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[3+2]-Cycloadditions of 1-Aza-2-azoniaallene Cations to Multiple Bonds

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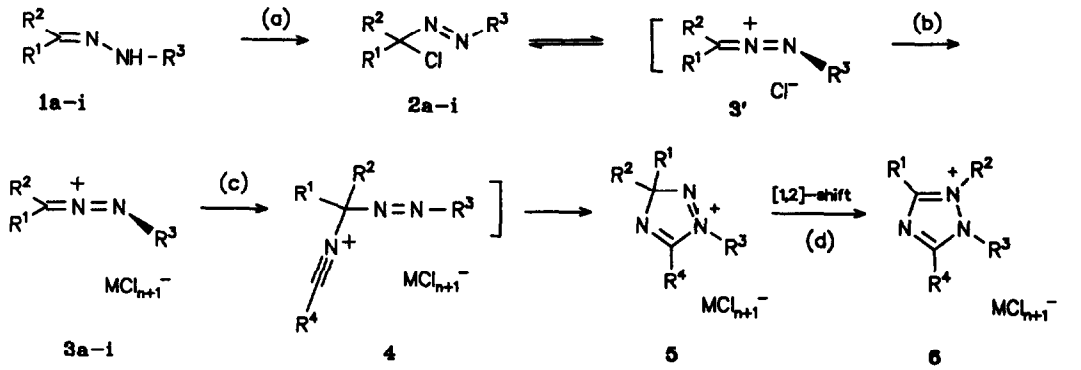
Abstract - Hydrazones of ketones, **1**, are transformed into 1-chloroalkylazo compounds, **2**, which react with Lewis acids to give transient 1-aza-2-azoniaallene salts, **3**. The cations **3** react with with acetylenes, olefins, isocyanates, carbodiimides, and nitriles under [3+2]-cycloadditions. The cycloadducts undergo consecutive reactions, e.g. [1,2]-shifts of alkyl groups.

Short-lived 1-aza-2-azoniaallene salts, **3**, were formed at low temperature from 1-chloroalkylazo compounds **2**[1,2] on treatment with Lewis acids like $SbCl_5$ or $AlCl_3$ (Scheme 1).[3] Occasionally, solutions of **3** (R^3 = alkyl) in CH_2Cl_2 showed strong IR absorptions around 1900 cm^{-1}, which were assigned to the antisymmetric stretching vibration of the C=N=N unit. However, during evaporation of the solvent the cumulenes **3** decomposed giving mixtures of compounds, e.g. diazonium salts $R^3\text{-}N_2^+ X^-$ have been identified for R^3 = aryl .[3]

1-Aza-2-azoniaallene cations, **3** (R^3 = aryl) have been postulated by Huisgen and Koch as intermediates in the reaction of aryldiazonium salts with diazoalkanes.[4] Benzing studied equilibria **2** ⇌ **3'** as well as the decomposition of chlorides **3'** (R^3 = $ClCR^1R^2$).[5-7] The stereoselective trans-1,4-addition of chlorine to ketazines $R^1R^2C{=}N\text{-}N{=}CR^1R^2$ was explained assuming cations **3'** as intermediates.[8] Similarly, the solvolysis of 1,1'-dichloroazoalkanes occurs via cations **3'**.[9,10] Oxidation of acylhydrazones of ketones with lead(IV)-acetate furnished 1,3,4-oxadiazolines via cations $R^1R^2C{=}N^+{=}N\text{-}C(=O)R^3$.[11] 1-Aza-2-azoniaallene ions are generated as reactive intermediates in many oxidative processes of hydrazones, **1**.[12-18] 1-Aza-2-azoniaallene ions prepared from amidrazones have been shown to cyclize to 1,3,4-triazoles or 1,2,4-triazines.[19] The zwitterionic reaction products of diazotropylidene with acetylenes contain an 1-aza-2-azoniaallene moiety.[20]

Recently, we reported polar [3+2]-cycloadditions[21] of 1-aza-2-azoniaallene salts, **3**, to nitriles (Scheme 1).[3] 1,2,4-Triazolium salts, **6**, were isolated in high yields. The reaction probably proceeds stepwise via nitrilium cations **4**. In most cases the primary cyclization products **5** could not be isolated because of fast rearrangement to **6**. It was found that for $R^1 \neq R^2$ the substituent forming the more stable carbenium ion migrated exclusively. Furthermore, migration occured exclusively to N-2 (and not to N-4).[3,22-28]

Here we report that [3 + 2] - cycloadditions of cations **3** are not limited to nitriles but can be carried out with many types of multiple bonds.



Scheme 1. (a) t-BuOCl, $CHCl_3$ or CH_2Cl_2, −50°C to 0°C, 3h, 78–99%; (b) $SbCl_5$ or $AlCl_3$, −60°C to 23°C, 3h, 78–99%; (c) + R^4–CN; (d) 41–99%.

1–3	R^1	R^2	R^3	MCl_n
a	Me	*i*–Pr	*t*–Bu	$AlCl_3$
b	Me	Me	Ar	$AlCl_3$
c	Me	Me	Ar	$SbCl_5$
d	$(CH_2)_5$		CO_2Et	$SbCl_5$
e	$(CH_2)_4$		CO_2Et	$SbCl_5$

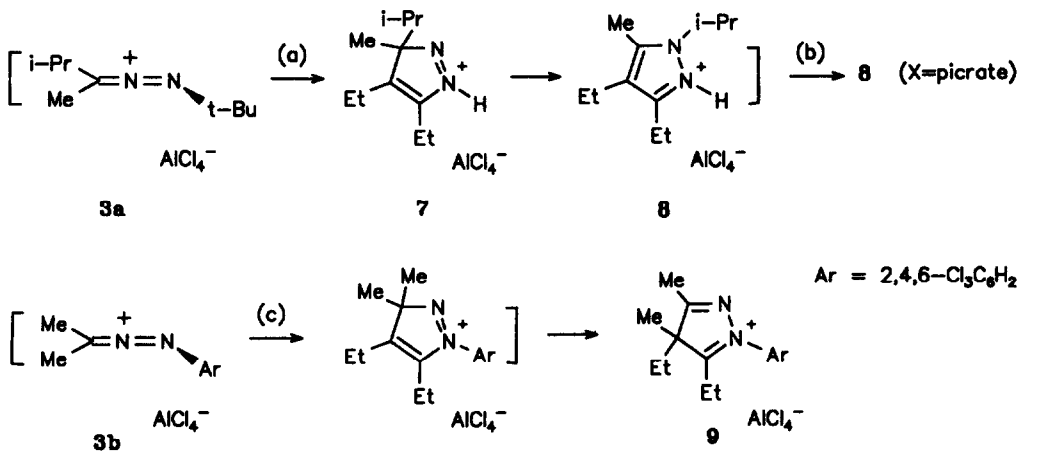
1–3	R^1	R^2	R^3	MCl_n
f	Ph	Me	Ar	$SbCl_5$
g	Me	cyclopropyl	Ar	$SbCl_5$
h	cyclopropyl	cyclopropyl	Ar	$SbCl_5$
i	Me	*t*–Bu	Ar	$SbCl_5$

Ar : 2,4,6–$Cl_3C_6H_2$

The chloroalkylazo compound **2a**[3] prepared by oxidation of the hydrazone **1a** with tert-butyl hypochlorite reacted with 3-hexyne in the presence of $AlCl_3$ to afford the *1H*-pyrazolium salt **8** (X = $AlCl_4$), which was characterized as the picrate, **8** (X = picrate) (Scheme 2). With $SbCl_5$ instead of $AlCl_3$ the reaction mixture turned black. Forming the more stable carbenium ion, the isopropyl group migrated exclusively and only migration to the adjacent nitrogen atom was observed. The tert-butyl substituent was lost during the reaction. Thus, tert-butyl hydrazones can be used to prepare pyrazoles unsubstituted at N-2. However, under similar reaction conditions **2b**[3] formed the *4H*-pyrazolium salt **9**. Here, migration of a methyl group occurred exclusively to the adjacent carbon atom.

