On the Reaction of 1-Aza-2-azoniaallene Salts with Isocyanates

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Received December 10, 1993

Key Words: 1-Aza-2-azoniaallene cations / Isocyanates / 4,5-Dihydro-5-oxo-1,2,4-triazolium salts / Cinnolinium salts / Cycloadditions / Calculations, AM1

1-Aza-2-azoniaallene salts **3**, prepared in situ from geminal chloroalkylazo compounds **2** with Lewis acids, react with isocyanates **4** to give 4,5-dihydro-5-oxo-3*H*-1,2,4-triazolium salts **6** and 4,5-dihydro-5-oxo-1*H*-1,2,4-triazolium salts **7**, respectively. The intramolecular cyclization of **3u** opens a new route to cinnolinium salts **11**. Allenes **3** react with isobutene to give pyrazolium salts **8**. According to AM1 calculations the cycloadditions of **3** to isocyanates proceed in two steps via acylium salts **5** as intermediates. Mechanistically, the rearrangements **6** → **7** resemble Wagner-Meerwein rearrangements rather than pericyclic [1,5]-sigmatropic shifts.

Isocyanates are mostly known for their electrophilic properties[1]. However, it should be recalled that towards strong electrophiles, e.g. carbenium ions or the nitronium ion, isocyanates behave as nucleophiles[2–5].

In preceding papers[6–9] we reported on the in situ preparation of 1-aza-2-azoniaallene salts **3** and their cycloadditions to the multiple bonds of nitriles, carbodiimides, and acetylenes producing five-membered heterocycles. We now found that the strongly electrophilic salts **3** react with isocyanates **4** to furnish 1,2,4-triazolium salts **7** (Scheme 1).

5-Oxo-4,5-dihydro-3*H*-1,2,4-triazolium salts **6** with R^4 = H were prepared by Schantl and his group by treatment of geminal azoalkyl isocyanates with acids[10,11]. Alternatively, salts **6** were obtained by alkylation of 5,5-disubstituted 4,5-dihydro-3*H*-1,2,4-triazol-3-ones[12]. An X-ray structural analysis for a compound **6** (R^4 = H) is reported[10]. On heating[13] or on treatment with acids[14–16] the salts **6** isomerize to the triazolium salts **7**.

When the chloroalkylazo compound **2a**, derived from the *tert*-butylhydrazone **1a**[17–19], was stirred at −60°C with $SbCl_5$ in dichloromethane the orange carbenium salt **3a** was formed[6–9]. After addition of methyl isocyanate the orange color faded, and at temperatures between −60 and +23°C the heterocycle **6a** was formed in 72% yield. Compounds **6b–d** were produced correspondingly.

However, from **3a** and *tert*-butyl isocyanate (**4e**) instead of **6e** a mixture of **6f** and the pyrazolium salt **8a** was obtained. During or after the cycloaddition of *tert*-butyl isocyanate to **3a**, isobutene must have been eliminated to give **6f**. Cycloaddition of isobutene to unreacted allene **3a** produced the pyrazolium salt **8a**. Indeed, compound **8a** could be prepared independently by reaction of **3a** with isobutene (Scheme 2).

Boiling a solution of **6b** under reflux in 1,2-dichloroethane resulted in loss of isobutene and rearrangement of one of the methyl groups. A mixture of two isomers (ratio 3:1) was formed, each of which containing an *N*-methyl, a *C*-methyl, and a propyl group. The NMR and analytical data are in agreement with constitutions **7v** and **9**. By crystallization the minor isomer, most likely **9**, was obtained pure.

On treatment of the chloroalkylazo compound **2g** at −60°C with $SbCl_5$ in dichloromethane in the presence of methyl isocyanate the orange color of the carbenium salt **3g** soon faded. However, instead of the expected compound **6g** the isomeric triazolium salt **7g** was isolated (90%). The salts **7h–n**, **p–u** were prepared correspondingly.

Noteworthy, even rather electron-deficient isocyanates like 3,4-dichlorophenyl isocyanate (**4m**) proved to be still nucleophilic enough to react with the cumulene **3g**. Furthermore, isocyanates with a moderately hindering substituent (**4n**) undergo the cycloaddition.

Thus, if R^3 is an electron-attracting substituent like 2,4,6-trichlorophenyl the 3*H*-triazolium salts **6** are unstable at room temperature rearranging to the more stable 1*H*-triazolium salts **7** by 1,2-alkyl shifts. An ethyl or isopropyl group migrated in preference to a methyl group. No traces of isomers of **7q–t** could be observed ^{1}H-NMR spectroscopically.

From *tert*-butyl isocyanate (**4e**) and the allenium salt **3g** a mixture of the expected *tert*-butyl compound **7o**, the N(4)-unsubstituted salt **7p** and the pyrazolium salt **8g** was obtained. Compound **7p** was prepared independently from **3g** and trimethylsilyl isocyanate, and pure **8g** could be produced by cycloaddition of isobutene to **3g**[20].

An interesting new synthesis for cinnolinium salts was found when the 2-azoniaallene **3u**, derived from phenylacetone, was submitted to reaction with methyl isocyanate. A mixture of the expected product **7u** and the two cinnolinium compounds **10**, **11** was obtained, from which pure **7u** could be separated. In the absence of methyl isocyanate the labile dihydro product **10** was produced almost quantitatively. In the presence of oxygen (air) the compound was quickly dehydrogenated to the cinnolinium *tetra*chloroantimonate **11**. Thus, an intramolecular electrophilic aromatic

