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Cycloadditions of 1-Aza-2-azoniaallene Salts Derived from Coumarin and Camphor

Nasser A. Hassan, Tahia K. Mohamed, and Omaima M. Abdel Hafez

Dokki, Cairo, A. R. Egypt, National Research Centre, Department of Photochemistry and Natural Products

Martin Lutz, Christoph C. Karl, Wolfgang Wirschun, Yaseen A. Al-Soud, and Johannes C. Jochims

Konstanz, Fakultät für Chemie der Universität

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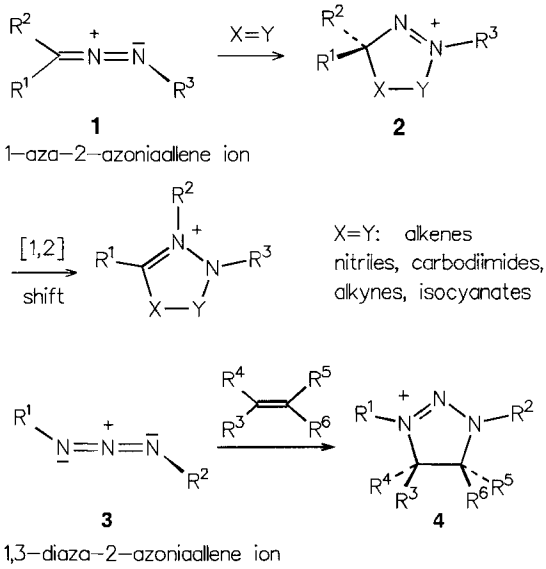
Abstract. The 1-aza-2-azoniaallene salt **8** prepared from 3-acetyl coumarin *via* the hydrazone **6** and the (chloroalkyl)azo derivative **7** reacts with nitriles to afford the 3-(3-chromenyl)-1,2,4-triazolium salts **11a–d**. With diisopropylcarbodiimide the triazolium salt **13** and with norbornene a tricyclic pyrazolium salt **14** are obtained. Concurrent to these cycloadditions the by-product **12** is formed by intramolecular cyclization of the cumulene **8**. Similarly, the intramolecular cyclization product **18** is isolated as the sole product when the 1-aza-2-azoniaallene salt **17a** (prepared from the ethyl carbazone of camphor by chlorination and treatment of the product **16a** with $SbCl_5$) was treated with nitriles, carbodiimides or alkenes. In contrast, 1,2,4-triazolium salts **20a–c**, **23c**, respectively pyrazolium salts **20d–f**, and 1,3,4-thiadiazolium salts **23a,b** are obtained by reaction of the 1-aza-2-azoniaallene salt **17b** with nitriles, respectively alkenes, alkynes, diisopropylcarbodiimide, and isothiocyanates. The constitutions of two of these products (**20e**, **23a**) were secured by X-ray structural analysis.

The novel heterocumulenes 1-aza-2-azoniaallene salts **1** and 1,3-diaza-2-azoniaallene salts **3**, readily prepared as reactive intermediates from hydrazones, respectively from 1,3-disubstituted triazenes, have been shown to undergo cycloaddition to many types of multiple bonds [1–9]. Thus, compounds **1** react with nitriles [1, 3, 6, 7], isocyanates [5], carbodiimides [2], as well as with electron-rich alkenes and alkynes [3, 4, 7] to give pyrazolium derivatives **2**, which frequently undergo successive transformations. In contrast, cumulenes **3** neither react with nitriles, nor with isocyanates. However, especially smooth reactions were observed with both electron-rich and electron-deficient alkenes affording 4,5-dihydro-1,2,3-triazolium salts **4** [8, 9]. So far only salts **1**, **3** with simple substituents, such as methyl, phenyl *etc.* were used as reactants for cycloadditions with conventional unsaturated compounds (acetonitrile, cyclopentene, 3-hexyne *etc.*). It seemed of interest to study the applicability of the cycloaddition protocol for heterocumulenes **1**, **3** derived from natural products with more sophisticated unsaturated reactants. Recently, we reported preparations of *C*- and *N*-glycosides by cycloaddition of **1**, **3** to glycosyl nitriles and a glucosyl alkyne [10]. In this communication we describe cycloadditions

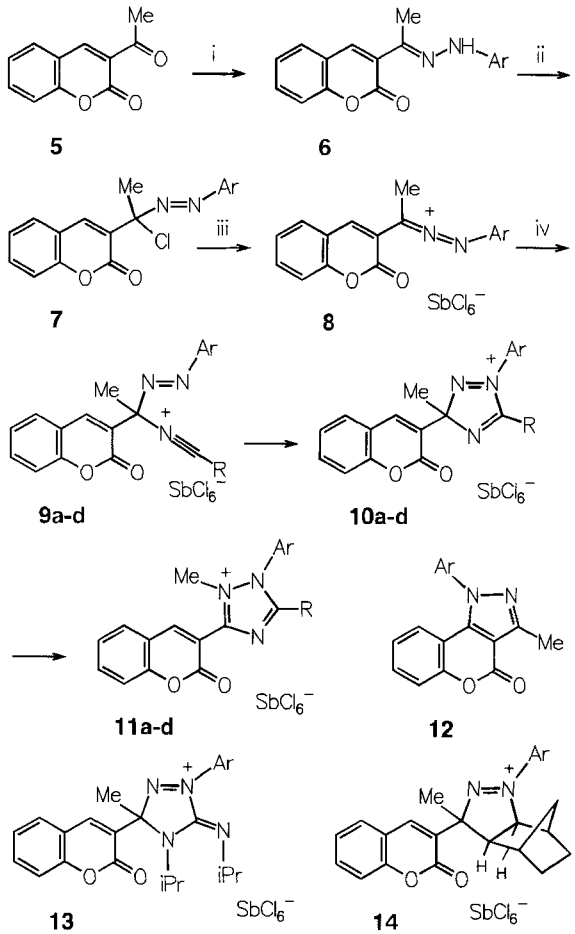


Scheme 1

of heterocumulenes **1** derived from 3-acetyl coumarin **5** and from camphor.

The hydrazone **6** prepared from 3-acetyl coumarin **5** was oxidized to the (chloroalkyl)azo compound **7** with *tert*-butyl hypochlorite (Scheme 2) [11–13]. Treatment of **7** at –60 °C with antimony pentachloride in dichloromethane afforded an orange precipitate **8**. On addition of acetonitrile and warming up to room temperature the precipitate dissolved and the color of the reaction mixture changed to brown. Workup afforded the *1H*-triazolium salt **11a** in 71% yield together with a small amount (8%) of the pyrazole **12**. Arguments have been put forward according to which formation of triazolium salts such as **11a** proceeds *via* nitrilium salts as intermediates (*e.g.* **9a**) undergoing cyclization to *3H*-triazolium salts (**10a**) [1, 3]. Wagner–Meerwein type [1, 2] shift of a methyl group completes the reaction sequence furnishing *1H*-triazolium salts (*e.g.* **11a**) [14–18]. Correspondingly, with pivalonitrile, dimethylcyanamide, and methyl thiocyanate the salts **11b–d** were obtained (46–90%). In all cases small amounts of **12** were formed as by-products indicating a concurrent intramolecular reaction of **8**, in which the azo group substitutes the proton in position 4. Compound **12** was obtained in 86% yield when the chloro compound **7** was treated with antimony pentachloride in the absence of a nitrile.

A clean reaction took place between **8** and diisopropylcarbodiimide to afford the iminium salt **13** in 87% yield. The ^{1}H NMR spectrum (in CD_3CN) of the crude product showed the presence of two isopropyl groups with diastereotopic methyl groups (doublets for CH_3 at 1.17, 1.29, 1.79, 1.81 ppm coupled to septets for CH at 3.41 and 4.97 ppm). A singlet for a C-methyl group was found at 3.00 ppm. Recrystallization at 23 °C from dichloromethane/ether afforded a clean product, however, with a quite different ^{1}H NMR spectrum again showing diastereotopic isopropyl methyl groups and one C-methyl group but no signal for *N*-methyl (doublets for CH_3 at 0.92, 0.89, 1.69, 1.70, septets for CH at 3.13 and 4.71 ppm, singlet for C–CH_3 at 2.66 ppm). According to these spectra, the ^{13}C NMR spectra and the elemental analyses the products must be assigned the structures of geometrically isomeric *3H*-1,2,4-triazolium salts **13**. Thus, in contrast to earlier results [2], the *3H*-triazolium salt **13** does not rearrange to a *1H*-triazolium salt by migration of the methyl group from carbon to nitrogen. The reaction of 1-aza-2-azoniaallene salts with carbodiimides was shown [2] to be most likely a two-step process with a cyanamidium salt as intermediate, which closes the ring stereoelectronically controlled [19, 20] in such a way that in the product the imine isopropyl group and the *N*-aryl group are *cis* oriented with respect to each other. Obviously, in the case of **13** recrystallization, even under mild conditions, effects isomerization of the primarily formed *cis* product to the more stable *trans* isomer shown in Scheme 2.