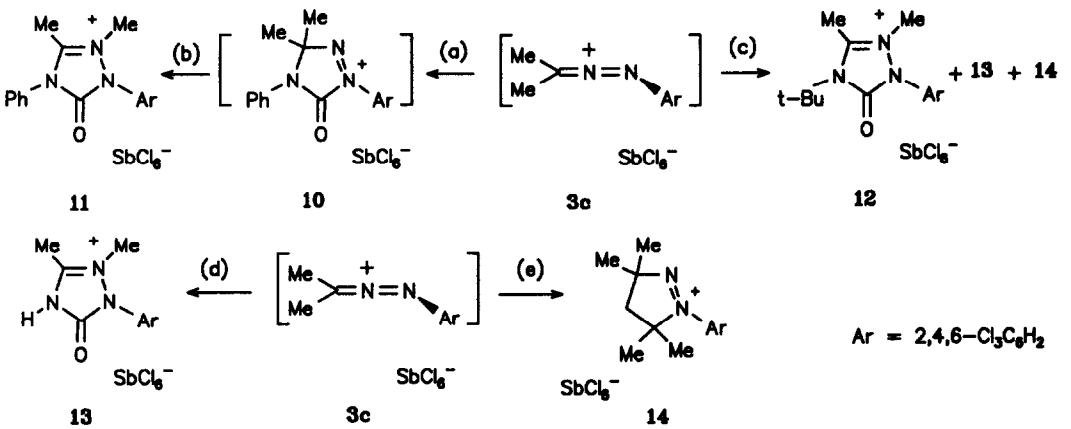
The ^1H NMR spectrum of **9** showed an AB-quartet for the aromatic protons and broad lines for one of the ethyl groups. In the ^{13}C NMR spectrum six well separated resonances for the aromatic carbon atoms were observed. This indicates hindered rotation around the aryl-C bond and unequal faces of the pyrazolium ring. Relatively little is known about *4H*-pyrazoles.[29-31]

With phenylisocyanate the hexachloroantimonate **3c** afforded the triazolium salt **11** Scheme 3). Noteworthy, the isocyanate acted as a nucleophile in this reaction.[32-34] An intermediate **10** was not observed. Exclusive methyl migration to N-2 was observed. With tert-butyl isocyanate **3c** reacted to give a mixture of compounds **12-14** (ratio 8:4:1, ^1H NMR).



Scheme 2. (a) + Et–C≡C–Et, $ClCH_2CH_2Cl$, reflux, 5h, – $Me_2C{=}CH_2$; (b) 1) NaOH/H_2O, 2) picric acid, 98%; (c) + Et–C≡C–Et, CH_2Cl_2, 0°C, 1h; 88%

Obviously, under the reaction conditions part of the tert-butyl isocyanate decomposed to isobutene and HNCO. The latter reacted with **3c** to furnish **13**, while isobutene added to **3c** producing **14**.



Scheme 3. (a) + PhNCO, CH_2Cl_2, 0°C, 2h; (b) 68%; (c) + t–BuNCO, CH_2Cl_2, 0°C to 25°C, 90min; (d) + Me_3SiNCO, CH_2Cl_2, 0°C, 3h, 42%; (e) + $Me_2C{=}CH_2$, CH_2Cl_2, 0°C, 2h, 42%.

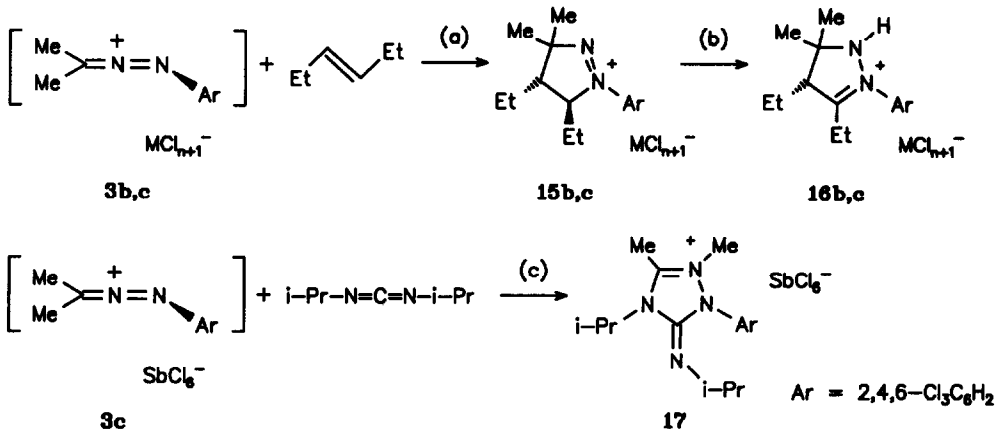
Compound **13** was prepared independently from **3c** and trimethylsilyl isocyanate, and **14** was obtained by direct reaction of **3c** with isobutene (Scheme 3).

The cycloaddition to isobutene occurred with complete Markovnikov regioselectivity. Noteworthy, the cycloaddition of the olefin was not followed by migration of a methyl group. Even with heating a rearrangement of **14** could not be achieved.

To test the stereoselectivity of the cycloaddition **3c** was treated with (E)-3-hexene (Scheme 4). A single stereoisomer, most likely the trans form **15c**, was obtained. In the ^1H NMR spectra of the reaction mixtures no trace of a second stereoisomer could be found. Thus, the cycloaddition of (E)-3-hexene to the cation **3c** proceeded completely stereoselective. This points to a concerted mechanism via a transition state with six rearranging electrons, two electrons being supplied by the olefin and four electrons coming from the C=N double bond and the lone pair on the sp^2-N of **3**. Such a mechanism could be regarded as an 1,3-dipolar cycloaddition with a positively charged "1,3-dipole" ("polar 1,3-dipolar cycloaddition" or "1,3-dipolar cycloaddition with reverse electron demand").[21,35]

Since only moderate yields (37%) of **15c** were obtained the corresponding transformation of the tetrachloroaluminate **3b** with (E)-3-hexene was studied. According to the ^1H NMR spectra stereochemically homogenious **15b** was formed. However, during the isolation procedure the compound rearranged to furnish **16b** (isolated yield 88%). A corresponding 1,3-hydrogen shift accompanied with considerable decomposition was observed for **15c** at higher temperature (boiling acetonitrile).[36,37]

Finally, cycloaddition of diisopropylcarbodiimide to **3c** provided the triazolium salt **17** (Scheme 4).[38]