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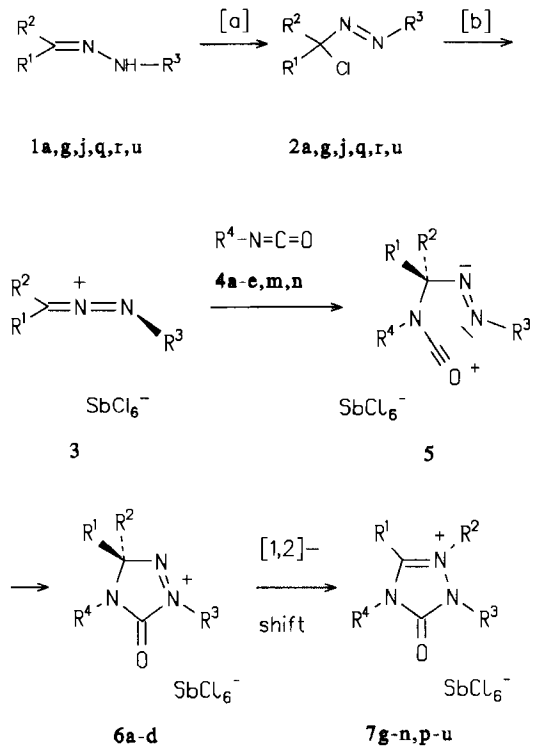
Scheme 1

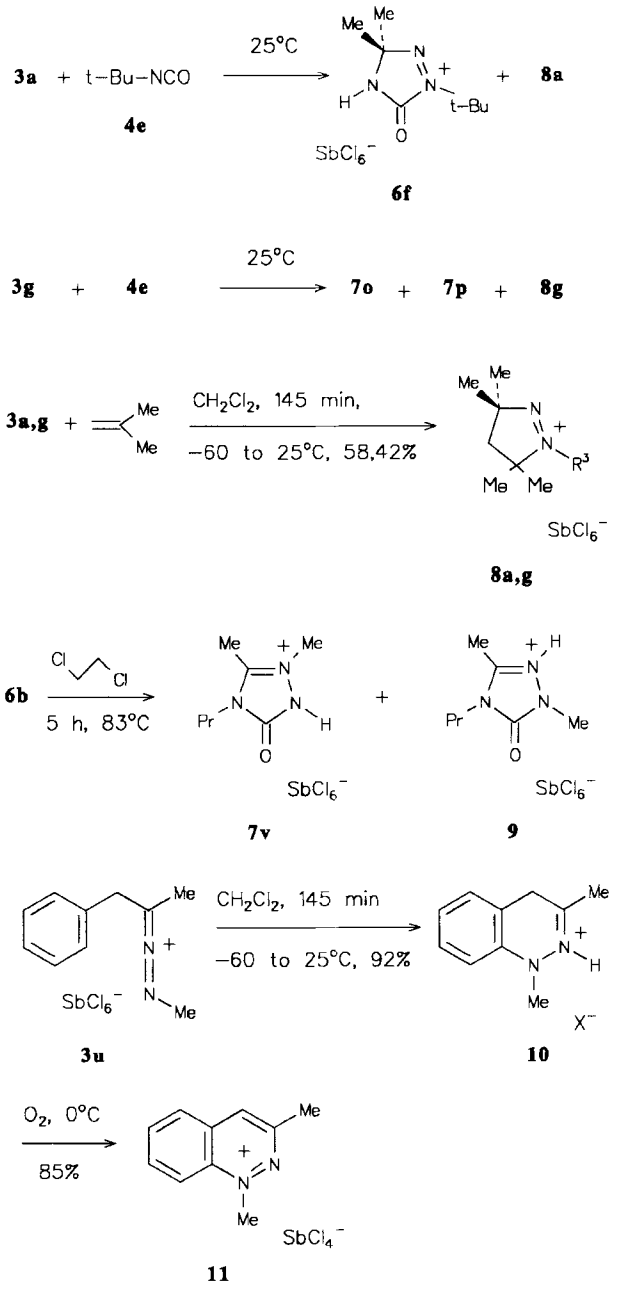


	R^1	R^2	R^3	R^4
a	Me	Me	t–Bu	Me
b	Me	Me	t–Bu	Pr
c	Me	Me	t–Bu	Ph
d	Me	Me	t–Bu	4–ClC_6H_4
e	Me	Me	t–Bu	t–Bu
f	Me	Me	t–Bu	H
g	Me	Me	2,4,6–$Cl_3C_6H_2$	Me
h	Me	Me	2,4,6–$Cl_3C_6H_2$	Pr
i	Me	Me	2,4,6–$Cl_3C_6H_2$	Pr*
j	$(CH_2)_5$		2,4,6–$Cl_3C_6H_2$	Me
k	Me	Me	2,4,6–$Cl_3C_6H_2$	Ph
l	Me	Me	2,4,6–$Cl_3C_6H_2$	4–ClC_6H_4
m	Me	Me	2,4,6–$Cl_3C_6H_2$	3,4–$Cl_2C_6H_3$
n	Me	Me	2,4,6–$Cl_3C_6H_2$	2–MeC_6H_4
o	Me	Me	2,4,6–$Cl_3C_6H_2$	t–Bu
p	Me	Me	2,4,6–$Cl_3C_6H_2$	H
q	Me	Et	2,4,6–$Cl_3C_6H_2$	Pr
r	Me	i–Pr	2,4,6–$Cl_3C_6H_2$	Me
s	Me	Et	2,4,6–$Cl_3C_6H_2$	Ph
t	Me	i–Pr	2,4,6–$Cl_3C_6H_2$	Ph
u	Me	$PhCH_2$	2,4,6–$Cl_3C_6H_2$	Me
v	Me	Me	H	Pr

* $AlCl_4^-$ as counterion.

[a] *t*-BuOCl, CH_2Cl_2, 0°C, 3 h, 80–90%. – [b] $SbCl_5$ or $AlCl_3$, CH_2Cl_2, −60°C to 23°C, 2–3 h, 68–93%.

Scheme 2



substitution in **3u** can compete with its intermolecular cycloaddition to methyl isocyanate.

AM1 Calculations and Reaction Mechanism

Reactions of cations **3** with the C=N bond of isocyanates could either proceed in a concerted manner or via acylium ions as intermediates. Recently, we suggested that cycloadditions of cations **3** to acetylenes are concerted reactions[9], in contrast to cycloadditions of **3** to the triple bond of nitriles[6] or to the double bonds of carbodiimides[8].