Scheme 2 Reagents and conditions: Ar = 2,4,6-$Cl_3C_6H_2$; i, $ArNHNH_2$, EtOH, AcOH, 1 h reflux, 87%; ii, *t*BuOCl, $CHCl_3$, –20 °C, 3 h, 88%; iii, $SbCl_5$, CH_2Cl_2, –60 °C; iv, RCN, – 60 °C to 23 °C, 3 h; **a**: R = Me, 71%; **b**: R = *t*Bu, 50%; **c**: R = Me_2N, 90%; **d**: R = SMe, 46%.

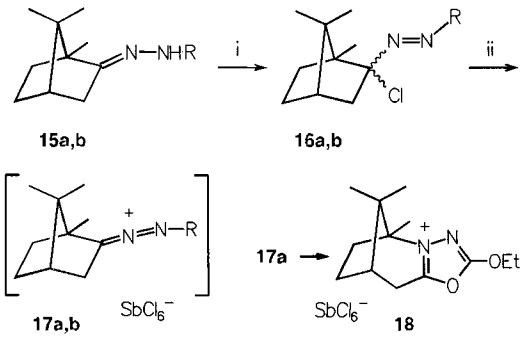
Reaction of **8** with phenyl isocyanate, cyclohexyl isothiocyanate, phenylacetylene, 1-hexyne or 3-hexyne unisonously afforded the product **12** of an intramolecular cyclization and no traces (NMR) of the expected cycloaddition products. In conclusion, compared to reactions with nitriles and carbodiimides cycloadditions of isocyanates, isothiocyanates and acetylenes to **8** are too slow to compete successfully with intramolecular cyclization to furnish **12**.

Similarly, only **12** was isolated when **8** was treated with methylene cyclopentane, 2-methyl-but-2-ene, with vinyl or allyl chloride. However, with the strained alkene norbornene the cycloadduct **14** was obtained as a mixture of the diastereomers (ca 2:1) in 92% yield. In the ^{1}H NMR spectrum (in CD_3CN) only signals for C-methyl groups (2.10 and 2.31 ppm) were observed in agreement with the *3H*-pyrazolium structure shown.

Resonances for the atoms H-5 of the pyrazolium rings appeared as sharp doublets at 6.10 ppm (J = 6.9 Hz), respectively 6.53 ppm (J = 7.9 Hz) indicating *cis* relationship to atoms H-4. In the ^{13}C NMR spectrum four signals between 95 and 101 ppm for saturated carbon atoms were assigned to C-3 and C-5 of the pyrazolium rings.

In conclusion, in concert with earlier observations, the rate of reactions of 1-aza-2-azoniaallene cations such as **8** with multiple bonds decreases in the order: nitriles ≈ carbodiimides ≈ strained alkenes >> unstrained alkenes, alkynes, isocyanates, isothiocyanates.

No difficulties were encountered in the preparation of the camphor hydrazones **15a,b** [21]. Chlorination with *tert*-butyl hypochlorite afforded the rather sensitive (chloroalkyl)azo compounds **16a,b** as mixtures of the diastereomers. With antimony pentachloride **16a** was transformed into colorless crystals, which according to the elemental analysis and the spectra were the oxadiazolium salt **18** (62%). In the IR spectrum (CH_2Cl_2) two strong bands at 1598 and 1661 cm^{-1} were assigned to C=N. No absorption between 1690 and 1740 cm^{-1} for urethane or around 1900 cm^{-1} for a 1-aza-2-azoniaallene salt were observed. In the ^{13}C NMR spectrum (in CD_3CN) two signals at 162.4 and 165.4 ppm assignable to C=N and two signals at 64.6 and 79.4 ppm arising from OCH_2 and C1 as well as nine resonances for saturated carbon atoms between 13 and 47 ppm are in concert with structure **18**. The ^1H NMR spectrum (in CD_3CN) showed three singlets for methyl groups and signals for an *O*-ethyl group. Compound **18** must have been formed from the heteroallene **17a**. Attempts to achieve cycloadditions of **17a** with nitriles, alkenes, alkynes *etc.* failed. In all cases only **18** was isolated.



Scheme 3 Reagents and conditions: **a**: R = COOEt; **b**: R = 2,4,6-$Cl_3C_6H_2$; i, *t*BuOCl, $CHCl_3$, –20 °C, 3 h, 92 and 99%; ii, $SbCl_5$, CH_2Cl_2, –60 °C.

In contrast, allene **17b**, prepared as reactive intermediate from **16b** with antimony pentachloride, reacted readily with nitriles, alkenes, alkynes, carbodiimides, and isothiocyanates to afford products **20a–f**, **23a–c** (Scheme 4).

With acetonitrile, dimethylcyanamide and methyl thiocyanate the cycloadducts **20a–c** were isolated (67–90%). With isobutene, respectively norbornene, the dihydropyrazolium salts **20d,e** were obtained (42,96%), and phenylacetylene afforded the pyrazolium salt **20f** in 53% isolated yield. Similar to the formation of **11a–d**, compounds **20a–f** must have been formed *via* intermediates **19**. Wagner–Meerwein type [1, 2] shift of the tertiary alkyl substituent on C-3 of the triazolium ring furnished **20a–f** (Scheme 4).

The structures of compounds **20a–f** follow from their elemental analyses and the ^1H and ^{13}C NMR spectra. However, the stereochemistry of **20e** could not be derived unambiguously from the NMR spectra. Therefore, **20e** was submitted to X-ray structural analysis (see below) confirming the configuration shown in Scheme 4. A different course took the reactions of **17b** with cyclohexyl and benzyl isothiocyanate as well as with di-*iso*propylcarbodiimide. In these cases the ß-campholeno derivatives **23a–c** (54–90%) were obtained. Reactions of 1-aza-2-azoniaallene cations with isothiocyanates have not been reported so far. Reaction of the isothiocyanates could have occurred either across the C=N double bond giving 1,2,4-triazolium salts or across the C=S double bond affording 1,3,4-thiadiazolium salts **23a,b**. Since we found it difficult to discriminate between these alternatives by NMR spectroscopy, X-ray structural analysis was carried out for **23a** (see below) confirming the thiadiazole structure shown.

To explain the formation of **23a–c** fragmentation of the primary cycloadduct **19** is assumed to give the tertiary carbenium ion **21**.