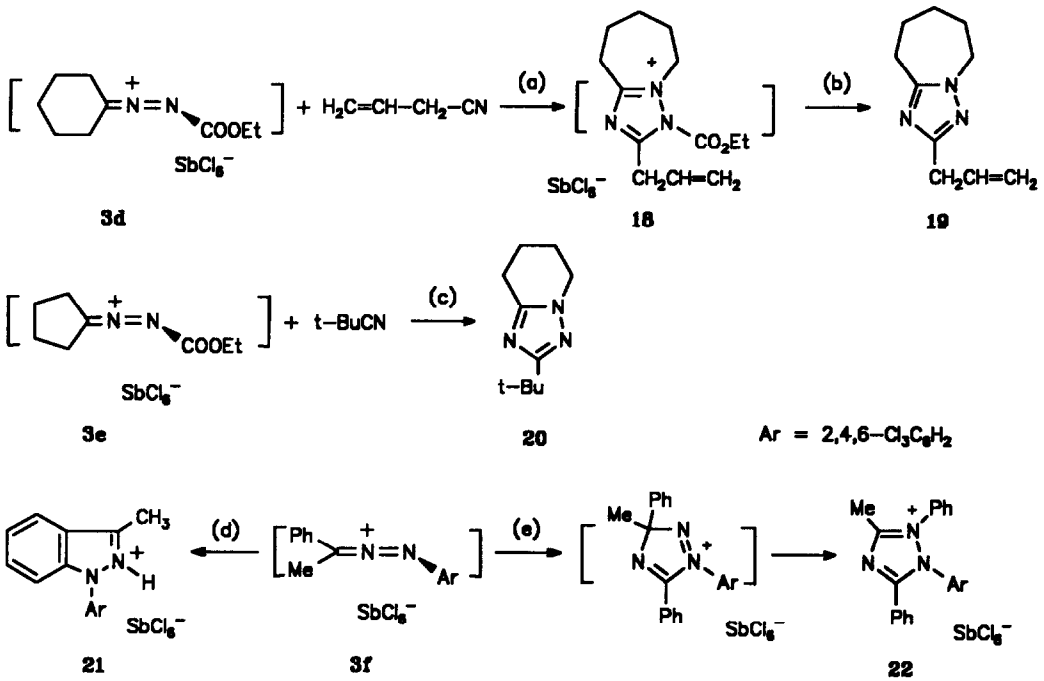
Scheme 4: (a) CH_2Cl_2, 0°C, 2–3h, **15c**: 37%; (b) **16b**: 88%; (c) CH_2Cl_2, 1h, 0°C, 65%.

In competitive experiments it was found that nitriles react especially fast with cations **3**. For instance, with **3d** allylcyanide reacted not as an olefin but exclusively as a nitrile to produce the triazole **19**, which was characterized as the picrate (Scheme 5).

The last reaction was accompanied by a site selective ring enlargement. The ester group of the intermediate **18** was removed with aqueous base. This sequence constitutes another new synthesis of N-2 unsubstituted *1H*-1,2,4-triazoles. Correspondingly, the triazole **20** was obtained from **3e** and pivalonitrile.

Indazolium salts are known to be formed on oxidation of hydrazones of *aryl* ketones in the

presence of a Lewis acid.[3,39,40] Thus, after treating the chloroalkylazo compound **2f** with $SbCl_5$ the indazolium hexachloroantimonate **21** was isolated in 65% yield (Scheme 5). However, when the reaction was carried out in the presence of one equivalent of benzonitrile only the intermolecular reaction product **22** was produced. Note the complete regioselectivity of the cycloaddition, the complete site selectivity of the rearrangement and the exclusive migration of phenyl.



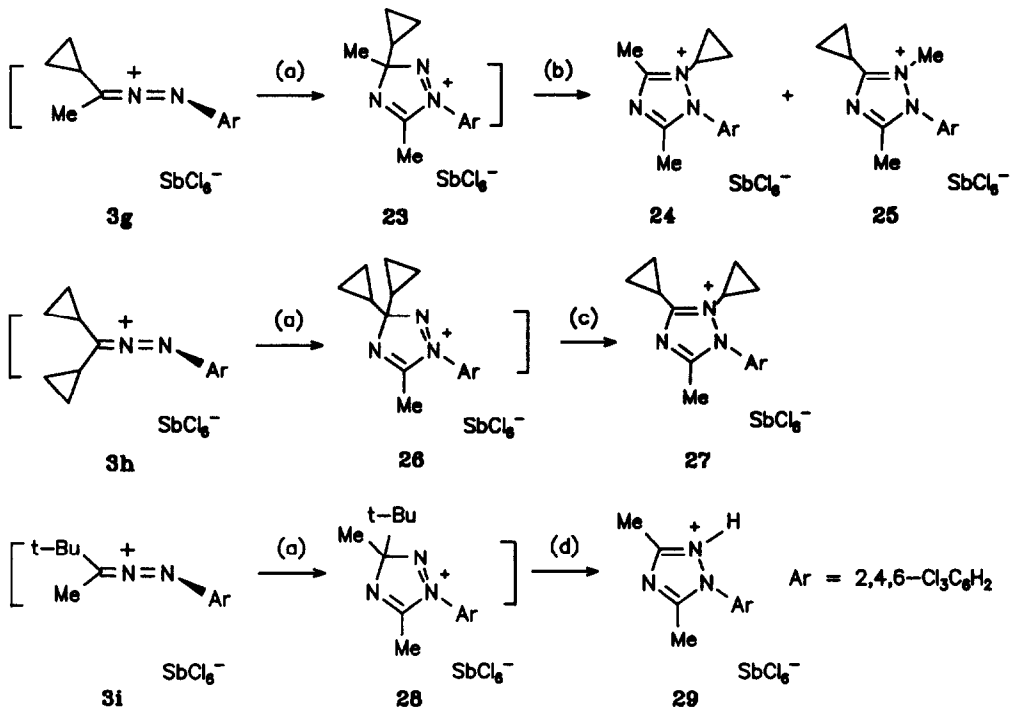
Scheme 5. (a) CH_2Cl_2, −60 to 0°C, 3h%; (b) NaOH/H_2O, −10°C, 1h, 56%; (c) as described for **19**, 85%; (d) CH_2Cl_2, −60 to 25°C, 130 min, 65%; (e) + PhCN, CH_2Cl_2, −60 to 0°C, 3h, 40%.

In addition to the mechanism of the [3 + 2]-cycloadditions of 1-aza-2-azoniaallene cations, **3**, to multiple bonds the mechanism of the subsequent [1,2]-shift of an alkyl or aryl group is of interest. The alkyl group, which forms the more stable carbenium ion migrates preferentially.[3] For closely related rearrangements Jefferson and Warkentin proposed a two-step mechanism, involving ion-pair intermediates.[41]

The cyclopropyl cation has been reported to rearrange to the allylic cation with almost no activation barrier.[42-45] If the [1,2] shift in **23** or **26** occurs through intermediate ion-pairs consisting of a cyclopropyl cation and an aromatic heterocycle one should expect products with an allyl substituent instead of a cyclopropyl group on N-2. When **3g** was treated with acetonitrile an equimolecular mixture of the triazolium salts **24** and **25** was formed showing that the migratory aptitudes of methyl and cyclopropyl are comparable. From the reaction of **3h** with acetonitrile the salt **27** was isolated in 90% yield (Scheme 6). No trace of an allylic

compound could be discovered in the reaction mixture (^{1}H NMR) indicating that an intermediate cyclopropyl cation was not formed. Thus, a *concerted* [1,5]-sigmatropic migration of cyclopropyl seems likely.