While we have no experimental results at hand, AM1 calculations[21,22] suggest that cycloadditions of **3** to isocyanates too are two-step reactions proceeding via acylium ions **5** as intermediates. The calculations were carried out for the

reactions of methyl isocyanate (**4a**) with the cations **3a** and **3g** (Figure 1). Both cycloadditions were calculated to be endothermic giving **6a, g** via intermediates **5a, g**. For an asynchronous concerted cycloaddition of **3g** to **4a** (reaction coordinate C(5)–N(1) = 1.2[C(3)–N(4)]) we calculated a 27 kJmol^{-1} higher enthalpy to activation than for a two-step reaction via **5g**. An even higher activation enthalpy was found for a synchronous concerted cycloaddition to **6a**. However, the preference for a stepwise cycloaddition of methyl isocyanate to **3g** (27 kJmol^{-1}) was calculated to be much less pronounced than that for the cycloaddition of diisopropylcarbodiimide to **3g** (97 kJmol^{-1})[8]. This probably reflects the higher energy of an aminoacylium ion[23] as compared to a cyanamidium ion[24,25]. Considering errors inherent in the AM1 method[21] and effects of the solvent etc. it seems premature to conclude that cycloadditions of isocyanates to 1-aza-2-azoniaallene cations generally occur in a non-concerted manner via acylium ions **5**.

Mechanistically, concerted cycloadditions of **3** to isocyanates would resemble 1,3-dipolar cycloadditions with the cumulene **3** acting as "1,3-dipole" to the isocyanate as dipolarophile. The dominant interaction would be that of HOMO of the dipolarophile with LUMO of the 1,3-dipole. Such "1,3-dipolar cycloadditions with reverse electron demand" ("type III" according to Sustmann's classification[26]) are known for certain sulfur-nitrogen compounds[27–29], e.g. for cycloadditions of the dithionitronium ion S=N$^+$=S to acetylenes, olefins and nitriles.

Discrepancies between calculations and experiment were encountered for the reaction enthalpies of the entropically unfavorable cycloadditions of **4a** to the cations **3a, g**. According to the calculations the heat of formation for the heterocycle **6g** is 61 kJmol^{-1} higher than the sum of the heats of formation for **4a** and **3g** (Figure 1). The formation of the *tert*-butyl-substituted cation **6a** was calculated to be less endothermic (32 kJmol^{-1}). Experimentally, **6a** was formed at 0°C in 72% yield, whilst **6g** could not at all be isolated. Instead, the rearranged product **7g** was obtained.

Experimentally, we found that the 1-*tert*-butyl-substituted allenes **3** generally give the 3*H*-triazolium salts **6**, while the 1-(2,4,6-trichlorophenyl)-substituted salts **3** afford 1*H*-triazolium compounds **7**. This poses the question for the mechanism of the 1,2-alkyl shift **6** → **7**. Corresponding alkyl shifts in triazolium salts unsubstituted at N(4) were observed by Schildknecht and recently by Schantl and Gstach et al.[10–16]. The latter authors reported on large differences in the rates of the rearrangements. The migratory aptitudes parallel the efficiency of the migrating group to stabilize a positive charge. Isopropyl migrates in preference to ethyl, which rearranges several orders of magnitude faster than a methyl group. Furthermore, the rates of the 1,2-shifts were found to be strongly dependent on the nature of the substituent on N(1). The more electron-withdrawing the substituent on N(1), the faster the rearrangement[14]. This is exactly what we observed for the rearrangement **6** → **7**: the *N(1)-tert*-butyl-substituted compounds **6** are stable at room temperature, while salts **6** with the electron-withdrawing trichlorophenyl substituent on

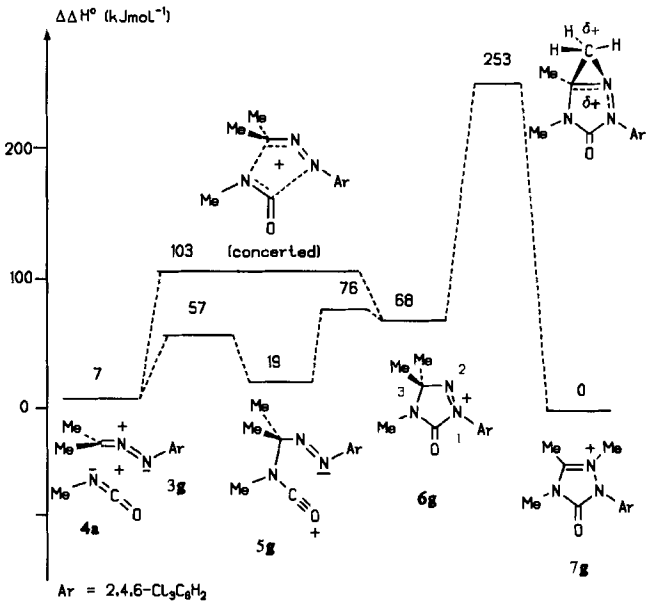


Figure 1. AM1-calculated heats of formation for the reaction **3g** + **4a** → **7g**, relative to ΔH_f^0 = 889 kJmol^{-1} for **7g**

N(1) rearrange to **7**. An ethyl, isopropyl, or a benzyl group migrates in preference to methyl. The differences in the migratory aptitudes are large enough to prevent formation of mixtures of products. Gstach's mechanism for the 1,2-shift requiring an unsubstituted N(4)[14] cannot be correct.