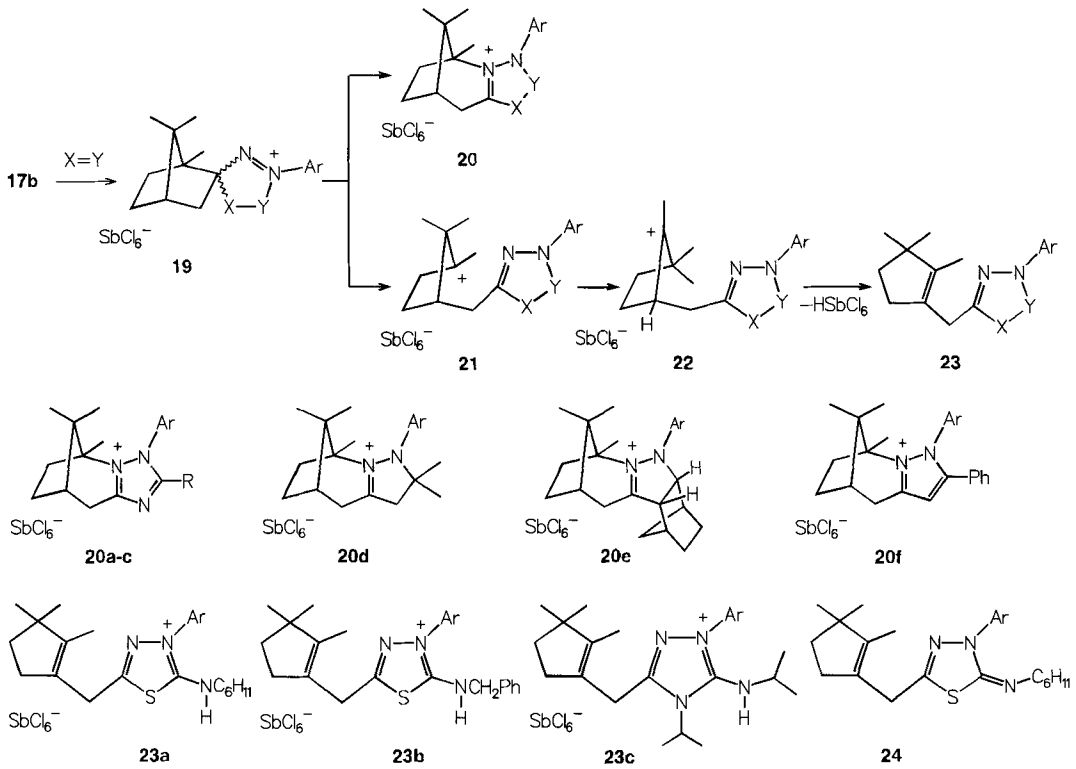
Wagner–Meerwein rearrangement of a methyl group followed by loss of a proton then furnishes the ß-campholene products **23**, which after reprotonation afford the salts **23a–c**.

From **23a** the free base **24** was prepared under mild conditions (82%).

The ^{13}C NMR data for the thiadiazole ring of **24** (C=N 149.7 and 152.0 ppm in $CDCl_3$) are very similar to data reported by L'abbé and coworkers for other 2,3-dihydro-2-imino-1,3,4-thiadiazoles [22, 23].

Fig.1,2 show ORTEP plots for the structures of the cations **20e** and **23a** as determined by X-ray crystallographic analysis [24]. Selected bond lengths, bond angles and torsional angles are given in Tables 1,2.

The asymmetric unit of the crystal **20e** consists of two independent molecules with rather similar structural data. In Table 1 structural data for only one of the cations are collected. A peculiarity is the long b-axis of 3671 pm of the monoclinic crystal (space group $P2_1$). With Mo-K_α radiation the distances between the reflections along the b-axis became rather small. Only after putting into the calculations a fragment $SbCl_3$ of known geometry a solution of the crystal structure by the Pat-



Scheme 4 **20a:** R = Me, 72%; **20b**: R = Me_2N, 90%; **20c**: R = MeS, 67%; **20d**: 42%; **20e**: 96%; **20f**: 53%; **23a**: 54%; **23b**: 68%; **23c**: 90%; **24**: 82%.

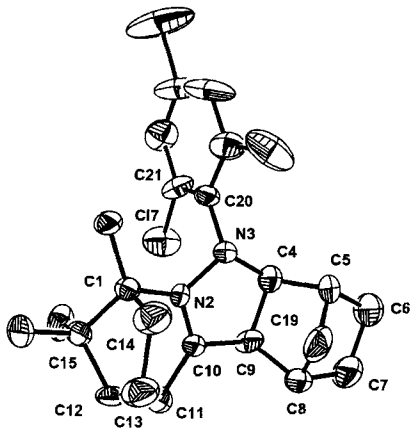


Fig. 1 ORTEP Plot of the cation **20e**

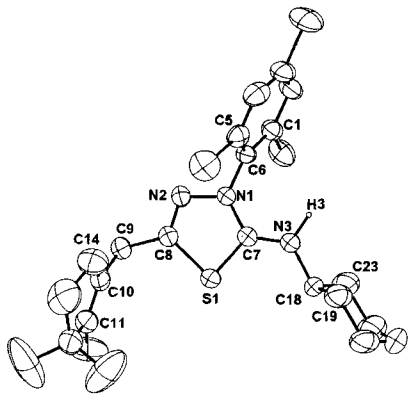


Fig. 2 ORTEP Plot of the cation **23a**

Tab. 1 Selected bond lengths (pm), bond angles (deg), and torsional angles (deg) of the cation **20e** [24]

N2-N3	143(1)	N2-N3-C20	116.9(8)	N2-C10-C9-C8	115(1)
N3-C4	150(2)	C4-C9-C10	103.7(9)	N2-N3-C4-C5	–112(1)
C4-C9	155(2)	C9-C10-N2	112(1)	N2-N3-C20-C21	–58(2)
C9-C10	148(2)	C10-N2-N3	112.8(9)	N2-N3-C4-C9	–4(1)
C10-N2	129(1)	C1-N2-N3	122.6(8)	N3-C4-C5-C6	–175(1)
N2-C1	155(1)	N2-N3-C20	116.9(8)	N3-C4-C5-C19	76(1)
N3-C20	143(1)	C15-C1-N2-N3	163(1)	N3-C4-C9-C10	1(1)
N2-N3-C4	107.0(8)	C14-C1-N2-N3	–87(1	C20-N3-C4-C5	117(1)
N3-C4-C9	104.2(9)	C1-N2-N3-C4	169(1)	C4-C9-C10-N2	3(1)

Tab. 2 Selected bond lengths (pm), bond angles (deg), and torsional angles (deg) of the cation **23a** [24]

S1-C7	172.2(3)	N2-C8-S1	115.2(3	N2-C8-S1-C7	–0.9(3)
C7-N1	133.5(4)	C8-S1-C7	88.3(2)	C8-S1-C7-N1	0.2(3)
N1-N2	138.5(4)	S1-C8-C9	121.0(3)	C8-S1-C7-N3	–179.8(3)
N2-C8	128.1(4)	S1-C7-N3	125.6(3)	C8-C9-C10-C11	–115.4(4)
C8-S1	175.2(4)	C7-N3-C18	124.1(3)	S1-C7-N3-C18	3.9(6)
C7-N3	131.1(4)	C7-N1-C6	125.8(3)	S1-C7-N1-C6	179.8(3)
S1-C7-N1	109.9(2)	S1-C7-N1-N2	0.4(4)	C7-N1-C6-C1	80.0(4)
C7-N1-N2	116.7(3)	C7-N1-N2-C8	–1.0(4)	C7-N3-C18-C19	–130.0(4)
N1-N2-C8	109.8(3)	N1-N2-C8-S1	1.2(4)	S1-C8-C9-C10	64.0(4)

terson method became possible. The structure **20e** may be compared with data for other 4,5-dihydropyrazolium cations [25–27].

The results of the crystal structural analysis of **23a** are comparable to X-ray analytical results for other 1,3,4-thiadiazolium salts [28–31]. The narrow angle C7-S1-C8 of 88.3(2)° is not exceptional.

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Experimental

All solvents were dried by standard methods. The experiments were carried out with exclusion of moisture. The melting points are uncorrected. – ^{1}H, ^{13}C NMR: Bruker AC-250 and WM-250 spectrometers; CD_3CN; 295 *K*; internal standard TMS; δ in ppm. – IR: Perkin-Elmer FTIR 1600 spectrometer; cm^{-1}. – br: broad, d: doublet; dd: doublet of doublets; m: multiplet; sh: shoulder.

X-Ray Diffraction Analysis of Compound 20e [24]

$[C_{23}H_{28}Cl_3N_2]^+ SbCl_6^-$, crystal size 0.1 × 0.2 × 0.2 mm^3, monoclinic, space group $P2_1$, $Z = 4$, $\alpha = 808.1(4)$, $b = 3670.9(3)$, $c = 1015.6(4)$ pm, $\beta = 93.11(2)$, $V = 3008(2) \times 10^6$ pm^3, $d_{calc} = 1.71$ M g m^{-3}, $T = 233$ K, $\mu_{Mo\text{-}K\alpha} = 17.34$ cm^{-1}, ω-scan, $2.01 \leq 2\Theta \leq 27.02°$, 7107 collected reflections, 6649 independent reflections, 5401 observed reflections [$I > 2\sigma(I)$]. The cell constants and the intensities of the reflections were measured on a Siemens P4 diffractometer with a graphite monochromator, $\lambda_{Mo\text{-}K\alpha} = 71.069$ pm. The structure was solved by the Patterson method with subsequent difference-Fourier synthesis (DIRDIF-96) and refined using the program SHELXL-93. The hydrogen atoms were fixed on calculated positions [d (C-H) = 0.96–0.98 pm] (riding model; refinement together with the attached C atoms). The anisotropic refinement of all other atoms (full-matrix least-squares on F^2) led to agreement factors $R(F) = 0.053$ [$I > 2\sigma(I)$], $R_w(F^2) = 0.078$ (all reflections).