On the other hand, from **3i** the triazolium salt **29** was obtained, which afforded the free base with aqueous NaOH. The tert-butyl group was probably lost during and not after the



Scheme 6. (a) + MeCN, CH_2Cl_2, −60 to 25°C, 3h; (b) 87%: (c) 90%; (d) 82%.

rearrangement **28** → **29**. The formation of **29** shows that sterically demanding substituents forming stable carbenium ions can escape during the [1,2]-shift.[3,25,26,41,46]

The question remains open concerning the sense of the migration - clockwise or anticlockwise - (the periselectivity of the [1,5]-sigmatropic rearrangement). What determines the sense of the rearrangement leading to compounds **8** and **9**?[47] Why is R^2 in **5** always shifted to N2 giving **6**, and not to N4? Free carbenium ions are known to alkylate 1,2,4-triazoles preferentially on N4.[26,48] Preliminary MNDO calculations showed no simple correlation between the π-electron densities or the HOMO p_z coefficients of the aromatic heterocycle and the site of attack by the positively polarized migrating group.

Experimental Section

IR: Perkin-Elmer spectrometers 1320 and 299 and Mattson Polaris FT-IR spectrometer; absorptions in cm^{-1}; sh = shoulder. ^1H and ^{13}C NMR spectra: Bruker AC-250 and WM-250 instruments; chemical shifts in δ units relative to internal TMS at 295 K, if not stated otherwise. All experiments were carried out with exclusion of moisture.

Preparation of the Hydrazones (**1**): A mixture of the ketone (100 mmol) and the hydrazine (100 mmol) in ethanol (80 ml) / acetic acid (1 ml) was boiled under reflux for 5h. Evaporation of the solvent and crystallization of the residue afforded the pure hydrazone.

Ethyl Cyclohexylidenecarbazate (**1d**):[49] From cyclohexanone (9.81 g, 100 mmol) and ethyl carbazate (10.41 g, 100 mmol). Yield: 18.30 g (99%) of a colorless oil, which slowly solidified. IR (CCl_4): 1700, 1760; ^1H NMR ($CDCl_3$): 1.31 (t, J = 7.1 Hz, CH_3), 1.65 (m, 6H), 2.33 (m, 4H), 4.27 (q, J = 7.1 Hz)(CH_2), 8.26 (NH); ^{13}C NMR ($CDCl_3$): 14.6 (CH_3), 25.6, 25.8, 26.4, 26.9, 35.4, 61.7 (CH_2), 154.9, 157.3 (C=N,C=O). (Found: C, 58.52; H, 8.73; N, 15.00. Calcd for $C_9H_{16}N_2O_2$ (MW = 184.2): C, 58.67; H, 8.75; N, 15.21%).

Ethyl Cyclopentylidenecarbazate (**1e**):[50] From cyclopentanone (8.41 g, 100 mmol) and ethyl carbazate (10.41 g, 100 mmol). Crystallization from ethanol (35 ml) afforded colorless leaflets (10.89 g, 64%); mp 101-102°C. IR (CCl_4): 1720 (sh), 1740, 1775; ^1H NMR ($CDCl_3$): 1.32 (t, J = 7.0 Hz, CH_3), 1.75 (m), 1.87 (m), 2.24 (m), 2.48 (m), 4.29 (q, J = 7.0 Hz)(CH_2), 7.72 (NH); ^{13}C NMR ($CDCl_3$): 14.6 (CH_3), 24.8, 24.9, 27.2, 33.4, 61.8 (CH_2), 154.3, 163.2 (C=N,C=O). (Found: C, 56.44; H, 8.23; N, 16.49. Calcd for $C_8H_{14}N_2O_2$ (MW = 170.2): C, 56.45; H, 8.29; N, 16.46%).

1-Phenylethanone 2,4,6-Trichlorophenylhydrazone (**1f**): From acetophenone (12.02 g, 100 mmol) and 2,4,6-trichlorophenylhydrazine (21.15 g, 100 mmol). Crystallization at -18°C from hot ethanol (50 ml) gave colorless prisms (26.58 g, 85%); mp 55-56°C. IR (CCl_4): 1440, 1465; ^1H NMR ($CDCl_3$): 2.23 (CH_3), 7.30 (trichlorophenyl); ^{13}C NMR ($CDCl_3$): 12.1 (CH_3). (Found: C, 53.65; H, 3.62; N, 8.94. Calcd for $C_{14}H_{11}Cl_3N_2$ (MW = 313.6): C, 53.62; H, 3.54; N, 8.93%).

1-Cyclopropylethanone 2,4,6-Trichlorophenylhydrazone (**1g**): From cyclopropylmethylketone (8.41 g, 100 mmol) and 2,4,6-trichlorophenylhydrazine (21.15 g, 100 mmol). The reaction mixture was boiled under reflux for 8h. Evaporation of the solvent gave an orange oil (27.48 g, 99%). IR (CCl_4): 1455, 3338; ^1H NMR ($CDCl_3$): mixture of the geometrical isomers, ratio 1:3; main isomer: 1.83 (CH_3), 7.26 (trichlorophenyl), 6.80 (NH); minor isomer: 1.81 (CH_3), 7.28 (trichlorophenyl), 7.42 (NH); ^{13}C NMR ($CDCl_3$): main isomer: 5.8, 13.2, 17.7 (CH_3, CH_2, CH), 154.1 (C=N); minor isomer: 4.72, 10.3, 19.7 (CH_3, CH_2, CH), 154.1 (C=N). (Found: C, 47.67; H, 3.91; N, 10.00. Calcd for $C_{11}H_{11}Cl_3N_2$ (MW = 277.6): C, 47.60; H, 3.99; N, 10.09%).

Dicyclopropylketone 2,4,6-Trichlorophenylhydrazone (**1h**): From dicyclopropylketone (27.54 g, 250 mmol) and 2,4,6-trichlorophenylhydrazine (21.15 g, 100 mmol); 30h boiling time. After cooling fine colorless leaflets (23.38 g, 77%) were filtered off and recrystallized from boiling ethanol (75 ml); mp 47-48°C. IR (CCl_4): 1478, 3334; ^1H NMR ($CDCl_3$): 0.59-1.02 (CH_2), 1.34 (m), 1.67 (m) (CH), 7.25 (trichlorophenyl), 7.63 (NH); ^{13}C NMR ($CDCl_3$): 4.8, 6.4 (CH_2), 10.4, 13.3 (CH), 125.5, 128.7 (m,o-C), 126.2, 139.0 (p,i-C), 155.3 (C=N). (Found: C, 51.46; H, 4.38; N, 9.21. Calcd for $C_{13}H_{13}Cl_3N_2$ (MW = 303.6): C, 51.43; H, 4.32; N, 9.23%).

3,3-Dimethyl-2-butanone 2,4,6-Trichlorophenylhydrazone (**1i**): From 3,3-dimethyl-2-butanone (10.02 g, 100 mmol) and 2,4,6-trichlorophenylhydrazine (21.15 g, 100 mmol), 15h boiling time. Crystallization from hot ethanol (35 ml) afforded yellowish prisms (16.52 g, 70%); mp 48-50°C. IR (CCl_4): 1463, 3346; ^{1}H-NMR ($CDCl_3$): 1.14 (9 H), 1.88 (CH_3), 7.26 (trichlorophenyl), 6.95 (NH); ^{13}C-NMR ($CDCl_3$): 10.6, 27.8(3 C) (CH_3), 38.7 (C), 125.6, 128.6 (o,m-C), 126.4, 139.2 (p,i-C), 157.7 (C=N). (Found: C, 48.96; H, 5.19; N, 9.46. Calcd for $C_{12}H_{15}Cl_3N_2$ (MW = 293.6): C, 49.08; H, 5.15; N, 9.54%).

