 g, 66%); mp 39–41 °C.

Propanal (2,4,6-Trichlorophenyl)hydrazone **(1m)**:

From propanal (6.39 g, 110 mmol) and (2,4,6-trichlorophenyl)hydrazine (21.15 g, 100 mmol). The mixture was filtered with added activated carbon. Evaporation of the solvent afforded a pale orange oil (23.90 g, 95%), which was used without further purification.[7]

Cyclohexanone (2,4,6-Trichlorophenyl)hydrazone **(1n)**:

From cyclohexanone (9.82 g, 100 mmol) and (2,4,6-trichlorophenyl)hydrazine (21.15 g, 100 mmol). From EtOH (100 mL) colorless needles (15.82 g, 54%); mp 69–70 °C (Lit.[40] 73 °C).

4-tert-Butylcyclohexanone (2,4,6-Trichlorophenylhydrazone) **(1q)**:

From 4-*tert*-butylcyclohexanone (15.43 g, 100 mmol) and (2,4,6-trichlorophenyl)hydrazine (21.15 g, 100 mmol). Before evaporating the solvent, activated carbon was added and the mixture was filtered. The ochreous residue (34.74 g, 100%) could be recrystallized from cyclohexane to give a colorless powder; mp 58–59 °C.

3,3,5,5-Tetramethylcyclohexanone (2,4,6-Trichlorophenyl)hydrazone **(1r)**:

From 3,3,5,5-tetramethylcyclohexanone (15.43 g, 100 mmol) and (2,4,6-trichlorophenyl)hydrazine (21.15 g, 100 mmol). From EtOH (90 mL) colorless needles (28.16 g, 81%); mp 93–94 °C.

Cyclododecanone (2,4,6-Trichlorophenyl)hydrazone **(1s)**:

From cyclododecanone (18.23 g, 100 mmol) and (2,4,6-trichlorophenyl)hydrazine (21.15 g, 100 mmol). Recrystallization from petroleum ether (50–70 °C) (60 mL) afforded colorless crystals (26.31 g, 70%); mp 65–66 °C.

Tricyclo[3.3.1.1^{3,7}]decan-2-one (2,4,6-Trichlorophenyl)hydrazone **(1t)**:

From adamantanone (15.02 g, 100 mmol) and (2,4,6-trichlorophenyl)hydrazine (21.15 g, 100 mmol). From EtOH (130 mL) colorless needles (26.47 g, 77%); mp 85–86 °C.

Acetone (4-Chlorophenyl)hydrazone **(1u)**.

From acetone (6.97 g, 120 mmol) and 4-chlorophenylhydrazine (17.91 g, 100 mmol). From EtOH/H_2O (1 : 1) colorless crystals (10.60 g, 58%); mp 77–80 °C (dec) (Lit.[41] mp 84 °C).

Acetone tert-Butylhydrazone **(1v)**:

A suspension of acetone *tert*-butylhydrazone hydrochloride[26] (32.94 g, 200 mmol) in Et_2O (150 mL) was shaken with aq Na_2CO_3 (10%, 200 mL). The organic layer was separated, and the aqueous layer was repeatedly extracted with Et_2O. The combined ether extracts were dried (Na_2SO_4). Evaporation of the solvent and distillation of the residue afforded a colorless oil (15.90 g, 62%); bp 133–136 °C (Lit.[42] 132–134 °C).

3-Methyl-2-butanone tert-Butylhydrazone **(1w)**:

A mixture of *tert*-butylhydrazine hydrochloride (12.56 g, 100 mmol) and NaOH (4.00 g, 100 mmol) in H_2O was saturated with NaCl. 3-Methyl-2-butanone (8.61 g, 100 mmol) was added and the mixture was stirred at 80 °C for 2 h. After cooling to 0 °C the product was extracted with Et_2O. Workup and distillation afforded an orange oil (8.93 g, 57%); bp 78–79 °C/14 Torr.

Benzophenone (2,4,6-Trichlorophenyl)hydrazone **(1x)**:

From benzophenone (9.11 g, 50 mmol) and (2,4,6-trichlorophenyl)hydrazine (10.57 g, 50 mmol). The mixture was boiled under reflux for 15 h. The crude product dissolved partly in boiling EtOH (180 mL). Filtration and keeping at −20 °C afforded colorless needles (9.54 g, 51%); mp 105–107 °C (Lit.[39] 106–107 °C).