X-Ray Diffraction Analysis of Compound 23a [24]

$[C_{23}H_{29}Cl_3N_3S]^+ SbCl_6^- \cdot CH_3CN$, crystal size 0.5 × 0.4 × 0.3 mm^3, triclinic, space group P-1, $Z = 2$, $a = 1248.1(4)$, $b = 1270.4(5)$, $c = 1385.2(4)$ pm, $\alpha = 100.55(3)$, $\beta = 106.41(2)$, $\gamma = 114.21(3)°$, $V = 1806(1) \times 10^6$ pm^3, $d_{calc} = 1.58$ M g m^{-3}, $T = 253$ K, $\mu_{Mo\text{-}K\alpha} = 15.11$ cm^{-1}, ω-scan, $2.02 \leq 2\Theta \leq 27.00°$, 8033 collected reflections, 7677 independent reflections, 6583 observed reflections [$I > 2\sigma(I)$]. The cell constants and the intensities of the reflections were measured on a Siemens P4 diffractometer with a graphite monochromator, $\lambda_{Mo\text{-}K\alpha} = 71.069$ pm. The structure was solved by the Patterson method (DIRDIF-96) with subsequent difference-Fourier synthesis using the program SHELXL-93. The positions of nine hydrogen atoms were fixed on calculated positions [d (C-H) = 0.95 pm]. The other hydrogen atoms were found by difference-Fourier synthesis. The anisotropic refinement of all other atoms (full-matrix least-squares on F^2) led to agreement factors $R_1 = 0.045$ [$I > 2\sigma(I)$], $R_2 = 0.053$ (all reflections).

3-Acetylcoumarin (2,4,6-Trichlorophenyl)hydrazone (**6**)

A mixture of 3-acetyl coumarin (18.82 g, 100 mmol) and (2,4,6-trichlorophenyl)-hydrazine (21.15 g, 100 mmol) in EtOH (100 ml) and AcOH (2 ml) was heated under reflux for 1 h. Cooling, filtration and recrystallization of the residue from MeCN (60 ml) afforded a yellow crystalline powder (33.00 g, 87%); *m.p.* 154–156 °C. – IR (CCl_4) ν/cm^{-1} = 1668, 1736. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.37 (CH_3), 7.35 (trichlorophenyl), 7.25–7.56 (m), 8.07 (H-4), 7.42 (NH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.2 (CH_3), 116.4, 119.3, 124.6, 126.8, 128.3, 128.6, 128.9, 131.8, 137.7, 140.6, 145.5, 153.9, 160.2 (C=).

$C_{17}H_{11}Cl_3N_2O_2$	calcd.:	C 53.50	H 2.91	N 7.34
(381.6)	found:	C 53.49	H 2.92	N 7.32.

[1-Chloro-1-(2-oxo-2H-chromen-3-yl)ethyl]azo(2,4,6-trichlorobenzene) (**7**)

In the dark, *t*-BuOCl [32] (1.63 g, 15 mmol) was added dropwise to a cold (–20 °C) solution of **6** (3.81 g, 10 mmol) in $CHCl_3$ (30 ml). After stirring at 0 °C for 3 h the solvent was evaporated and the residue was crystallized at –15 °C from $CHCl_3$ (8 ml) to afford a yellow powder (3.66 g, 88%); *m.p.* 159–161 °C. – IR (KBr): ν/cm^{-1} = 1731. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.41 (CH_3), 7.40 (trichlorophenyl), 7.27–7.61(m), 8.10 (aryl). – ^{13}C NMR ($CDCl_3$): δ/ppm =27.8 (CH_3), 92.3 (CCl), 116.5, 118.2, 124.7, 127.4, 127.8, 128.8, 129.1, 132.6, 134.2, 141.4, 145.3, 153.9, 157.7(C=).

$C_{17}H_{10}Cl_4N_2O_2$	calcd.:	C 49.07	H 2.42	N 6.73
(416.1)	found:	C 48.99	H 2.45	N 7.03.

2,5-Dimethyl-3-(2-oxo-2H-chromen-3-yl)-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**11a**)

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (–60 °C) solution of **7** (4.16 g,

10 mmol) and MeCN (0.41 g, 10 mmol) in CH_2Cl_2 (30 ml). After stirring at −60 °C for 1 h, then at 0 °C for 1 h, and finally at 23 °C for 1 h the solvent was evaporated. The residue was suspended in CH_2Cl_2 (10 ml). After stirring for 5 min **12** (0.53 g, 14%) was isolated by filtration. The filtrate was evaporated and the residue was stirred in $CHCl_3$ (30 ml) for 5 min. Filtration afforded a colorless powder, which was crystallized at 23 °C from CH_2Cl_2 (6 ml)/Et_2O (60 ml) to furnish a colorless powder (5.40 g, 71%); *m.p.* 273–275 °C. – IR(KBr): ν/cm^{-1} = 1608, 1721(br). – ^{1}H NMR (CD_3CN): δ/ppm = 2.62, 3.84 (CH_3), 7.97 (trichlorophenyl), 7.49–7.95 (m), 8.75 (aryl). – ^{13}C NMR (CD_3CN): δ/ppm = 13.6, 37.9 (CH_3), 113.5, 117.8, 118.2, 119.0, 124.1, 126.7, 131.5, 131.8, 136.8, 142.7, 152.8, 156.1, 156.8, 158.1, 162.1 (C=).

$C_{19}H_{13}Cl_9N_3O_2Sb$	calcd.:	C 30.18	H 1.73 N 5.56
(756.2)	found:	C 30.10	H 1.68 N 5.44.

5-tert-Butyl-2-methyl-3-(2-oxo-2H-chromen-3-yl)-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**11b**)

From Me_3CCN (0.83 g, 10 mmol) in the manner described for **11a**. After evaporation of the solvent the residue (3:1 mixture of **11b** and **12**) was stirred in CH_2Cl_2 (20 ml) for 5 min. Filtration, evaporation of the filtrate and stirring of the residue in $CHCl_3$ (20 ml) for 5 min afforded a pale brown powder (**11b**, 3.98 g, 50%); *m.p.* 245–247 °C. – IR (KBr): ν/cm^{-1} = 1610, 1721(br). – ^{1}H NMR (CD_3CN): δ/ppm = 1.40 (9H), 3.70 (CH_3), 7.96 (trichlorophenyl), 7.49–7.95 (m's, aryl), 8.78 (H-4). – ^{13}C NMR (CD_3CN): δ/ppm = 28.9 (3C), 36.8, 37.3 (CH_3,C), 113.8, 117.9, 119.1, 126.6, 126.8, 131.5, 132.1, 136.9, 137.1, 142.8, 153.0, 156.2, 156.3, 158.3, 171.1 (C=).

$C_{22}H_{19}Cl_9N_3O_2Sb$	calcd.:	C 33.10	H 2.40 N 5.26
(798.2)	found:	C 32.95	H 2.41 N 5.38.

2-Methyl-5-(dimethylamino)-3-(2-oxo-2H-chromen-3-yl)-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**11c**)

From Me_2NCN (0.70 g, 10 mmol) in the manner described for **11a**. Evaporation of the solvent and precipitation of the residue from CH_2Cl_2 (10 ml)/Et_2O (100 ml) and reprecipitation at −15 °C from CH_2Cl_2 (10 ml)/Et_2O (100 ml) afforded a yellow powder (7.07 g, 90%); *m.p.* 156–158 °C. – IR (CH_2Cl_2): ν/cm^{-1} = 1611, 1655, 1731. – ^{1}H NMR (CD_3CN): δ/ppm = 3.07 (6H), 3.50 (CH_3), 7.88 (trichlorophenyl), 7.47–7.91(m's, aryl), 8.66 (H-4). – ^{13}C NMR (CD_3CN): δ/ppm = 36.1, 40.2 (2C) (CH_3), 114.3, 117.8, 119.1, 126.6, 126.9, 131.3, 131.6, 136.5, 138.3, 141.7, 152.2, 156.2, 157.4, 158.2, 160.1 (C=).