The rearrangements **6a, g** → **7a, g** were simulated by AM1 calculations [reaction coordinate: distance C(3)–CH$_3$]. The calculated activation enthalpies [185 kJmol^{-1} for **6g** → **7g** (Figure 1), and 210 kJmol^{-1} for **6a** → **7a**] are too high. The calculations did not take into account solvation of the rather polar transition structures (**6a**: dipole moment 2.42 D, transition structure **6a** → **7a**: dipole moment 7.28 D). In agreement with the experiment the enthalpy to activation for **6a** is higher than for **6g** reflecting the different electron deficiencies of N(2) (**6a**: net atomic charge: +0.10 e, **6g**, +0.13 e). In the transition structures the migrating methyl group is planar. Going from **6a** to the transition structure **6a** → **7a** the positive charge of the migrating methyl group increases from +0.14 to +0.55 e. Geometrically, the transition structures resemble π complexes of a methyl cation and a N(2)–C(3) double bond. This is exactly what we calculated for 1,2-alkyl shifts in other saturated and unsaturated five-membered heterocycles[8,9] suggesting similar mechanisms in all cases. Pericyclic [1,5]-sigmatropic mechanisms seem unlikely for rearrangements **6** → **7** because conjugated double bonds for a cation **6** can only be drawn invoking unlikely canonical forms. Rather, the shifts can be regarded as generalized Wagner-Meerwein rearrangements, that is, the rate of the alkyl migration increases a) with increasing ability of the migrant to stabilize a positive charge, and b) with increasing electron deficiency of an atom [here N(2)] adjacent to the center, to which the migrant was originally bound[30,31]. It has been reported by Warkentin and Gstach[16,32,33] that a migrant forming an extraordinarily stable carbenium ion

can escape from the coordination sphere of the heterocycle to undergo intermolecular alkylation reactions.

This work was supported by the *Fonds der Chemischen Industrie*. We thank Mr. *S. Herzberger* for technical assistance.

Experimental

Melting points: uncorrected. – IR: Mattson Polaris FT-IR spectrometer. – ^1H and ^{13}C NMR: Bruker WM 250 and AC 250 spectrometers (Table 1). – All experiments were carried out with exclusion of moisture in solvents dried by standard methods. The hydrazones **1** and the α-chloroalkylazo compounds **2** were prepared according to the general procedures given in ref.[6]

Phenylacetone (2,4,6-Trichlorophenyl)hydrazone (**1u**): From phenylacetone (13.42 g, 100 mmol) and (2,4,6-trichlorophenyl)hydrazine (21.15 g, 100 mmol)[6]. Recrystallization of the product from hot EtOH (40 ml) afforded pale brown prisms (29.49 g; 90%); m.p. 80–85°C. According to the ^{13}C-NMR spectrum the compound was a 1:1 mixture of the geometrical isomers. – $C_{15}H_{13}Cl_3N_2$ (327.6): calcd. C 54.99, H 4.00, N 8.55; found C 54.59, H 4.05, N 8.50.

(1-Chloro-1-methyl-2-phenylethyl)(2,4,6-trichlorophenyl)diazene (**2u**): From **1u** (32.76 g, 100 mmol). The oily product (34.40 g, 95%) slowly solidified at −20°C. – $C_{15}H_{12}Cl_4N_2$ (362.1): calcd. C 49.76, H 3.34, N 7.73; found C 49.69, H 3.35, N 7.44.

Formation of the Triazolium Salts **6**, **7** *from the α-Chloroalkylazo Compounds* **2** *and Isocyanates* **4**. *General Procedure:* 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 **2** (10 mmol) and **4** (12 mmol) in CH_2Cl_2 (20 ml). After stirring at −60°C for 1 h and then at 0°C for 75 min and finally at 23°C for 10 min the mixture was cooled to −20°C and ether (80 ml) was added dropwise. The product was filtered off.

1-tert-Butyl-4,5-dihydro-3,3,4-trimethyl-5-oxo-3H-1,2,4-triazolium Hexachloroantimonate (**6a**): From **2a**[6] (1.63 g, 10 mmol) and **4a** (0.69 g, 12 mmol). After stirring at 0°C for 90 min a colorless powder (3.73 g, 72%) was filtered off. Precipitation at −20°C from CH_3CN (12 ml)/ether (20 ml) afforded a colorless powder; m.p. 133–136°C (dec.). – $C_9H_{18}Cl_6N_3OSb$ (518.7): calcd. C 20.84, H 3.50, N 8.10; found C 20.85, H 3.50, N 8.05.

1-tert-Butyl-4,5-dihydro-3,3-dimethyl-5-oxo-4-propyl-3H-1,2,4-triazolium Hexachloroantimonate (**6b**): From **2a** (1.63 g, 10 mmol) and **4b** (1.02 g, 12 mmol). Yield: 4.92 g (90%) of a pale yellow powder. Crystallization at −20°C from CH_2Cl_2 (6 ml)/ether (10 ml) afforded a colorless powder (4.53 g); m.p. 96–98°C (dec.). – $C_{11}H_{22}Cl_6N_3OSb$ (546.8): calcd. C 24.16, H 4.06, N 7.68; found C 24.17, H 4.01, N 7.58.

1-tert-Butyl-4,5-dihydro-3,3-dimethyl-5-oxo-4-phenyl-3H-1,2,4-triazolium Hexachloroantimonate (**6c**): From **2a** (1.63 g, 10 mmol) and **4c** (1.43 g, 12 mmol). Yield: 4.78 g (82%) of an orange powder. Reprecipitation at −20°C from CH_2Cl_2 (25 ml)/ether (10 ml) afforded an orange powder (4.68 g); m.p. 116–120°C (dec.). – $C_{14}H_{20}Cl_6N_3OSb$ (580.8): calcd. C 28.95, H 3.47, N 7.23; found C 28.73, H 3.50, N 6.97.

1-tert-Butyl-4-(4-chlorophenyl)-4,5-dihydro-3,3-dimethyl-5-oxo-3H-1,2,4-triazolium Hexachloroantimonate (**6d**): From **2a** (1.63 g, 10 mmol) and **4d** (1.84 g, 12 mmol). Yield: 4.16 g (68%) of an orange powder. Reprecipitation at −20°C from CH_2Cl_2 (15 ml)/ether (10 ml) afforded yellow crystals (3.06 g), which soon turned orange; m.p. 112–116°C (dec.). – $C_{14}H_{19}Cl_7N_3OSb$ (615.3): calcd. C 27.33, H 3.11, N 6.83; found C 25.56, H 2.89, N 6.93.