Preparation of the α-Chloro Azo Compounds 2:

The reaction was carried out in the dark. *t*-BuOCl[43] (6.51 g, 60 mmol) was added dropwise to a cold (−10 °C) solution of the hydrazone (50 mmol) in $CHCl_3$ (60 to 200 mL, depending on the solubility of the hydrazone). After stirring at 0 °C for 3 h the solvent was removed under reduced pressure. The oily residue crystallized spontaneously on cooling or after trituration with cold MeOH (5 to 20 mL) or was used without further purification.

1-[(1-Chloro-1-methylethyl)azo]-2,4,6-trichlorobenzene **(2a)**.[7,44]

From **1a** (12.58 g, 50 mmol). Evaporation of the solvent afforded an analytically pure yellow oil (14.16 g, 99%).

1-[(1-Chloro-1-methylpropyl)azo]-2,4,6-trichlorobenzene **(2k)**:

From **1k** (13.28 g, 50 mmol). Yield: 14.70 g (98%) of an orange oil.

1-[(1-Chloro-1,2-dimethylpropyl)azo]-2,4,6-trichlorobenzene **(2l)**:

From **1l** (13.98 g, 50 mmol). Yield: 13.82 g (88%) of an orange oil.

1-[(1-Chloropropyl)azo]-2,4,6-trichlorobenzene **(2m)**:

From **1m** (12.58 g, 50 mmol). However, 13.03 g (120 mmol) of *t*-BuOCl was used. The mixture was stirred at 23 °C for 90 min. Evaporation of the solvent afforded an orange oil (13.16 g, 92%), which couldn't be distilled without decomposition.

1-[*(1-Chlorocyclohexyl)azo*]-*2,4,6-trichlorobenzene* **(2n)**:

From **1n** (14.58 g, 50 mmol). The oily product crystallized when treated with cold (0 °C) MeOH (5 mL) to afford yellow needles (12.72 g, 78%); mp 50–51 °C.

1-[(4-tert-Butyl-1-chlorocyclohexyl)azo]-2,4,6-trichlorobenzene **(2q)**:

From **1q** (17.40 g, 50 mmol). Yield: 18.73 g (98%) of a red oil.

1-[(1-Chloro-3,3,5,5-tetramethylcyclohexyl)azo]-2,4,6-trichlorobenzene (**2r**):

From **1r** (17.39 g, 50 mmol). Yield: 18.34 g (96%) of yellow crystals; mp 92–95°C. With MeOH **2r** reacted quickly to give a geminal methoxy azo compound.

1-[(1-Chlorocyclododecyl)azo]-2,4,6-trichlorobenzene (**2s**):

From **1s** (18.79 g, 50 mmol). The product crystallized after evaporation of the solvent. Washing with MeOH (5 mL) afforded a yellow powder (19.28 g, 94%); mp 106–107°C.

1-[(2-Chlorotricyclo[3.3.1.1^{5,7}]dec-2-yl)azo]-2,4,6-trichlorobenzene (**2t**):

From **1t** (17.19 g, 50 mmol). The oily product crystallized on trituration with cold MeOH (20 mL) giving orange needles (17.39 g, 92%), mp 92–95°C.

1-[(1-Chloro-1-methylethyl)azo]-4-chlorobenzene (**2u**):

From **1u** (9.14 g, 50 mmol). Yield: 10.20 g (94%) of an orange oil, which solidified below 0°C.

1-[(1-Chloro-1-methylethyl)azo]-1,1-dimethylethane (**2v**):

t-BuOCl (6.51 g, 60 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a cold (−50°C) solution of **1v** (6.41 g, 50 mmol) in CH_2Cl_2 (20 mL). After stirring at −50°C for 2 h and then at 0°C for 1 h the solvent was evaporated at 0°C/14 Torr leaving a volatile orange oil (6.54 g, 80%), for which a correct elemental analysis could not be obtained; bp 42–51°C/14 Torr.

1-[(1-Chloro-1,2-dimethylpropyl)azo]-1,1-dimethylethane (**2w**):

From **1w** (7.81 g, 50 mmol) in $CHCl_3$ (50 mL) as described for **2v**. Yield: 8.96 g (94%) of a volatile orange oil, for which a correct elemental analysis could not be obtained.