Preparation of the α-Chloroalkylazo Compounds (**2**): The reaction was carried out in the dark. tert-Butylhypochlorite[51] (13.03 g, 120 mmol) was added dropwise to a cold (-10°C) solution of the hydrazone (100 mmol) in $CHCl_3$ (120 ml). The mixture was stirred for 3h at 0°C. Evaporation of the solvent afforded the orange-yellow compound **2**.

Ethyl (1-Chlorocyclohexyl)azocarboxylate (**2d**): From **1d** (18.42 g, 100 mmol). Yield: 20.80 g (96%) of a yellow oil. IR (CCl_4): 1770, 1830 (sh); ^{1}H NMR ($CDCl_3$): 1.42 (t, J = 7.1 Hz, CH_3), 1.74-2.25 (5 CH_2), 4.45 (q, J = 7.1 Hz)(CH_2); ^{13}C NMR ($CDCl_3$): 14.1 (CH_3), 22.1, 24.7, 37.3, 64.8 (CH_2), 97.7 (CCl), 161.8 (C=O). (Found: C, 48.96; H, 6.87; N, 12.50. Calcd for $C_9H_{15}ClN_2O_2$ (MW = 218.7): C, 49.43; H, 6.91; N, 12.81%).

Ethyl (1-Chlorocyclopentyl)azocarboxylate (**2e**): From **1e** (17.02 g, 100 mmol). Yield: 19.44 g (95%) of a yellow oil. IR (CCl_4): 1555, 1575, 1729; ^{1}H NMR ($CDCl_3$): 1.43 (t, J = 7.1 Hz, CH_3), 1.97-2.63 (4 CH_2), 4.45 (q, J = 7.1 Hz) (CH_2); ^{13}C NMR ($CDCl_3$): 14.1 (CH_3), 24.4, 41.5, 64.8 (CH_2), 102.4 (CCl), 161.7 (C=O). (Found: C, 46.49; H, 6.37; N, 13.50. Calcd for $C_8H_{13}ClN_2O_2$ (MW = 204.7): C, 46.95; H, 6.40; N, 13.69%).

(1-Chloro-1-phenylethyl)azo(2,4,6-trichlorobenzene) (**2f**): From **1f** (31.36 g, 100 mmol). Yield: 34.11 g (98%) of a yellow oil, which solidified at -20°C to give a yellow powder; mp 38-40°C. IR (CCl_4): 1425, 1440, 1450 (sh); ^{1}H NMR ($CDCl_3$): 2.34 (CH_3), 7.35 (trichlorophenyl); ^{13}C NMR ($CDCl_3$): 29.5 (CH_3), 95.9 (CCl), 126.8, 127.1, 128.5, 128.9, 133.7, 139.9, 145.6 (aryl). (Found: C, 48.39; H, 2.93; N, 7.84. Calcd for $C_{14}H_{10}Cl_4N_2$ (MW = 348.1): C, 48.31; H, 2.90; N, 8.05%).

(1-Chloro-1-cyclopropylethyl)azo(2,4,6-trichlorobenzene) (**2g**): A mixture of **1g** (3.12 g, 10 mmol) and tert-butylhypochlorite (1.30 g, 12 mmol) in CH_2Cl_2 (20 ml) was stirred at -60°C for 1h. Work-up afforded an orange oil (2.81 g, 90%). IR (CCl_4): 1540 (sh), 1578, 1725; ^{1}H NMR ($CDCl_3$): 0.61-0.80 (m, 2 CH_2), 1.70 (m, CH), 1.96 (CH_3), 7.38 (aryl); ^{13}C NMR ($CDCl_3$): 2.8, 3.1 (CH_2), 21.8, 28.0 (CH, CH_3), 97.8 (CCl), 126.8, 128.8, 133.5, 145.9 (aryl). (Found: C, 42.31; H, 3.32; N, 9.00. Calcd for $C_{11}H_{10}Cl_4N_2$ (MW = 312.0): C, 42.34; H, 3.23; N, 8.98%).

(Chlorodicyclopropylmethyl)azo(2,4,6-trichlorobenzene) (**2h**): From **1h** (3.04 g, 10 mmol) as described for **2g**. Evaporation of the solvent afforded a yellow powder (3.11 g, 92%), which can be crystallized at -20°C from ether to give orange needles; mp 56-58°C. IR (CCl_4): 1536 (sh), 1578, 1725; ^{1}H NMR ($CDCl_3$): 0.57-0.86 (m, 4 CH_2), 1.71 (m, 2 CH), 7.39 (aryl); ^{13}C NMR ($CDCl_3$): 2.4, 3.1 (CH_2), 20.3 (CH), 102.0 (CCl), 126.7, 128.9, 133.5, 146.2 (aryl). (Found: C, 46.23; H, 3.58; N, 8.16. Calcd for $C_{13}H_{12}Cl_4N_2$ (MW = 338.1): C, 46.19; H, 3.58; N, 8.29%).

(1-Chloro-1,2,2-trimethylpropyl)azo(2,4,6-trichlorobenzene) (**2i**): From **1i** (29.36 g, 100 mmol). Evaporation of the solvent afforded an oil, which slowly solidified to give an orange powder (30.50 g, 93%); mp 38-39°C. IR (CCl_4): 1540, 1578, 1725; ^{1}H NMR ($CDCl_3$): 1.24 (9 H), 1.88

(CH_3), 7.38 (aryl); ^{13}C NMR ($CDCl_3$): 24.9, 26.2 (3 C) (CH_3), 40.7 (C), 104.9 (CCl), 126.9, 128.9, 133.4, 146.1 (aryl). (Found: C, 43.94; H, 4.19; N, 8.02. Calcd for $C_{12}H_{14}Cl_4N_2$ (MW = 328.1): C, 43.93; H, 4.30; N, 8.54%).

Reactions of the α-Chloroalkylazo Compounds with Multiple Bonds: 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 α-chloroalkylazo compound (10 mmol) and the unsaturated compound (12 mmol) in CH_2Cl_2 (20 ml). Alteratively, a solution of the α-chloroalkylazo compound (10 mmol) and the unsaturated compound (12 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (-60°C) suspension of $AlCl_3$ (1.33 g, 10 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at -60°C for 2h, then at 0°C for 1h, and finally at a temperature and for a time as specified. a) The solvent was evaporated under reduced pressure and the remaining salt was purified by crystallization or precipitation.

b) Alternatively, a solution of NaOH (2.80 g, 70 mmol) in H_2O (10 ml) was added dropwise at -10°C to the solution of the condensation product. After stirring at -10°C for 1h the solvent was evaporated and the residue was extracted with $CHCl_3$ (2x30 ml). The combined $CHCl_3$ extracts were dried over Na_2SO_4 and the solvent was evaporated. The residue was dissolved in a saturated solution of picric acid (2.75 g, 12 mmol) in ethanol / H_2O. Crystallization at -18°C afforded the picrate, which can be recrystallized (-18°C) from $CHCl_3$.