4,5-Dihydro-2,3,4-trimethyl-5-oxo-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7g**): From **2g** (2.86 g, 10 mmol) and **4a** (0.69 g, 12 mmol). Reprecipitation from CH_3CN (15 ml)/ether (25 ml) afforded a colorless powder (5.78 g, 90%); m.p. 166–167°C. – $C_{11}H_{11}Cl_9N_3OSb$ (642.1): calcd. C 20.58, H 1.73, N 6.54; found C 20.58, H 1.82, N 6.31.

4,5-Dihydro-2,3-dimethyl-5-oxo-4-propyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7h**): From **2g** (2.86 g, 10 mmol) and **4b** (1.02 g, 12 mmol). Reprecipitation at −20°C from CH_3CN (15 ml)/ether (50 ml) afforded a colorless crystalline powder (6.23 g, 93%); m.p. 167–170°C. – $C_{13}H_{15}Cl_9N_3OSb$ (670.1): calcd. C 23.30, H 2.26, N 6.27; found C 23.39, H 2.21, N 6.34.

4,5-Dihydro-2,3-dimethyl-5-oxo-4-propyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Tetrachloroaluminate (**7i**): A solution of **2g** (2.86 g, 10 mmol) in CH_2Cl_2 (10 ml) was added at −60°C to a suspension of $AlCl_3$ (1.33 g, 10 mmol) in CH_2Cl_2 (10 ml). After 5 min a solution of **4b** (1.02 g, 12 mmol) in CH_2Cl_2 (5 ml) was added. After stirring at −60°C for 1 h and then at 0°C for 90 min CCl_4 (40 ml) was added. Filtration afforded a moisture-sensitive pale yellow powder (4.45 g, 88%), which was crystallized at −20°C from CH_3CN (5 ml)/ether (15 ml) to furnish a colorless powder; m.p. 148–151°C (dec.). – $C_{13}H_{15}AlCl_7N_3O$ (504.4): calcd. C 30.95, H 3.00, N 8.33; found C 31.23, H 3.14, N 8.37.

2,3,5,6,7,8-Hexahydro-3-methyl-2-oxo-1-(2,4,6-trichlorophenyl)-1H,4H-[1,2,4]triazolo[1,5-a]azepinium Hexachloroantimonate (**7j**): From **2j**[6] (3.26 g, 10 mmol) and **4a** (0.69 g, 12 mmol). After stirring at 23°C for 30 min the reaction mixture was concentrated to a volume of 30 ml. At −20°C fine brown needles precipitated, which were recrystallized at −20°C from CH_2Cl_2 (20 ml) to give colorless needles (5.64 g, 83%); m.p. 172–174°C (dec.). – $C_{14}H_{15}Cl_9N_3OSb$ (682.1): calcd. C 24.65, H 2.22, N 6.16; found C 24.43, H 2.27, N 6.12.

4,5-Dihydro-2,3-dimethyl-5-oxo-4-phenyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7k**): From **2g** (2.86 g, 10 mmol) and **4c** (1.43 g, 12 mmol). After stirring at 0°C for 2 h 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; m.p. 193–196°C. – $C_{16}H_{13}Cl_9N_3OSb$ (704.1): calcd. C 27.29, H 1.86, N 5.97; found C 27.13, H 1.89, N 5.97.

4-(4-Chlorophenyl)-4,5-dihydro-2,3-dimethyl-5-oxo-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7l**): From **2g** (2.86 g, 10 mmol) and **4d** (1.84 g, 12 mmol). Reprecipitation from CH_3CN (15 ml)/ether (50 ml) afforded a colorless powder (5.74 g, 78%); m.p. 202–206°C. – $C_{16}H_{12}Cl_{10}N_3OSb$ (738.6): calcd. C 26.02, H 1.64, N 5.69; found C 25.93, H 1.69, N 5.67.

4-(3,4-Dichlorophenyl)-4,5-dihydro-2,3-dimethyl-5-oxo-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7m**): From **2g** (2.86 g, 10 mmol) and **4m** (2.26 g, 12 mmol). Reprecipitation from CH_3CN (15 ml)/ether (100 ml) afforded brownish leaflets (6.52 g, 84%); m.p. 187–191°C. – $C_{16}H_{11}Cl_{11}N_3OSb$ (773.0): calcd. C 24.86, H 1.43, N 5.44; found C 24.71, H 1.49, N 5.34.

4,5-Dihydro-2,3-dimethyl-4-(2-methylphenyl)-5-oxo-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7n**): From **2g** (2.86 g, 10 mmol) and **4n** (1.60 g, 12 mmol). Reprecipitation at −20°C from CH_3CN (15 ml)/ether (100 ml) afforded colorless needles (5.08 g, 71%); m.p. 189–192°C. – $C_{17}H_{15}Cl_9N_3OSb$ (718.1): calcd. C 28.43, H 2.11, N 5.85; found C 28.27, H 2.09, N 5.74.