1-[(1-Chloro-1,1-diphenylmethyl)azo]-2,4,6-trichlorobenzene (**2x**):

From **1x** (3.75 g, 10 mmol). However, a larger excess of *t*-BuOCl was used (2.60 g, 24 mmol). The reaction mixture was stirred at 23°C for 1 h. The oily product crystallized on trituration with petroleum ether (110–140°C) (3 mL). Recrystallization from petroleum ether (110–140°C) (15 mL) afforded yellow needles (2.50 g, 61%); mp 73–75°C (Lit.[44] 74–76°C).

General Procedures for the Preparations of the Triazolium Salts 5, 6:

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (30 mL) was added dropwise to a cold (−60°C) solution of **2** (10 mmol) and the nitrile (12 mmol) in CH_2Cl_2 (30 mL). The mixture was stirred at −60°C for 1 h, then at 0°C for 1 h, and then at 23°C for 10 min. Et_2O (100 mL) was added dropwise. The mixture was kept for 2 h at −20°C. Filtration afforded in most cases an analytically pure product.

Alternatively, instead of precipitating the product with Et_2O, the solvent was removed under reduced pressure and the residue was purified.

1-tert-Butyl-3,3,5-trimethyl-3H-1,2,4-triazolium Hexachloroantimonate (**5v**):

From **2v** (1.63 g, 10 mmol) and MeCN (0.49 g, 12 mmol). Yield: 3.80 g, 76%) of a colorless powder, which could be crystallized at −20°C from MeCN (7 mL)/Et_2O (20 mL) to furnish colorless needles; mp 92–94°C (dec).

2,3,5-Trimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**6a**):

From **2a** (8.58 g, 30 mmol) and MeCN (1.44 g, 36 mmol). However, the solution of **2a** was added dropwise to the suspension of $SbCl_5$ in CH_2Cl_2. Precipitation with Et_2O afforded a colorless powder (18.23 g, 97%), which could be recrystallized from MeCN (55 mL)/Et_2O (36 mL); mp 261–263°C (dec).

2,3,5-Trimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Tetrachloroaluminate (**6b**):

As described for **6a**, however with $AlCl_3$ (4.00 g, 30 mmol) instead of $SbCl_5$. Precipitation with Et_2O yielded a colorless powder (11.13 g, 82%). Reprecipitation from MeCN (10 mL)/Et_2O (70 mL) furnished colorless crystals; mp 163–165°C.

After stirring a mixture of **2a** and $AlCl_3$ in CH_2Cl_2 at −50°C for 20 min the clear yellow solution showed a strong and broad IR absorption at 1899 cm^{-1}, which disappeared on addition of MeCN.

5-Ethyl-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Tetrachloroaluminate (**6c**):

From **2a** (8.58 g, 30 mmol) and EtCN (1.98 g, 36 mmol) as described for **6b**. Yield: 11.90 g (84%) of a colorless powder: mp 146–148°C. Reprecipitation from MeCN (15 mL)/Et_2O (80 mL) afforded colorless crystals.

5-Isopropyl-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**6d**):

From **2a** (2.86 g, 10 mmol) and *i*-PrCN (0.83 g, 12 mmol). Precipitation with Et_2O afforded a colorless powder (6.40 g, 98%). Crystallization at −20°C from MeCN (35 mL) gave a colorless powder (5.89 g); mp 259–262°C (dec).

5-tert-Butyl-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**6e**):

From **2a** (2.86, 10 mmol) and *t*-BuCN (1.00 g, 12 mmol). Precipitation with Et_2O gave a colorless crystalline powder (6.08 g, 91%). Recrystallization from CH_2Cl_2 (32 mL)/Et_2O (12 mL) gave colorless leaflets (4.81 g); mp 208–214°C (dec).

2,3-Dimethyl-5-phenyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**6f**):

From **2a** (8.58 g, 30 mmol) and benzonitrile (1.24 g, 12 mmol). Yield: 6.48 g (94%) of a colorless powder, which can be crystallized at −20°C from MeCN (6 mL) to give colorless needles; mp 222–225°C.

5-(Cyanomethyl)-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**6g**):

From **2a** (1.43 g, 5 mmol) and $CH_2(CN)_2$ (3.30 g, 50 mmol). Evaporation of the solvent and precipitation of the residue from MeCN (10 mL)/Et_2O (60 mL) gave a colorless powder (1.32 g, 41%); mp 165–175°C (dec).