3,4-Diethyl-1-isopropyl-5-methyl-*1H*-pyrazolium Picrate (**8**): From **2a**[3] (1.91 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and 3-hexyne (0.99 g, 12 mmol) in $ClCH_2CH_2Cl$ as solvent. The reaction mixture was boiled under reflux for 5h. Yield of the picrate: 4.00 g (98%) of a yellow crystalline powder; mp 97-99°C; IR (CCl_4) of the base: 1455, 1551. IR (KBr) of the picrate: 1560, 1620; ^1H NMR ($CDCl_3$) of the base: 1.07 (t, J=7.6 Hz), 1.21 (t, J=7.4 Hz), 1.44 (d, J=6.7 Hz, 6H), 2.15(CH_3), 2.36 (q, J=7.6 Hz), 2.59 (q, J=7.4 Hz)(CH_2), 4.33 (sept, J= 6.7 Hz, CH); ^{13}C NMR ($CDCl_3$) of the base: 9.3, 14.8, 15.9, 16.7, 20.2, 22.4 (CH_3, CH_2), 49.3 (CH), 116.8, 134.0, 150.6 (C=); ^1H NMR ($CDCl_3$) of the picrate: 1.16 (t, J = 7.6 Hz), 1.22 (t, J = 7.6 Hz), 1.63 (d, J = 6.9 Hz, 6H), 2.39 (CH_3), 2.49 (q, J = 7.6 Hz), 2.72 (q, J = 7.6 Hz) (CH_2), 4.75 (sept, J = 6.9 Hz, CH), 8.92 (aryl), 13.30 (NH); ^{13}C NMR ($CDCl_3$) of the picrate: 9.6, 13.2, 15.0, 17.9, 21.2 (2C) (CH_3, CH_2), 52.9 (CH), 120.1, 126.3, 129.6, 140.5, 141.3, 148.4, 160.5 (C=). (Found: C, 49.56; H, 5.58; N, 16.83. Calcd for $C_{17}H_{23}N_5O_7$ (MW = 409.4): C, 49.87; H, 5.66; N, 17.11%).

4,5-Diethyl-3,4-dimethyl-1-(2,4,6-trichlorophenyl)-*4H*-pyrazolium Tetrachloroaluminate (**9**): From **2b**[1,3] (2.86 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and 3-hexyne (0.99 g, 12 mmol). After stirring at 0°C for 1h pentane (40 ml) was added dropwise to the reaction mixture. The precipitating orange oil crystallized at -20°C to give fine pale yellow needles (4.40 g, 88%), which decomposed at -20°C within a few days; mp 115-120°C (dec); IR (CH_2Cl_2): 1567, 1598; ^1H NMR (CD_3CN): 0.79 (t, J=7.6 Hz), 1.20 (very broad), 1.70, 2.42 (CH_3), 2.41 (m), 3.05 (very broad) (CH_2), 7.87 (q, J=2 Hz, aryl); ^{13}C NMR (CD_3CN): 10.0, 10.5, 13.3, 21.0, 23.0, 30.2 (CH_3, CH_2), 73.1 (C), 130.7, 131.3, 131.4, 132.9, 133.3, 140.8 (aryl), 189.0, 200.9 (C=). (Found: C, 35.49; H, 3.69; N, 5.51. Calcd for $C_{15}H_{18}AlCl_7N_2$ (MW = 501.5): C, 35.93; H, 3.62; N, 5.59%).

4,5-Dihydro-2,3-dimethyl-5-oxo-4-phenyl-1-(2,4,6-trichlorophenyl)-*1H*-1,2,4-triazolium Hexachloroantimonate (**11**): From **2b** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol) and phenyl

isocyanate (1.43 g, 12 mmol). After stirring at 0°C for 2h a yellow powder was filtered off (4.79 g, 68%), which was crystallized at -15°C from acetonitrile (50 ml) / ether (200 ml) to give colorless leaflets; mp 193-196°C. IR (KBr): 1771; ^{1}H NMR (CD_3CN): 2.59, 3.67 (CH_3), 7.87 (trichlorophenyl); ^{13}C NMR (CD_3CN): 13.3, 35.6 (CH_3), 148.0, 155.0 (C=O,C=N). (Found: C, 27.13; H, 1.89; N, 5.77. Calcd for $C_{16}H_{13}Cl_9N_3OSb$ (MW = 704.1): C, 27.29; H, 1.86; N, 5.97%).

4,5-Dihydro-2,3-dimethyl-5-oxo-1-(2,4,6-trichlorophenyl)-*1H*-1,2,4-triazolium Hexachloroantimonate (**13**): From **2b** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol) and trimethylsilylisocyanate (1.38 g, 12 mmol). After stirring at 0°C for 3h the product was precipitated at -20°C by slow addition of ether (100 ml). The product was dissolved in acetonitrile (30 ml) containing H_2O (3 ml). After stirring at 25°C for 1h the solvent was evaporated under reduced pressure and the residue was dissolved in acetonitrile (4 ml). Slow addition of ether (30 ml) and cooling to -20°C for 12h afforded a pale ochreous powder (2.64 g, 42%); mp 250-252°C (dec). IR (KBr): 1756; ^{1}H NMR (CD_3CN): 2.69, 3.53 (CH_3), 7.82 (trichlorophenyl), NH 10.25 (very broad); ^{13}C NMR (CD_3CN): 12.7, 35.1 (CH_3), 124.2, 131.1, 138.7, 141.3 (aryl), 147.6, 154.4 (C=O, C=N). (Found: C, 19.12; H, 1.48; N, 6.43. Calcd for $C_{10}H_9Cl_9N_3OSb$ (MW = 628.0): C, 19.12; H, 1.44; N, 6.69%).

4,5-Dihydro-3,3,5,5-tetramethyl-1-(2,4,6-trichlorophenyl)-*3H*-pyrazolium Hexachloroantimonate (**14**): a) From **2b** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol) and isobutene (0.67 g, 12 mmol). After stirring at 0°C for 2h the product was precipitated from the dark green solution by slow addition of ether (100 ml) to afford a yellow powder (2.69 g, 42%), which can be crystallized at -20°C from acetonitrile / ether; mp 182-184°C (dec). IR (KBr): 1567; ^{1}H NMR (CD_3CN): 1.91, 1.93 (CH_3), 2.58 (CH_2), 7.88 (aryl); ^{13}C NMR (CD_3CN, 273 K): 28.0, 28.9 (CH_3), 45.7 (CH_2), 91.3, 105.5 (C-N), 131.7, 131.8, 133.2 (broad), 140.7 (aryl). (Found; C, 24.10; H, 2.41; N, 4.28. Calcd for $C_{13}H_{16}Cl_9N_2Sb$ (MW = 641.1): C, 24.35; H, 2.52; N, 4.37%).

b) From **2b** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol) and tert-butylisocyanate (1.19 g, 12 mmol). The reaction mixture was stirred at 0°C for 75 min and then at 25°C for 15 min. After addition of ether (100 ml) at -20°C a yellow powder (5.28 g) was formed, which according to the ^{1}H NMR spectrum (CD_3CN) was a mixture of **12-14**, integral ratio 8:4:1. ^{1}H NMR: **12**: 1.77 (3 CH_3), 2.84, 3.57 (CH_3), 7.81 (aryl); **13**: 2.68, 3.53 (CH_3), 7.81 (?, aryl); **14**: 1.91, 1.93 (CH_3), 2.58 (CH_2), 7.88 (aryl); ^{13}C NMR (CD_3CN): **12**: 15.9, 28.9 (3 C), 35.3 (CH_3), 66.6 (C), 124.8, 131.1, 138.5, 141.2 (aryl), 148.7, 154.8 (C=O,C=N); **13**: 12.7, 35.1 (CH_3), 124.2, 131.6 (?), 138.7, 141.3 (aryl), 147.5, 154.4 (C=O,C=N); **14**: 28.0, 29.0 (CH_3), 45.9 (CH_2), 91.4, 105.6 (C), 131.8, 131.9, 133.2, 140.9 (aryl).