$C_{20}H_{16}Cl_9N_4O_2Sb$	calcd.:	C 30.59	H 2.05 N 7.14
(785.2)	found:	C 30.81	H 2.13 N 7.31.

2-Methyl-5-(methylthio)-3-(2-oxo-2H-chromen-3-yl)-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**11d**)

From MeSCN (0.73 g, 10 mmol) in the manner described for **11a**. Some **12** crystallized form the reaction mixture and was removed by filtration. Et_2O (100 ml) was added to the filtrate. At −15 °C a yellow powder (**11d**, 3.61 g, 46%) crystallized, which can be recrystallized from MeCN to yield yellow prisms; *m.p.* 262–264 °C. – IR(KBr): ν/cm^{-1} = 1608, 1723 (br). – ^{1}H NMR (CD_3CN, 333 *K*): δ/ppm = 2.91, 3.83 (CH_3), 7.92 (trichlorophenyl), 7.49–7.94 (m's, aryl), 8.81 (H-4). – ^{13}C NMR (CD_3CN, 333 *K*): δ/ppm = 14.9, 37.1 (CH_3), 112.7, 118.3, 123.2, 126.0, 130.7, 131.2, 136.1, 136.4, 142.4, 152.4, 155.6, 156.4, 157.2, 166.0 (C=).

$C_{19}H_{13}Cl_9N_3O_2SSb$	calcd.:	C 28.95	H 1.66 N 5.33
(788.2)	found:	C 28.93	H 1.67 N 5.30.

3-Methyl-1-(2,4,6-trichlorophenyl)-1H,4H-chromeno[4,3-c]pyrazol-4-one (**12**)

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (−60 °C) solution of **7** (4.16 g, 10 mmol) in CH_2Cl_2 (40 ml). After stirring at −60 °C for 1 h, then at 0 °C for 1 h, and finally at 23 °C for 1 h the solvent was evaporated, and the residue was crystallized at 23 °C from MeCN (15 ml) to afford colorless needles (3.25 g, 86%); *m.p.* 209–211 °C. – IR (KBr): ν/cm^{-1} = 1730 (br). – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.72 (CH_3), 7.63 (trichlorophenyl), 6.80–7.56 (m's, aryl). – ^{13}C NMR ($CDCl_3$): δ/ppm = 13.1 (CH_3), 106.5, 111.4, 118.2, 120.9, 124.6, 129.3, 131.6, 133.9, 135.9, 137.6, 143.3, 152.2, 153.3, 157.5 (C=).

$C_{17}H_9Cl_3N_2O_2$	calcd.:	C 53.78	H 2.39 N 7.38
(379.6)	found:	C 53.85	H 2.50 N 7.35.

4,5-Dihydro-4-isopropyl-5-(isopropylimino)-3-methyl-3-(2-oxo-2H-chromen-3-yl)-1-(2,4,6-trichlorophenyl)-3H-1,2,4-triazolium Hexachloroantimonate (**13**)

From diisopropylcarbodiimide (1.26 g, 10 mmol) in the manner described for **11a**. Evaporation of the solvent and crystallization of the residue at 23 °C from CH_2Cl_2 (20 ml)/Et_2O (100 ml) afforded a yellow powder (7.32 g, 87%); *m.p.* 184–186 °C (dec). – IR (KBr): ν/cm^{-1} = 1609, 1722, 1748. – ^{1}H NMR (CD_3CN): δ/ppm = 0.89 (d, *J*=6.1), 0.92 (d, *J*=6.1), 1.69 (d, *J*=7.0), 1.70 (d, *J*=7.0), 2.66 (CH_3), 3.13 (sept, *J*=6.1), 4.71 (sept, *J*=7.0) (CH), 7.44–7.85 (m's, aryl), 8.21 (H-4). – ^{13}C NMR (CD_3CN): δ/ppm = 13.1, 18.8, 19.2, 24.37, 24.41 (CH_3), 49.3, 53.1 (CH), 117.98, 118.02, 118.2, 126.9, 129.9, 131.3, 131.5, 131.7, 136.8, 138.1, 139.0, 140.2, 149.6, 155.4, 157.7, 163.6 (C=).

$C_{24}H_{24}Cl_9N_4O_2Sb$	calcd.:	C 34.26	H 2.88 N 6.66
(841.3)	found:	C 34.40	H 2.84 N 6.55.

5-Methyl-5-(2-oxo-2H-chromen-3-yl)-3-(2,4,6-trichlorophenyl)-4-aza-3-azoniatricyclo[5.2.1.0^{2,6}]dec-3-ene Hexachloroantimonate (**14**)

From norbornene (0.94 g, 10 mmol) in the manner described for **11a**. Precipitation at 23 °C from CH_2Cl_2 (40 ml)/Et_2O (100 ml) afforded a colorless powder (7.42 g, 92%); *m.p.* 165–167 °C (dec). – IR (KBr): ν/cm^{-1} = 1711. – ^{1}H NMR (CD_3CN): δ/ppm = ca. 2:1 mixture of the diastereomers: main component: 2.10 (CH_3), 3.13 (d, *J*=6.9, H-6), 6.10 (d, *J*=6.9, H-2), 8.01 (vinyl); minor component: 2.31 (CH_3), 2.97 (d, *J*≈7, H-6), 6.53 (d, *J*=7.8, H-2), 8.36 (vinyl). – ^{13}C NMR(CD_3CN): δ/ppm = 20.3, 25.5, 26.0, 27.7, 27.8, 29.6, 35.1, 36.8, 39.8, 41.4, 41.8, 42.9, 50.4, 52.2 (CH_3, CH_2, CH), 95.3, 98.9, 99.3, 100.9 (C-2,5), 117.3–154.8 (24 lines, C=C), 159.8, 160.5 (C=O).

$C_{24}H_{20}Cl_9N_2O_2Sb$	calcd.:	C 35.62	H 2.49 N 3.46
(809.3)	found:	C 35.95	H 2.58 N 3.81.

Ethyl Norbornylidenecarbazate (**15a**)

A mixture of camphor (1.52 g, 10 mmol) and ethyl carbazate (1.04 g, 10 mmol) in EtOH (10 ml) and AcOH (1 ml) was boiled under reflux for 9 h. Cooling to 5 °C, and filtration afforded a colorless crystalline powder (2.10 g, 88%); *m.p.* 141–143 °C. – $[\alpha]_D^{23} = -40°$; $[\alpha]_{546}^{23} = -48°$ (c = 1.0, CH_2Cl_2). – IR (CCl_4): ν/cm^{-1} = 1757, 1716, 1701. – ^1H NMR ($CDCl_3$): δ/ppm = 0.75, 0.93, 1.07, 1.30 (t, J = 7.1) (CH_3), 1.21–2.39 (m's, 7H), 4.24 (q, J = 7.1, CH_2), 7.50 (br, NH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 11.1, 14.6, 18.6, 19.6, 27.3, 32.5, 33.3, 44.0, 48.0, 52.6 (CH_3, CH_2, CH, C), 61.5 (br, OCH_2), 154.1 (br), 166.1 (C=N, C=O).

$C_{13}H_{22}N_2O_2$	calcd.: C 65.52	H 9.31	N 11.75
(238.3)	found: C 65.27	H 9.36	N 11.64.