Table 1. Selected NMR and IR data for the new compounds

No. IR[a]	^{1}H NMR (CD_3CN, 295 K) δ, J[Hz] [b]	^{13}C NMR (CD_3CN, 295 K) δ[b]
1u 1460, 3335[c]	1.84, 2.07 (CH_3), 3.53, 3.73 (CH_2), 6.96 (NH), 7.22-7.37 (aryl) [d,e]	14.2, 24.3, 36.9, 45.1 (CH_3,CH_2), 152.3, 153.1 (C=N) [d,e]
2u 1547, 1571[c]	1.91 (CH_3), 3.54 (q, J=13.9, CH_2), 7.30 (m, phenyl), 7.38 (aryl) [d]	28.0 (CH_3), 48.1 (CH_2), 96.8 (CCl), 126.9, 127.3, 128.1, 128.9, 131.2, 133.6, 134.6, 145.7 [d]
6a 1837	1.88 (9H), 1.89 (6H), 3.16 (CH_3)	22.5 (2C), 27.1 (3C), 29.2 (CH_3), 79.0, 97.5 (C), 148.2 (C=O)
6b 1837	0.98 (t, J=7.4), 1.88 (9H), 1.91 (6H) (CH_3), 1.75 (m), 3.53 (m, CH_2)	11.4, 21.0, 22.9 (2C), 27.1 (3C), 46.0 (CH_3, CH_2), 78.8, 97.7 (C), 148.4 (C=O)
6c 1837	1.96 (15 H, CH_3), 7.43-7.68 (phenyl)	23.3 (2C), 27.4 (3C) (CH_3), 80.0, 98.6 (C), 128.3, 131.0, 131.5, 132.0 (phenyl), 147.6 (C=O) [f]
6d 1829	1.95 (15 H, CH_3), 7.43-7.72 (aryl) [f]	23.1 (2C), 27.4 (3C) (CH_3), 80.2, 98.8 (C), 129.9, 130.5, 131.8, 137.7 (aryl), 147.7 (C=O) [f]
7g 1775	2.71, 3.49, 3.57 (CH_3), 7.84 (aryl)	12.5, 30.4, 35.2 (CH_3), 124.3, 131.2, 138.6, 141.3, 148.4, 155.2 (aryl, C=N, C=O)
7h 1775	1.00 (t, J=7.3), 2.73, 3.57 (CH_3), 1.81 (m), 3.93 (t, J=7.3) (CH_2), 7.83 (aryl)	11.1, 12.4, 22.2, 35.2, 46.2 (CH_3, CH_2), 124.2, 131.0, 138.4, 141.2, 148.3, 154.6 (aryl, C=N, C=O)
7i 1787[g]	1.00 (t, J=7.4), 2.71, 3.55 (CH_3), 1.81 (m), 3.92 (t, J=7.3) (CH_3), 7.83 (aryl)	11.1, 12.4, 22.2, 35.2, 46.3 (CH_3, CH_2), 124.4, 131.2, 138.7, 141.4, 148.6, 154.9 (aryl, C=N, C=O)
7j 1779	3.52 (CH_3), 1.85-1.98 m, 6H), 3.20 (m, 2H), 3.97 (m, 2H) (CH_2), 7.82 (aryl)	22.9, 26.2, 26.3, 28.6, 30.4, 51.1 (CH_3, CH_2), 124.2, 131.1, 138.8, 141.3, 148.5, 159.4 (aryl, C=N, C=O)
7k 1771	2.59, 2.67 (CH_3), 7.87 (aryl)	13.3, 35.6 (CH_3), 148.0, 155.0 (C=O, C=N)
7l 1787	2.63, 3.69 (CH_3), 7.55 (m), 7.71 (m) (4-ClC_6H_4), 7.85 (2,4,6-$Cl_3C_6H_2$)	13.3, 35.7 (CH_3), 124.1, 128.8, 130.1, 131.2, 131.6, 138.2, 138.6, 141.6, 147.6, 154.8 (aryl, C=N, C=O)
7m 1787	2.66, 3.71 (CH_3), 7.85 (2,4,6-$Cl_3C_6H_2$)	13.4, 35.8 (CH_3), 124.0, 128.5, 129.4, 130.5, 131.2, 133.3, 134.8, 136.8, 138.6, 141.7, 147.3, 154.7 (aryl, (C=N, C=O)
7n 1767	2.30, 2.55, 3.70 (CH_3), 7.84 (2,4,6-$Cl_3C_6H_2$)	13.0, 17.6, 35.8 (CH_3), 123,8, 128.8, 128.9, 131.0, 131.1, 132.9, 137.4, 138.2, 138.7, 141.4, 147.0, 154.6 (aryl, C=N, C=O)
7o[h]	1.77 (9 H), 2.83 (3H), 3.56 (3H) (CH_3), 7.82 (aryl)	
7p 1756	2.69, 3.53 (CH_3), 7.82 (aryl), 10.25 (NH)	12.7, 35.1 (CH_3), 124.2, 131.1, 138.7, 141.3 (aryl), 147.6, 154.4 (C=N, C=O)
7q 1756	1.00 (t, J=7.5), 1.27 (t, J=7.3), 2.77 (CH_3), 1.82 (m), 3.92 (t, J=7.4), 4.04 (q, J=7.3) (CH_2), 8.10 (aryl)	11.2, 12.2, 14.0, 22.1, 45.0, 46.3 (CH_3, CH_2), 124.5, 131.3, 138.4, 141.3, 148.7, 154.4 (aryl, C=N, C=O)
7r 1775	1.52 (d, J=7.0), 2.78, 3.46 (CH_3), 4.32 (sept, J=7.0, CH), 7.83 (aryl)	13.4, 21.0 (2C), 30.1, 56.9 (CH_3, CH), 125.1, 131.3, 138.7, 141.4, 148.6, 154.9 (aryl, C=N, C=O)
7s 1771	1.36 (t, J=7.3), 2.63 (CH_3), 4.14 (q, J=7.3, CH_2), 7.85 (2,4,6-$Cl_3C_6H_2$)	13.0, 13.9, 45.5 (CH_3, CH_2), 124.5, 128.2, 130.0, 131.2, 131.3, 132.5, 138.4, 141.4, 148.0, 154.2 (aryl, C=N, C=O)
7t 1767	1.60 (d, J=7.0), 2.66 (CH_3), 4.43 (sept, J=7.0, CH), 7.86 (2,4,6-$Cl_3C_6H_2$)	14.1, 20.8, 57.6 (CH_3, CH), 125.0, 128.5, 129.9, 131.2, 131.3, 132.5, 138.7, 141.4, 148.2, 154.1 (aryl, C=N, C=O)
7u 1764	2.89, 3.53 (CH_3), 5.24 (CH_2), 7.01-7.41 (phenyl), 7.61 (aryl)	13.0, 30.6 (CH_3), 53.0 (CH_2), 124.6, 129.3, 129.8, 130.3, 130.5, 130.7, 138.4, 141.0, 148.1, 155.4 (aryl, C=N, C=O)
7v[i] 1574	0.97 (t, J=7.4), 2.61, 3.83 (CH_3), 1.82 (m), 4.08 (t, J=7.7) (CH_2), 9.59 (NH)	10.8, 11.1, 22.7, 38.1, 46.6 (CH_3, CH_2), 149.1, 156.3 (C=N, C=O)
8a 1459	1.65 (6H), 1.79 (9H), 1.91 (6H) (CH_3), 2.28 (CH_2)	27.2 (2C), 29.9 (2C), 30.3 (3C) (CH_3), 49.4 (CH_2), 81.8, 84.4, 100.0 (C)
8g 1567	1.91 (6H), 1.93 (6H) (CH_3), 2.58 (CH_2), 7.88 (aryl)	28.0, 28.9 (CH_3), 45.7 (CH_2), 91.3, 105.5 (C), 131.7, 131.8, 133.2[j], 140.7 (aryl) [k]
9[l] 1644	0.94 (t, J=7.4), 2.55, 3.74 (CH_3), 1.72 (m), 3.84 (t, J=7.4) (CH_2), 9.76 (NH) [f]	10.5, 11.1, 22.5, 37.6, 46.1 (CH_3, CH_2), 149.8, 155.4 (C=O, C=N) [f]
10 1567	2.45 (CH_3), 4.21 (CH_2), 6.39 (m, 1H), 7.23 (m, 3H) (phenylene), 7.81 (2,4,6-$Cl_3C_6H_2$), 12.65 (NH)	21.6 (CH_3), 32.6 (CH_2), 113.5, 114.3, 127.4, 129.7, 130.1, 131.2, 131.7, 136.1, 138.8, 139.6 (aryl), 165.0 (C=N)
11 1567	3.08 (CH_3), 9.28 (H4), 7.92 (2,4,6-$Cl_3C_6H_2$), 7.87 (m), 8.27 (m), 8.37 (m), 8.55 (m) (phenylene) [m]	22.1 (CH_3), 118.7, 130.9, 131.4, 133.7, 134.8, 136.2, 136.3, 140.6, 141.4, 143.0, 144.6, 159.7 (aryl) [m]