t-4,5-Diethyl-4,5-dihydro-3,3-dimethyl-1-(2,4,6-trichlorophenyl)-*3H*-pyrazolium Hexachloroantimonate (**15c**): From **2b** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol) and (E)-3-hexene (1.01 g, 12 mmol). The reaction mixture was stirred at 0°C for 2h. Slow addition of ether (100 ml) afforded a pale yellow powder (2.48 g, 37%), which can be crystallized at -20°C from acetonitrile (10 ml) to give colorless prisms; mp 122-126°C (dec). IR (CH_2Cl_2): 1570; ^{1}H NMR (CD_3CN): 0.98 (t, J = 7.5 Hz), 1.07 (t, J = 7.4 Hz), 1.70, 1.97 (CH_3), 1.60-2.16 (m, 4H, CH_2), 2.50 (m, J ≈ 7.7, 7.6 and 7.0 Hz), 5.43 (m, J ≈ 7.7, 7.0 and 5.2 Hz)(CH), 7.88 (aryl); ^{13}C NMR (CD_3CN): 10.5, 12.6, 20.4, 21.9, 26.0, 28.2 (CH_3, CH_2), 50.5, 93.2, 95.9 (CH, C), 130.8 (broad), 131.7, 134.5 (broad), 141.5 (aryl). (Found: C, 26.70; H, 3.02; N, 4.22. Calcd for $C_{15}H_{20}Cl_9N_2Sb$ (MW = 669.2): C, 26.92; H,

3.01; N, 4.19%).

3,4-Diethyl-4,5-dihydro-5,5-dimethyl-1-(2,4,6-trichlorophenyl)-*1H*-pyrazolium Tetrachloroaluminate (**16b**): From **2b** (2.86 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol) and (E)-3-hexene (1.68 g, 20 mmol). After stirring at 0°C for 3h and addition of ether (140 ml) the product crystallized at -20°C to form very moisture sensitive colorless fine prisms (4.43 g, 88%); mp 68-72°C (dec). ^1H NMR (CD_3CN): 1.18 (t, J= 7.6 Hz), 1.21 (t, J = 7.7 Hz), 1.42, 1.52 (CH_3), 1.97 (m), 2.59 (m) (CH_2), 3.45 (t, J = 6.9 Hz, CH), 6.97 (NH), 7.80 (aryl); ^{13}C NMR (CD_3CN): 10.5, 12.9, 19.9, 21.0, 23.5, 27.9 (CH_3, CH_2), 59.1, 65.5 (CH, C), 128.8, 131.1 (m-C), 131.4 (m-C), 133.4 (o-C), 133.5 (o-C), 140.6 (aryl), 183.6 (C=N). (Found: C, 35.36; H, 4.33; N, 5.53. Calcd for $C_{15}H_{20}AlCl_7N_2$ (MW = 503.5): C, 35.78; H, 4.00; N, 5.57%).

4,5-Dihydro-4-isopropyl-5-(isopropylimino)-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-*1H*-1,2,4-triazolium Hexachloroantimonate (**17**): From **2b** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol) and diisopropylcarbodiimide (1.51 g, 12 mmol). After stirring at 0°C for 1h the reaction mixture was evaporated under reduced pressure. The yellow residue was precipitated from CH_2Cl_2 (10 ml) / pentane (80 ml). Crystallization at -20°C from CH_2Cl_2 (30 ml) / ether (200 ml) afforded fine yellow needles (4.62 g, 65%); mp 163-165°C (dec). IR (KBr): 1717; ^1H NMR ($CDCl_3$): 0.88 (d, J = 6.1 Hz), 1.66 (d, J = 6.9 Hz), 2.90, 3.51 (CH_3), 3.05 (sept, J = 6.1 Hz), 4.64 (sept, J = 6.9 Hz)(CH), 7.60 (aryl); ^{13}C NMR ($CDCl_3$, 273 K): 12.6, 19.3 (2 C), 24.2 (2 C), 34.0 (CH_3), 48.0, 50.8 (CH), 128.4, 130.2, 135.1, 137.9, 139.7, 155.4 (aryl, C=N). (Found: C, 27.00; H, 3.22; N, 7.53. Calcd for $C_{16}H_{22}Cl_9N_4Sb$ (MW = 711.2): C, 27.02; H, 3.12; N, 7.88%).

2-Allyl-5,6,7,8-tetrahydro-*4H*-1,2,4-triazolo[1,5-a]azepine (**19**) and Picrate: The salt **18** was prepared from **2d** (2.17 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol) and allylcyanide (0.81g, 12 mmol). After evaporation of the solvent the crude product was dissoved in acetonitrile (25 ml). At -10°C a solution of NaOH (2.80 g, 70 mmol) in H_2O (10 ml) was added. Stirring at -10°C for 1h, evaporation of the solvent, and extraction of the residue with $CHCl_3$ (2 x 30 ml) afforded after usual work-up **19** as a brown oil (0.99 g, 56%), which was transformed into the picrate with a saturated solution of picric acid in ethanol / H_2O. Crystallization at -18°C gave a yellow powder (2.30 g, 35%); mp 98-100°C. IR(KBr): 1490, 1520 (sh), 1540, 1590, 1610 (sh); ^1H NMR ($CDCl_3$): 1.93-2.06 (m, 3 CH_2), 3.35 (m), 3.70 (m, J = 6.7 and 1.3 Hz), 4.46 (m), 5.22 (m) (CH_2), 5.93 (m, CH), 8.86 (aryl); ^{13}C NMR ($CDCl_3$): 23.8, 24.9, 26.4, 29.4, 30.0, 53.4, 119.5 (CH_2), 130.1 (CH), 155.7, 161.1 (C=N), 126.0, 129.1, 141.6, 154.0 (aryl). (Found: C, 47.39; H, 4.54; N, 20.47. Calcd for $C_{16}H_{18}N_6O_7$ (MW = 406.4): C, 47.29; H, 4.47; N, 20.69%).

2-tert-Butyl-4,5,6,7-tetrahydro-1,2,4-triazolo[1,5-a]pyridine (**20**) and Picrate: The base **20** was prepared from **2e** (2.05 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol) and pivalonitrile (1.00g, 12 mmol). Yield: 1.52 g (85%) of a colorless powder, which was recrystallized from petroleum ether; mp 74-75°C. IR (CCl_4): 1430, 1450, 1485; ^1H NMR ($CDCl_3$): 1.36 (CH_3), 1.93-2.07 (m, 2 CH_2), 2.89 (t, J = 6.1 Hz), 4.10 (t, J = 6.0 Hz) (CH_2); ^{13}C NMR ($CDCl_3$): 20.6, 23.0, 23.7, 29.7 (3 C), 32.6, 46.7 (CH_3, CH_2, C), 152.2, 171.1 (C=N). (Found: C, 66.98; H, 9.33; N, 23.28. Calcd for $C_{10}H_{17}N_3$ (MW = 179.3): C, 67.00; H, 9.56; N, 23.45%). The picrate **20** (95%) was recrystallized from $CHCl_3$; mp 153-154°C. IR (KBr): 1560, 1600; ^1H NMR ($CDCl_3$): 1.42 (CH_3), 2.08-2.28 (m, 2 CH_2), 3.18 (t, J = 6.1 Hz), 4.28 (t, J = 6.0 Hz) (CH_2), 8.87 (aryl); ^{13}C NMR ($CDCl_3$): 18.3, 21.4,

21.8, 28.3 (3 C), 32.6, 47.9 (CH_3, CH_2, C), 126.3, 128.7, 141.7, 151.3, 161.5, 163.6 (aryl, C=N). (Found: C, 47.17; H, 4.89; N, 20.69. Calcd for $C_{16}H_{20}N_6O_7$ (MW = 408.4): C, 47.06; H, 4.94; N, 20.58%).