Camphor (2,4,6-Trichlorophenyl)hydrazone (**15b**)

A mixture of camphor (15.22 g, 100 mmol), (2,4,6-trichlorophenyl) hydrazine (21.15 g, 100 mmol) in EtOH (60 ml) and conc. HCl (2 ml) was boiled under reflux for 12 h. After cooling to 5 °C H_2O (100 ml) was added. The mixture was neutralized with saturated aqueous $NaHCO_3$ solution and kept at 5 °C for 2 h. Filtration and crystallization of the residue at –15 °C from EtOH (100 ml) afforded a colorless powder (22.40 g, 65%); *m.p.* 67–68 °C. – $[\alpha]_D^{23} = +29°$; $[\alpha]_{546}^{23} = +37°$ (c = 0.5, CH_2Cl_2). – IR (CCl_4): ν/cm^{-1} = 1757, 1716, 1701. – IR (KBr): ν/cm^{-1} = 1474, 3334 (NH). – ^1H NMR ($CDCl_3$): δ/ppm = 0.79, 0.93, 1.02 (CH_3), 1.18–2.03 (m's, 6H), 2.48 (m, 1H), 6.68 (br, NH), 7.26 (aryl). – ^{13}C NMR ($CDCl_3$): δ/ppm = 11.1, 18.7, 19.5 (CH_3), 27.4, 32.4, 33.1, 44.1, 48.1, 52.5 (C-1,3-7), 126.2, 126.7, 128.6, 139.2 (aryl), 166.0 (C-1).

$C_{16}H_{19}Cl_3N_2$	calcd.: C 55.59	H 5.54	N 8.10
(345.7)	found: C 55.71	H 5.61	N 8.08.

Ethyl [2-Chloro-2-bornyl]azocarboxylate (**16a**)

From **15a** (2.38 g, 10 mmol) as described for **7** (in 10 ml of $CHCl_3$). Evaporation of the solvent afforded a yellow oil (2.71 g, 99%), which was used without further purification. – IR (CCl_4): ν/cm^{-1} = 1745, 1765. – ^1H NMR ($CDCl_3$): mixture of the diastereomers + impurities. – ^{13}C NMR ($CDCl_3$): main component: δ/ppm = 12.2, 14.1, 20.3, 21.1, 26.2, 30.5, 44.0, 46.6, 50.7, 56.3 (CH_3, CH_2, CH, C), 64.6 (OCH_2), 103.0 (CCl), 162.2 (C=O). – $C_{13}H_{21}ClN_2O_2$ (272.8).

[2-Chloro-2-bornyl]azo(2,4,6-trichlorobenzene) (**16b**)

From **15a** (3.46 g, 10 mmol) in the manner described for **7**. The yellow oily product (3.45 g, 91%) solidified at 5 °C to give an orange powder; *m.p.* 57–59 °C. – IR(KBr): ν/cm^{-1} = 1553, 1577. – ^1H NMR($CDCl_3$): δ/ppm = 2:1 mixture of the diastereomers: 0.88, 1.00, 1.05, 1.06, 1.14, 1.34 (CH_3), 7.38, 7.39 (aryl). – ^{13}C NMR($CDCl_3$): δ/ppm = 10.6, 12.4, 20.4, 21.2, 21.3, 22.4 (CH_3), 104.1, 106.0 (CCl), 126.7, 127.1, 128.8, 128.9, 133.2, 133.4, 145.9, 146.4 (aryl).

$C_{16}H_{18}Cl_4N_2$	calcd.: C 50.55	H 4.77	N 7.37
(380.1)	found: C 50.86	H 4.88	N 7.44.

4-Ethoxy-1,11,11-trimethyl-3-aza-2-azonia-5-oxatricyclo [6.2.1.0^{2,6}]undeca-2(6),3-diene Hexachloroantimonate (**18**)

From **16a** (2.73 g, 10 mmol) – with or without MeCN – in the manner described for **11a**. The product was suspended in CH_2Cl_2 (20 ml). After slow addition of Et_2O (80 ml) the mixture was kept at –15 °C for 12 h. Filtration furnished a colorless powder (3.56 g, 62%); *m.p.* 165–167 °C (dec). – $[\alpha]_D^{23} = -26°$; $[\alpha]_{546}^{23} = -29°$ (c = 1.0, CH_2Cl_2). – IR (CCl_4): ν/cm^{-1} = 1757, 1716, 1701. – IR (CH_2Cl_2): ν/cm^{-1} = 1598, 1661. – ^1H NMR (CD_3CN): δ/ppm = 1.00, 1.17, 1.52 (t, J = 7.1), 1.55 (CH_3), 1.60 (m, 1H), 2.26 (m,3H), 2.49 (m, 1H), 3.03 (dd, J = 2.0 and 20.0, 1H), 3.32 (ddd, J = 1.9 and 4.5 and 20.0, 1H), 4.69 (q, J = 7.1, OCH_2). – ^{13}C NMR (CD_3CN): δ/ppm = 13.6, 14.3, 17.1, 23.7, 27.7, 30.0, 40.2, 42.0, 46.7 (CH_3, CH_2, CH, C), 74.6, 79.4 (OCH_2, C-1), 162.4, 165.4 (C=N).

$C_{13}H_{21}Cl_6N_2O_2Sb$	calcd.: C 27.31	H 3.70	N 4.90
(571.8)	found: C 27.24	H 3.72	N 5.04.

1,4,11,11-Tetramethyl-3-(2,4,6-trichlorophenyl)-3,5-diaza-2-azoniatricyclo[6.2.1.0^{2,6}]undeca-2(6),4-diene Hexachloroantimonate (**20a**)

From **16b** (3.80 g, 10 mmol) and MeCN (0.41 g, 10 mmol) in the manner described for **11a**. Crystallization at –15 °C from CH_2Cl_2 (15 ml)/Et_2O (60 ml) afforded a colorless powder (5.19 g, 72%); *m.p.* 205–207 °C (dec). – $[\alpha]_D^{23} = -18°$; $[\alpha]_{546}^{23} = -20°$ (c = 1.0, CH_2Cl_2). – IR (KBr): ν/cm^{-1} = 1537, 1558, 1569. – ^1H NMR (CD_3CN): δ/ppm = 1.00, 1.20, 1.84, 2.73 (CH_3), 1.67 (m, 1H), 2.25–2.46 (m, 4H), 3.03 (dd, J = 18.3 and 1.9, H-7), 3.34 (ddd, J = 18.3 and 4.8 and 1.7, H-7'), 7.82 (q, J = 2.2, aryl). – ^{13}C NMR (CD_3CN): δ/ppm = 13.6, 16.5, 18.2, 24.5, 27.8, 29.6, 40.2, 41.9, 47.1 (CH_3, C-7-11), 80.1 (C-1), 129.6, 130.9, 131.0, 135.3, 135.4, 140.4 (aryl), 154.3, 155.5 (C=N).

$C_{18}H_{21}Cl_9N_3Sb$	calcd.: C 30.02	H 2.94	N 5.83
(720.2)	found: C 30.14	H 3.03	N 6.19.

4-(Dimethylamino)-1,11,11-trimethyl-3-(2,4,6-trichlorophenyl)-3,5-diaza-2-azoniatricyclo[6.2.1.0^{2,6}]undeca-2(6),4-diene Hexachloroantimonate (**20b**)

From **16b** (3.80 g, 10 mmol) and Me_2NCN (0.70 g, 10 mmol) in the manner described for **11a**. Precipitation at 23 °C from CH_2Cl_2 (15 ml)/Et_2O (60 ml) afforded a colorless powder (7.09 g, 90%); *m.p.* 156–158 °C (dec). – $[\alpha]_D^{23} = -45°$; $[\alpha]_{546}^{23} = -57°$ (c = 1.0, CH_2Cl_2). – IR (CH_2Cl_2): ν/cm^{-1} = 1569, 1611, 1654, 1731. – ^1H NMR (CD_3CN): δ/ppm = 0.95, 1.18, 1.75, 2.85 (6H) (CH_3), 1.70 (m, 1H), 2.22–2.45 (m, 4H), 2.93 (m, H-7), 3.29 (ddd, J = 18.3 and 5.2 and 2.1, H-7'), 7.79 (s, aryl). – ^{13}C NMR (CD_3CN): δ/ppm = 14.5, 18.1, 24.8, 28.2, 30.5, 38.6, 40.8, 42.6, 48.2 (CH_3, C-7-11), 79.1 (C-1), 130.8, 130.9, 131.2, 135.3, 135.7, 140.0 (aryl), 153.8, 154.8 (C=N).

$C_{19}H_{24}Cl_9N_4Sb$	calcd.: C 30.46	H 3.23	N 7.48
(749.3)	found: C 30.58	H 3.34	N 7.49.