Bis[2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium-5-yl]-methane Bis(hexachloroantimonate) (**6h**):

From **2a** (2.86 g, 10 mmol) and $CH_2(CN)_2$ (0.33 g, 5 mmol). Evaporation of the solvent and precipitation of the brown residue from acetone (10 mL)/Et_2O (60 mL) afforded a pale yellow powder (5.95 g, 96%); mp 144–152°C (dec).

5-(Dimethylamino)-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**6i**):

From **2a** (8.58 g, 30 mmol) and Me_2NCN (0.84 g, 12 mmol). Evaporation of the solvent and precipitation of the residue from CH_2Cl_2 (20 mL)/Et_2O (30 mL) afforded pale yellow needles (4.98 g, 76%), which could be recrystallized at −20°C from CH_2Cl_2 (8 mL)/Et_2O (5 mL) to furnish orange needles; mp 201–204°C.

2,3-Dimethyl-5-methylthio-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**6j**):

From **2a** (2.86 g, 10 mmol) and MeSCN (0.88 g, 12 mmol). Precipitation with Et_2O gave a colorless powder (6.24 g, 95%). Crystallization of 1.0 g at −20°C from MeCN (6 mL)/Et_2O (12 mL) afforded colorless needles (0.5 g); mp 235–240°C (dec).

2-Ethyl-3,5-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**6k**):

From **2k** (3.00 g, 10 mmol) and MeCN (0.50 g, 12 mmol). Precipitation with Et_2O afforded a colorless powder (6.32 g, 99%), which could be reprecipitated from MeCN (20 mL)/Et_2O (160 mL); mp 218–220°C.

2-Isopropyl-3,5-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**6l**):

From **21** (3.14 g, 10 mmol) and MeCN (0.50 g, 12 mmol). Precipitation with Et_2O gave a colorless powder (3.79 g, 58%), which could be crystallized at −20°C from MeCN (15 mL)/Et_2O (15 mL) to afford colorless prisms; mp 204–206°C.

3-Ethyl-5-methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate **(6m)**:

From **2m** (2.86 g, 10 mmol) and MeCN (0.50 g, 12 mmol). Precipitation with Et_2O gave a colorless powder (6.02 g, 96%), which crystallized from CH_2Cl_2 (10 mL)/pentane (50 mL) affording brownish crystals; mp 167–169 °C.

6,7,8,9-Tetrahydro-2-methyl-3-(2,4,6-trichlorophenyl)-5H-[1,2,4]triazolo[5,1-a]azepinium Hexachloroantimonate **(6n)**:

From **2n** (3.26 g, 10 mmol) and MeCN (0.50 g, 12 mmol). Precipitation with Et_2O yielded a colorless powder (6.54 g, 98%); mp 230–233 °C. Slow crystallization at −20 °C from MeCN (1 g in 10 mL) afforded colorless prisms suitable for an X-ray diffraction analysis.

2-Ethyl-6,7,8,9-hexahydro-3-(2,4,6-trichlorophenyl)-5H-[1,2,4]triazolo[5,1-a]azepinium Hexachloroantimonate **(6o)**:

From **2n** (3.26 g, 10 mmol) and EtCN (0.66 g, 12 mmol). Precipitation with Et_2O provided a pale brown powder (6.50 g, 96%), which was crystallized at −20 °C from MeCN (35 mL) affording pale brown crystals; mp 208–213 °C (dec).

6,7,8,9-Tetrahydro-2-phenyl-3-(2,4,6-trichlorophenyl)-5H-[1,2,4]triazolo[5,1-a]azepinium Hexachloroantimonate **(6p)**.

From **2n** (3.26 g, 10 mmol) and PhCN (1.24 g, 12 mmol). Precipitation with Et_2O furnishes a colorless powder (7.12 g, 98%); mp 209–212 °C.

7-tert-Butyl-6,7,8,9-tetrahydro-2-methyl-3-(2,4,6-trichlorophenyl)-5H-[1,2,4]triazolo[5,1-a]azepinium Hexachloroantimonate **(6q)**:

From **2q** (3.82 g, 10 mmol) and MeCN (0.50 g, 12 mmol). Precipitation with Et_2O gave a colorless powder (6.54 g, 91%), which could be crystallized at −20 °C from MeCN (30 mL) affording colorless prisms; mp 234–238 °C.