[a] In KBr, cm^{-1}. – [b] TMS as internal standard. – [c] In CCl_4. – [d] In $CDCl_3$. – [e] Mixture of the geometric isomers. – [f] At 263 K. – [g] In CH_2Cl_2. – [h] Spectrum read from a mixture of **7o**, **7p**, and **8g**. – [i] The isomeric constitution **9** cannot be excluded. The data are extracted from the spectra of a mixture of **7v** and **9**. – [j] Broad. – [k] At 273 K. – [l] The isomeric constitution **7v** cannot be excluded. – [m] At 353 K.

4-tert-Butyl-4,5-dihydro-2,3-dimethyl-5-oxo-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7o**), *4,5-Dihydro-2,3-dimethyl-5-oxo-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate* (**7p**), *and 4,5-Dihydro-3,3,5,5-tetramethyl-1-(2,4,6-trichlorophenyl)-3H-pyrazolium Hexachloroantimonate* (**8g**): From **2g** (2.86 g, 10 mmol) and **4e** (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) consisted of a mixture of **7o**, **p** and **8g**, integral ratio 8:4:1.

7p: From **2g** (2.86 g, 10 mmol) and trimethylsilyl isocyanate (1.38 g, 12 mmol). After stirring at 0°C for 3 h 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 1 h 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 12 h afforded a pale ochreous powder (2.64 g, 42%); m.p. 250−252°C (dec.). − $C_{10}H_9Cl_9N_3OSb$ (628.0): calcd. C 19.12, H 1.44, N 6.69; found C 19.12, H 1.48, N 6.43.

2-Ethyl-4,5-dihydro-3-methyl-5-oxo-4-propyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7q**): From **2q**[6] (3.00 g, 10 mmol) and **4b** (1.02 g, 12 mmol). After stirring at 0°C for 1 h a colorless powder (6.36 g, 93%) was precipitated at −20°C by slow addition of ether (100 ml). Crystallization at −20°C from CH_2Cl_2 (15 ml)/ether (50 ml) afforded fine colorless prisms (5.22 g); m.p. 171−173°C. − $C_{14}H_{17}Cl_9N_3OSb$ (684.1): calcd. C 24.58, H 2.50, N 6.14; found C 24.19, H 2.43, N 5.98.

4,5-Dihydro-2-isopropyl-3,4-dimethyl-5-oxo-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7r**): From **2r**[6] (3.14 g, 10 mmol) and **4a** (0.69 g, 12 mmol). Yield: 4.83 g (72%) of a pale yellow powder, which was crystallized at −20°C from acetonitrile (10 ml)/CCl_4 (20 ml) to afford colorless needles (2.42 g); m.p. 214−216°C (dec.). − $C_{13}H_{15}Cl_9N_3OSb$ (670.1): calcd. C 23.30, H 2.26, N 6.27; found C 23.45, H 2.34, N 6.05.

2-Ethyl-4,5-dihydro-3-methyl-5-oxo-4-phenyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7s**): From **2q** (3.00 g, 10 mmol) and **4c** (1.43 g, 12 mmol). Yield: 5.98 g (83%) of an orange powder, which was crystallized at −20°C from warm acetonitrile (12 ml) to afford colorless needles (5.66 g); m.p. 208−210°C (dec.). − $C_{17}H_{15}Cl_9N_3OSb$ (718.1): calcd. C 28.43, H 2.11, N 5.85; found C 28.40, H 2.11, N 5.86.

4,5-Dihydro-2-isopropyl-3-methyl-5-oxo-4-phenyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7t**): From **2r** (3.14 g, 10 mmol) and **4c** (1.43 g, 12 mmol). Yield: 6.22 g (85%) of a pale yellow powder, which was crystallized at −20°C from warm acetonitrile (16 ml)/ether (40 ml) to afford a colorless powder (4.11 g); m.p. 205−208°C (dec.). − $C_{18}H_{17}Cl_9N_3OSb$ (732.2): calcd. C 29.53, H 2.34, N 5.74; found C 29.38, H 2.33, N 5.70.