1,11,11-Trimethyl-4-(methylthio)-3-(2,4,6-trichlorophenyl)-3,5-diaza-2-azoniatricyclo[6.2.1.0^{2,6}]undeca-2(6),4-diene Hexachloroantimonate (**20c**)

From **16b** (3.80 g, 10 mmol) and MeSCN (0.73 g, 10 mmol) in the manner described for **11a**. Crystallization at –15 °C from CH_2Cl_2 (10 ml)/CCl_4 (60 ml) and recrystallization at –15 °C from MeCN (15 ml) afforded a colorless crystalline powder (5.28 g, 67%); *m.p.* 167–169 °C (dec). – $[\alpha]_D^{23} = -21°$; $[\alpha]_{546}^{23} = -25°$ (c = 1.1, CH_2Cl_2). – IR (KBr): ν/cm^{-1} = 1555, 1563 (sh). – ^1H NMR (CD_3CN): δ/ppm = 0.99, 1.20, 2.06, 2.50 (CH_3), 1.69 (m, 1H), 2.34 (m, 4H), 3.05 (dd, J = 18.6 and 1.8, H-7), 3.39 (ddd, J = 18.6 and 4.9 and 1.5, H-7'), 7.83 (q, J = 2.2, aryl), 1.97 (MeCN). – ^{13}C NMR (CD_3CN): δ/ppm =

16.9, 18.2, 19.8, 24.6, 27.9, 30.1, 40.1, 41.6, 47.5 (CH_3, C-7-11), 82.2 (C-1), 130.9, 131.0, 131.2, 135.0, 135.3, 140.5 (aryl), 154.2, 157.6 (C=N).

$C_{18}H_{21}Cl_9N_3SSb \cdot CH_3CN$	calcd.: C 30.28	H 3.05 N 7.06
(793.3)	found: C 30.06	H 3.18 N 6.89.

1,4,4,11,11-Pentamethyl-3-(2,4,6-trichlorophenyl)-3-aza-2-azoniatricyclo[6.2.1.$0^{2,6}$]-2(6)-undec-2(6)-ene Hexachloroantimonate (**20d**)

From **16b** (3.80 g, 10 mmol) and *iso*butene (1.68, 30 mmol) in the manner described for **11a**. After evaporation of the solvent the dark brown residue was crystallized at −15 °C from CH_2Cl_2 (20 ml)/Et_2O (120 ml) to furnish a pale brown crystalline powder (3.09 g, 42%); *m.p.* 176–179 °C (dec). – $[\alpha]_D^{23}$ = −137°; $[\alpha]_{546}^{23}$ = −177° (c = 1.0, CH_2Cl_2). – IR (CH_2Cl_2): ν/cm^{-1} = 1543, 1567, 1617. – ^{1}H NMR [CD_3CN/CD_2Cl_2 (2:1)]: δ/ppm = 1.06, 1.09, 1.18, 1.25, 1.48 (CH_3), 1.64 (m, 1H), 2.23 (m, 4H) (H8-10), 2.90 (br, d, J = 22.2, 1H), 3.25 (br, d, $J \approx 22$, 1H) (H-7,7'), 3.45 (AB-q, J = 20.1, H-5,5'), 7.64 (AB-q, J = 2.4, aryl). – ^{13}C NMR [CD_3CN/CD_2Cl_2 (2:1)]: δ/ppm = 14.1, 18.3, 24.3 (2C), 28.8, 29.3, 36.5, 38.5, 40.6, 47.7, 51.9 (CH_3, CH_2, CH, C), 68.2 (C-4), 83.9 (C-1), 131.4, 131.6, 135.8, 136.6, 137.1, 138.4 (aryl), 179.9 (C=N). – MS (FAB,DMSO/*m*-nitrobenzyl alcohol): *m/z* 399/401/403(M^+–$SbCl_6$).

$C_{20}H_{26}Cl_9N_2Sb$	calcd.: C 32.67	H 3.56 N 3.81
(735.3)	found: C 32.78	H 3.15 N 4.07.

1,11,11-Trimethyl-3-(2,4,6-trichlorophenyl)-3-aza-2-azoniapentacyclo[10.2.1.$1^{5,8}$.$0^{2,10}$.$0^{4,9}$]hexadeca-2(6)-ene Hexachloroantimonate (**20e**)

From **16b** (3.80 g, 10 mmol) and norbornene (0.94 g, 10 mmol) in the manner described for **11a**. Crystallization at −15 °C from CH_2Cl_2 (30 ml)/Et_2O (100 ml) afforded a yellow powder (7.45 g, 96%); *m.p.* 173–175 °C (dec). – $[\alpha]_D^{23}$ = +110°; $[\alpha]_{546}^{23}$ = +138° (c = 1.1, CH_2Cl_2). – IR (CH_2Cl_2): ν/cm^{-1} = 1547, 1567, 1606. – ^{1}H NMR [CD_3CN/CD_2Cl_2 (2:1), 313*K*]: δ/ppm = 0.96, 1.05, 1.16 (CH_3), 1.20–2.90 (m's, 14H), 3.14 (dt, J = 21.5 and 3.3, H-11), 3.80 (br, CH_2-16), 7.60 (q, J = 2.3, aryl). – ^{13}C NMR [CD_3CN/CD_2Cl_2 (2:1), 313*K*]: δ/ppm = 15.2, 18.9, 24.5, 25.0, 28.5, 28.8, 34.8, 35.3, 40.8, 42.6, 43.5, 44.6, 47.6, 58.9, 74.2 (CH_3, C-4-9, 11-16), 87.3 (C-1), 130.9, 131.7, 135.7, 137.4, 138.1, 140.0 (aryl), 176.4 (C=N). – FAB-MS (DMSO/*m*-nitrobenzyl alcohol): *m/z* 439 (M^+–$SbCl_6$).

$C_{23}H_{28}Cl_9N_2Sb$	calcd.: C 35.72	H 3.65 N 3.62
(773.5)	found: C 35.88	H 3.70 N 3.79.

1,11,11-Trimethyl-4-phenyl-3-(2,4,6-trichlorophenyl)-3-aza-2-azoniatricyclo[6.2.1.$0^{2,6}$]undeca-2(6),4-diene Perchlorate (**20f**)

At −60 °C a solution of **16b** (3.80 g, 10 mmol) and PhC≡CH (1.02 g, 10 mmol) in CH_2Cl_2 (30 ml) was added dropwise to $AlCl_3$ (1.33 g, 10 mmol) in CH_2Cl_2 (30 ml). After stirring at −60 °C for 1 h, then at 0 °C for 1 h, and finally at 23 °C for 1 h the solvent was removed and the residue was dissolved in MeCN (80 ml). At −5 °C a solution of $NaClO_4$ (1.84 g, 15 mmol) in MeCN (20 ml) was added. After stirring for 12 h the suspension was filtered and the solvent was evaporated. The residue was stirred for 10 min in $CHCl_3$ (80 ml). Filtration and evaporation of the solvent afforded a residue, which was dissolved in CH_2Cl_2 (10 ml). After addition of Et_2O (100 ml) at −15 °C within 12 h a brownish powder precipitated (2.95 g, 53%); *m.p.* 177–179 °C (dec). – $[\alpha]_D^{23}$ = −23°; $[\alpha]_{546}^{23}$ = −29° (c = 1.0, CH_2Cl_2). – IR (CH_2Cl_2): ν/cm^{-1} = 1556, 1568. – ^{1}H NMR (CD_3CN): δ/ppm = 1.13, 1.16, 1.18 (CH_3), 1.68 (m, 1H), 2.08–2.35 (m, 3H), 2.59 (m, 1H), 3.13 (dd, J = 18.8 and 1.7, H-7), 3.40 (ddd, J = 2.1 and 4.3 and 18.8, H-7'), 7.04 (H-5), 7.35–7.75 (aryl). – ^{13}C NMR (CD_3CN): δ/ppm = 15.6, 18.5, 25.0, 28.4, 31.8, 41.1, 42.2, 49.1 (CH_3, C-7-11), 85.8 (C-1), 111.4 (C-5), 126.1, 129.6, 130.2, 131.1, 131.3, 131.7, 132.8, 137.5, 137.9, 141.0, 154.3, 154.4 (aryl, C-4,6).