6,7,8,9-Tetrahydro-2,6,6,8,8-pentamethyl-3-(2,4,6-trichlorophenyl)-5H-[1,2,4]triazolo[5,1-a]azepinium Hexachloroantimonate **(6r)**:

From **2r** (3.82 g, 10 mmol) and MeCN (0.50 g, 12 mmol). Precipitation with Et_2O afforded colorless fine needles (6.40 g, 89%), which were recrystallized from MeCN (25 mL) to give colorless prisms (5.50 g); mp 215–218 °C.

2-Methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolo[2,3-a]-1-azoniacyclotridec-1-ene Hexachloroantimonate **(6s)**:

From **2s** (4.10 g, 10 mmol) and MeCN (0.50 g, 12 mmol). Yield: 6.68 g (89%) of a colorless powder, which could be crystallized at −20 °C from MeCN (10 mL per g) to afford colorless needles; mp 223–224 °C.

2-Methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolo[2.3-b]tricyclo[4.3.1^{1,6}.1^{4,8}]-2-azoniaundec-2-ene Hexachloroantimonate **(6t)**:

From **2t** (3.78 g, 10 mmol) and MeCN (0.50 g, 12 mmol). Precipitation with Et_2O gave a colorless powder (5.82 g, 81%), which was crystallized at −20 °C from MeCN (20 mL) affording colorless prisms; mp 217–219 °C.

1-(4-Chlorophenyl)-2,3,5-trimethyl-1H-1,2,4-triazolium Hexachloroantimonate **(6u)**:

From **2u** (2.17 g, 10 mmol) and MeCN (0.50 g, 12 mmol). Precipitation with Et_2O afforded a yellow powder, which according to the ^1H NMR spectrum (CD_3CN) was a 4:1 mixture of **5u** and **6u**. The product was dissolved in MeCN (20 mL). The solution was boiled under reflux for 1 h. Evaporation of the solvent and precipitation of the residue from MeCN (6 mL)/Et_2O (60 mL) furnished colorless leaflets (3.76 g, 68%); mp 157–160 °C.

1-Isopropyl-3,5-dimethyl-1H-1,2,4-triazolium Hexachloroantimonate **(6y)**:

From **2w** (1.91 g, 10 mmol) and MeCN (0.50 g, 12 mmol). Evaporaton of the solvent gave a red oil, which crystallized at −20 °C after addition of Et_2O (20 mL) to afford pale brown prisms (3.84 g, 81%); mp 129–132 °C. According to the ^1H NMR spectrum (CD_3CN) the compound was contaminated with about 5% of a compound, which we were not able to separate.

3-Phenyl-1-(2,4,6-trichlorophenyl)indazolium Hexachloroantimonate (7):

$SbCl_5$ (1.50 g, 5 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a cold (−30 °C) solution of **2x** (2.05 g, 5 mmol) in CH_2Cl_2 (10 mL). After stirring at 0 °C for 1 h a yellow powder (3.30 g, 93%) was filtered off, which was dissolved in boiling CH_2Cl_2 (20 mL)/MeCN (7 mL). Cooling to −20 °C and slow addition of pentane (70 mL) afforded a pale yellow powder; mp 217–218 °C (dec).

1-Isopropyl-3,5-dimethyl-1*H*-1,2,4-triazole (9):

NaOH (16.00 g, 400 mmol) in H_2O (200 mL) was added to a cold (0 °C) solution of **6y** (23.74 g, 50 mmol) in CH_2Cl_2 (200 mL). After shaking for 5 min the organic layer was separated. The aqueous layer was repeatedly extracted with CH_2Cl_2. Workup of the combined organic extracts and distillation of the crude product afforded a colorless oil (5.65 g, 81%); bp 102–103 °C/14 Torr.

3-Ethyl-5-methyl-1-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazole (10):

A mixture of NaOH (1.60 g, 40 mmol) in H_2O (10 mL) and **6m** (3.13 g, 5 mmol) in MeCN (20 mL) was stirred for 10 min. After addition of H_2O (30 mL) the mixture was extracted with $CHCl_3$ (3 × 50 mL). Workup gave a red solid (1.33 g, 92%), which was dissolved in boiling EtOH (3 mL). At −20 °C colorless prisms were formed (1.09 g, 75%); mp 91–92 °C.

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