3-Methyl-1-(2,4,6-trichlorophenyl)-*1H*-indazolium Hexachloroantimonate (**21**): 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 **2f** (3.48 g, 10 mmol) in CH_2Cl_2 (30 mL). The mixture was stirred at -60°C for 1h, then at 0°C for 1h, finally at 25°C for 10 min. The solvent was evaporated and the residue was crystallized at -18°C from CH_2Cl_2 (20 ml) / ether (30 ml) to yield colorless prisms (4.19 g, 65%); mp 193-205°C. IR (KBr): 1450, 1480, 1510 (sh), 1560, 1630; ^1H NMR (CD_3CN): 2.95 (CH_3), 7.88 (trichlorophenyl), 7.46 (m, $^3J \sim 8.8$ Hz, H-7 or -4), 7.1 (m, H-6 or -5), 7.95 (m, H-5 or -6), 8.19 (m, $^3J \sim 8.5$ Hz, H-4 or 7), 10.33 (NH); ^{13}C NMR (CD_3CN): 11.4 (CH_3), 111.6, 121.4, 124.5, 126.7, 128.2, 131.0, 136.6, 137.4, 140.6, 141.5, 148.2 (aryl, C=N). (Found: C, 24.71; H, 1.80; N, 4.30. Calcd for $C_{14}H_{10}Cl_9N_2Sb$ (MW = 647.1): C, 25.99; H, 1.56; N, 4.33%).

3-Methyl-2,5-diphenyl-1-(2,4,6-trichlorophenyl)-*1H*-1,2,4-triazolium Hexachloroantimonate (**22**): From **2f** (3.48 g, 10 mmol), $SbCl_5$ (2-99 g, 5 mmol) and benzonitrile (1.24 g, 12 mmol). The solvent was evaporated and the residue was dissolved in hot acetonitrile (15 ml). At 23°C colorless prisms (3.02 g, 40%) were formed; mp 218-220°C. IR (KBr): 1390, 1450, 1480, 1520, 1560, 1600 (sh); ^1H NMR (CD_3CN): 2.69 (CH_3), 7.55-7.78 (aryl); ^{13}C NMR (CD_3CN): 14.9 (CH_3), 123.5, 126.4, 129.0, 129.7, 131.1, 131.6, 131.8, 135.0, 135.6, 136.8, 142.3 (aryl), 160.5, 163.5 (C=N). (Found: C, 33.66; H, 2.04; N, 5.58. Calcd for $C_{21}H_{15}Cl_9N_3Sb$ (MW = 750.2): C, 33.62; H, 2.02; N, 5.60%).

Mixture of 2-Cyclopropyl-3,5-dimethyl-1-(2,4,6-trichlorophenyl)-*1H*-1,2,4-triazolium Hexachloroantimonate (**24**) and 3-Cyclopropyl-2,5-dimethyl-1-(2,4,6-trichlorophenyl)-*1H*-1,2,4-triazolium Hexachloroantimonate (**25**): From **2g** (3.12 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol) and acetonitrile (0.50 g, 12 mmol). After stirring at 0°C for 1h ether was added slowly (100 ml) and a colorless precipitate (5.70 g, 87%) was filtered off. Reprecipitation from CH_2Cl_2 (30 ml) / ether (250 ml) afforded a colorless powder; mp 194-200°C. ^1H NMR (CD_3CN): mixture of **24, 25** in the ratio of 7:10; **24**: 2.47, 2.77 (CH_3), 3.38 (m, NCH), 7.92 (aryl); **25**: 2.41 (CH_3), 3.80 (NCH_3), 2.28 (m, CH), 7.93 (aryl); ^{13}C NMR (CD_3CN): 8.1, 8.8, 12.3, 13.2, 15.1 (CH_3, CH_2, CH), 29.4 (NCH), 34.9 (NCH_3), 124.3, 126.3, 131.6, 131.7, 136.6, 137.1, 142.1, 142.3 (aryl), 161.2, 164.0, 166.4 (C=N). (Found: C, 23.90; H, 2.04; N, 6.35. Calcd for $C_{13}H_{13}Cl_9N_3Sb$ (MW = 652.1): C, 23.94; H, 2.01; N, 6.44%).

2,3-Dicyclopropyl-5-methyl-1-(2,4,6-trichlorophenyl)-*1H*-1,2,4-triazolium Hexachloroantimonate (**27**): From **2h** (3.38 g, 10 mmol) as described for **24/25**. Yield: 6.12 g (90%) of a colorless powder, which can be reprecipitated from CH_2Cl_2 (30 ml) / ether (120 ml) to afford a colorless powder; mp 197-200°C. IR (KBr): 1532, 1563; ^1H NMR (CD_3CN): 1.12-1.55 (m's, CH_2), 2.40 (CH_3), 2.49 (m), 3.42 (m) (CH), 7.91 (aryl); ^{13}C NMR (CD_3CN): 8.5, 9.5, 12.9, 13.2 (CH_3, CH_2, CH), 28.7 (NCH), 125.4, 131.5, 136.7, 141.8 (aryl), 161.2, 168.3 (C=N). (Found: C, 26.58; H, 2.24; N, 6.18. Calcd for $C_{15}H_{15}Cl_9N_3Sb$ (MW = 678.1): C, 26.57; H, 2.23; N, 6.20%).

3,5-Dimethyl-1-(2,4,6-trichlorophenyl)-*1H*-1,2,4-triazolium Hexachloroantimonate (**29**) and Free Base: From **2i** (3.28 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol) and acetonitrile (0.50 g, 12 mmol).

After stirring at 25°C for 10 min ether (150 ml) was added dropwise. The mixture was kept at -20°C for 2h. Filtration afforded a colorless powder (5.00 g, 82%), which can be crystallized at -18°C from CH_2Cl_2 to give colorless needles; mp 227-228°C. IR (CH_2Cl_2): 1567, 1609; ^1H NMR (CD_3CN): 2.62, 2.63 (CH_3), 7.82 (aryl); ^{13}C NMR (CD_3CN): 10.9, 11.8 (CH_3), 129.1, 130.9, 135.3, 140.4 (aryl), 154.7, 155.8 (C=N). (Found: C, 19.59; H, 1.66; N, 6.86. Calcd for $C_{10}H_9Cl_9N_3Sb$ (MW = 612.0): C, 19.62; H, 1.48; N, 6.87%).

A suspension of **29** (6.12 g, 10 mmol) in $CHCl_3$ (40 ml) was shaken with NaOH (2.80 g, 70 mmol) in H_2O (40 ml) for 15 min. Separation of the organic layer and usual work-up afforded a colorless powder (2.49 g, 90%), which was crystallized at -18°C from CH_2Cl_2 to give colorless needles of 3,5-dimethyl-1-(2,4,6-trichlorophenyl)-*1H*-1,2,4-triazole; mp 91-92°C. IR (CCl_4): 1466, 1517; ^1H NMR ($CDCl_3$): 2.28, 2.44 (CH_3), 7.53 (aryl); ^{13}C NMR ($CDCl_3$): 11.7, 14.0 (CH_3), 128.9, 132.0, 135.4, 137.0 (aryl), 154.4, 161.6 (C=N). (Found: C, 43.23; H, 2.99; N, 15.29. Calcd for $C_{10}H_8Cl_3N_3$ (MW = 276.6): C, 43.43; H, 2.92; N, 15.20%).

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