$C_{24}H_{24}Cl_4N_2O_4$	calcd.: C 52.77	H 4.43 N 5.13
(546.3)	found: C 52.65	H 4.47 N 5.00.

2-(Cyclohexylamino)-3-(2,4,6-trichlorophenyl)-5-[(2,3,3-trimethyl-1-cyclopentenyl)methyl]-1,3,4-thiadiazolium Hexachloroantimonate (**23a**)

From **16b** (3.80 g, 10 mmol) and cyclohexyl isothiocyanate (1.41 g, 10 mmol) in the manner described for **11a**. Evaporation of the solvent afforded a yellow foam, which solidified when stirred at 23 °C for 12 h in CH_2Cl_2 (20 ml)/Et_2O (120 ml). Yield 4.06 g (54%) of a pale yellow powder; *m.p.* 105–107 °C (dec). – Slow crystallization at −15 °C of **23a** (0.05 g) from MeCN (1 ml) afforded crystals suitable for X-ray structural analysis. – IR (KBr): ν/cm^{-1} = 1555, 1603, 3275 (NH). – ^{1}H NMR (CD_3CN): δ/ppm = 1.04 (6H), 1.68 (br) (CH_3), 1.09–2.31 (m's, 14H), 3.31 (br, coupl. to 8.09, 1H), 3.73 (br, CH_2), 7.83 (aryl), 8.09 (br, d, J = 7.6, NH). – ^{13}C NMR (CD_3CN): δ/ppm = 10.2, 25.3, 25.4, 26.4, 30.8, 32.3, 33.0, 39.4, 48.0 (CH_3, CH_2, C), 64.4 (NCH), 127.9, 129.7, 131.3, 136.5, 140.6, 147.7, 160.8, 169.6 (aryl, C=C, C=N). – MS (FAB, *m*-nitrobenzyl alcohol): *m/z* 470/471/473(M^+–$SbCl_6$).

$C_{23}H_{29}Cl_9N_3SSb$	calcd.: C 33.67	H 3.56 N 5.12
(820.4)	found: C 34.04	H 3.61 N 5.36.

2-(Benzylamino)-3-(2,4,6-trichlorophenyl)-5-[(2,3,3-trimethyl-1-cyclopentenyl)methyl]-1,3,4-thiadiazolium Hexachloroantimonate (**23b**)

From **16b** (3.80 g, 10 mmol) and benzyl isothiocyanate (1.49 g, 10 mmol) in the manner described for **11a**. The solvent of the suspension was evaporated and the residue was stirred at −15 °C for 12 h in CH_2Cl_2 (20 ml)/Et_2O (80 ml). Filtration afforded a pale yellow crystalline powder (5.63 g, 68%); *m.p.* 186–188 °C (dec). – IR (KBr): ν/cm^{-1} = 1557, 1605, 3288 (NH). – ^{1}H NMR (CD_3CN): δ/ppm = 1.00 (6H), 1.61 (t, J = 1.9) (CH_3), 1.66 (t, J = 7.1), 2.22 (m, coupl. to 1.61 and 1.66), 3.69, 4.64 (br, coupl. to 8.67) (CH_2), 7.37 (m, phenyl), 7.85 (aryl), 8.67 (br, NH). – ^{13}C NMR (CD_3CN): δ/ppm = 10.2, 26.3 (2C), 30.7, 33.1, 39.4, 47.9, 53.9 (CH_3, CH_2, C), 128.1, 129.4, 129.5, 130.2, 131.3, 133.4, 136.4, 140.8, 147.8, 161.3, 170.9 (aryl, C=C, C=N). – MS(FAB, *m*-nitrobenzyl alcohol): *m/z* 492/494/496 (M^+–$SbCl_6$).

$C_{24}H_{25}Cl_9N_3SSb$	calcd.: C 34.80	H 3.04 N 5.07
(828.4)	found: C 34.54	H 2.98 N 5.06.

4-Isopropyl-5-(isopropylamino)-1-(2,4,6-trichlorophenyl)-3-[(2,3,3-trimethyl-1-cyclopentenyl)methyl]-1H-1,2,4-triazolium Hexachloroantimonate (**23c**)

From **16b** (3.80 g, 10 mmol) and diisopropylcarbodiimide (1.26 g, 10 mmol) in the manner described for **11a**. After

evaporation of the solvent the residue was stirred at 23 °C in CH_2Cl_2 (20 ml)/Et_2O (120 ml) to afford a colorless powder (7.25 g, 90%); *m.p.* 185–187 °C (dec). – $[\alpha]_D^{23} = 0°$ (c = 1.0, CH_2Cl_2). – IR (CH_2Cl_2): ν/cm^{-1} = 1570, 1631. – ^{1}H NMR (CD_3CN): δ/ppm = 1.00 (s, 6H), 1.15 (d, J = 6.5, 6H), 1.57 (d, J = 7.1, 6H), 1.65 (m, $J \approx 2.1$, 3H) (CH_3), ca 1.64 (m, 2H), 2.15 (m, 2H), 3.62 (br, 2H) (CH_2), 3.29 (m, coupl. to 1.15 and 6.29, 1H), 4.45 (sept, J = 7.1, 1H) (CH), 6.29 (br, d, J = 9.5, NH), 7.78 (aryl). – ^{13}C NMR (CD_3CN, gated decoupling): δ/ppm = 10.2 (q, J = 131), 19.7 (q, J = 128), 23.4 (q, J = 127), 26.5 (q, J = 125) (CH_3), 27.1 (t, J = 131), 32.8 (t, J = 130), 39.2 (t, J = 128) (CH_2), 48.0 (br, C), 50.2 (d, J = 140), 51.1 (d, J = 141) (CH), 131.0 (dd, J = 177 and 6, *m*-C), 131.3 (t, J = 8, *i*-C), 135.9 (t, J = 3, *o*-C), 139.8 (t, J = 5, *p*-C), 126.0 (br), 145.3 (br), 150.0 (br), 152.9 (br) (C=C, C=N). – MS(FAB, *m*-nitrobenzyl alcohol): *m/z* 470/471/473 (M^+–$SbCl_6$).

$C_{23}H_{32}Cl_9N_4Sb$	calcd.:	C 34.30	H 4.00 N 6.96
(805.4)	found:	C 34.41	H 4.08 N 7.20.

2-(Cyclohexylimino)-3-(2,4,6-trichlorophenyl)-5-[(2,3,3-trimethyl-1-cyclopentenyl)methyl]-1,3,4-thiadiazole (**24**)

A solution of **23a** (8.20 g, 10 mmol) in H_2O (80 ml)/MeCN (100 ml) containing $NaHCO_3$ (8.40 g, 100 mmol) and aqueous NH_3 (25%, 20 ml) was stirred between 0° and 23 °C for 4 h. The solvent was evaporated and the residue was extracted with CH_2Cl_2 (3×30 ml). Drying of the combined extracts over Na_2SO_4 and evaporation of the solvent afforded an oil, which slowly crystallized at 23 °C from EtOH (40 ml) to furnish a colorless powder (4.01 g, 82%); *m.p.* 89–91°C. – IR (KBr): ν/cm^{-1} = 1644 (C=N). – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.02 (6H), 1.61 (t, J = 1.9) (CH_3), 1.04–1.73 (m's, 12H), 2.25 (br, 2H), 2.53 (br, 1H), 3.41 (2H), 7.41 (aryl). – ^{13}C NMR ($CDCl_3$): δ/ppm = 9.7, 24.9, 25.6, 26.3, 31.9, 32.5, 33.3, 38.6, 47.2 (CH_3, CH_2, C), 68.4 (NCH), 127.7, 128.8, 134.1, 135.3, 136.5, 143.8 (aryl, C=C), 149.7, 152.0 (C=N).

$C_{23}H_{28}Cl_3N_3S$	calcd.:	C 56.97	H 5.82 N 8.67
(484.9)	found:	C 56.70	H 5.78 N 8.63.

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Address for correspondence:
Prof. Dr. J. C. Jochims
Universität Konstanz, Fakultät für Chemie
Postfach 5560
D-78434 Konstanz
E-mail: johannes.jochims@uni-konstanz.de
Fax Int. 7531/883898