2-Benzyl-4,5-dihydro-3,4-dimethyl-5-oxo-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7u**): From **2u** (3.62 g, 10 mmol) and **4a** (0.69 g, 12 mmol). Yield: 6.48 g of a yellow powder. According to the ^{1}H-NMR spectrum this product consisted of a mixture of **7u**, **10**, and **11** (ratio 3.1:1.1:1.0). The product was suspended in CH_2Cl_2 (20 ml). Decantation and stirring of the residue under CH_2Cl_2 (20 ml) afforded a colorless powder (4.24 g, 59%); m.p. 201−204°C (dec.). − $C_{17}H_{15}Cl_9N_3OSb$ (718.2): calcd. C 28.43, H 2.11, N 5.85; found C 28.41, H 2.12, N 5.78.

1-tert-Butyl-4,5-dihydro-3,3,5,5-tetramethyl-3H-pyrazolium Hexachloroantimonate (**8a**)

a) From **2a** (1.63 g, 10 mmol) and **4e** (1.19 g, 12 mmol). The reaction mixture was stirred at 25°C for 40 min during which the color changed from yellow to orange. Slow addition of ether (40 ml) afforded a colorless precipitate of **8a** (2.54 g, 49%). Slow addition of ether (40 ml) to the mother liquor furnished a greenish powder (1.42 g, 28%), which according to the ^{1}H-NMR spectrum (CD_3CN) consisted mainly of one compound, probably **6f** [1.86 (s, 9H), 1.88 (s, 6H), 9.70 (NH)]. The compound was not obtained in pure form.

b) From **2a** (1.63 g, 10 mmol) and isobutene (ca. 0.67 g, 12 mmol) according to the general procedure. Yield: 3.02 g (58%) of a pale yellow powder, which was reprecipitated at −20°C from CH_2Cl_2 (80 ml)/ether (60 ml) to give a colorless powder; m.p. 120−162°C (dec.): − $C_{11}H_{23}Cl_6N_2Sb$ (517.8): calcd. C 25.51, H 4.48, N 5.41; found C 25.21, H 4.42, N 5.17.

4,5-Dihydro-3,3,5,5-tetramethyl-1-(2,4,6-trichlorophenyl)-3H-pyrazolium Hexachloroantimonate (**8g**): From **2g** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and isobutene (0.67 g, 12 mmol) as described in the general procedure for the preparation of the triazolium salts **7**. After stirring at 0°C for 2 h the product was precipitated from the dark green solution by slow addition of ether (100 ml) affording a yellow powder (2.69 g, 42%), which was crystallized at −20°C from acetonitrile/ether; m.p. 182−184°C (dec.). − $C_{13}H_{16}Cl_9N_2Sb$ (641.1): calcd. C 24.35, H 2.52, N 4.37; found C 24.10, H 2.41, N 4.28.

4,5-Dihydro-1,3-dimethyl-5-oxo-4-propyl-1H-1,2,4-triazolium (**9**) *or 4,5-Dihydro-2,3-dimethyl-5-oxo-4-propyl-1H-1,2,4-triazolium Hexachloroantimonate* (**7v**): A solution of **6b** (5.47 g, 10 mmol) in 1,2-dichloroethane (50 ml) was boiled under reflux for 5 h. The solvent was evaporated under reduced pressure. The oily residue consisted according to the ^{1}H-NMR spectrum of a mixture (3:1) of two isomers. Two crystallizations at −20°C from CH_2Cl_2 (10 ml each) afforded the pure minor isomer, probably **9**. Yield: 0.69 g (14%) of yellow prisms; m.p. 128−134°C. − $C_7H_{14}Cl_6N_3OSb$ (490.7): calcd. C 17.13, H 2.88, N 8.57; found C 17.37, H 3.16, N 8.41.

3-Methyl-1-(2,4,6-trichlorophenyl)cinnolinium Tetrachloroantimonate (**11**): From **2u** (3.62 g, 10 mmol) as described for **7u**, however without addition of **4a**. Yield: 6.08 g of **10** as an air-sensitive orange powder; m.p. 85−88°C (dec. giving **11**). The product was dissolved in CH_2Cl_2 (250 ml). The solution was cooled in an ice bath while oxygen was bubbled through the mixture for 1 h. An exothermic reaction took place, and **11** started to precipitate. The mixture was left at −20°C for 12 h. Filtration afforded a yellow powder (4.98 g, 85%) sparingly soluble in most organic solvents; m.p. 213−220°C (dec.). − $C_{15}H_{10}Cl_7N_2Sb$ (588.2): calcd. C 30.63, H 1.71, N 4.76; found C 30.64, H 1.78, N 4.80.

[1] S. Patai (Ed.), *The Chemistry of Cyanates and their Thio Derivatives*, Part I + II, J. Wiley, New York, **1977**.
[2] J. C. Bottaro, P. E. Penwell, R. J. Schmitt, *Synthetic Commun.* **1991**, *21*, 945−949.
[3] L. V. Cherednichenko, B. A. Ledebev, B. V. Gidaspov, *Zh. Org. Khim.* **1978**, *14*, 735−737.
[4] A. El-Hamid Ismail, A. Hamed, M. Taha Abdel-Aal, I. Zeid, M. Al-Talib, Q. Wang, J. C. Jochims, *J. Prakt. Chem.* **1992**, *334*, 661−668, and references therein.
[5] J. C. Jochims, C. Troll, H. Fischer, Q. Wang, A. Hamed, A. El-Hamid Ismail, M. Taha Abdel-Aal, I. Zeid, M. Al-Talib, *J. Prakt. Chem.* **1992**, *334*, 669−675, and references therein.
[6] Q. Wang, J. C. Jochims, S. Köhlbrandt, L. Dahlenburg, M. Al-Talib, A. Hamed, A. El-Hamid Ismail, *Synthesis* **1992**, 710−718.
[7] Q. Wang, A. Amer, S. Mohr, E. Ertel, J. C. Jochims, *Tetrahedron* **1993**, *49*, 9973−9986.

[8] Q. Wang, A. Amer, C. Troll, H. Fischer, J. C. Jochims, *Chem. Ber.* **1993**, *126*, 2519–2524.
[9] Q. Wang, M. Al-Talib, J. C. Jochims, *Chem. Ber.* **1994**, *127*, 541–547.
[10] H. Gstach, P. Seil, J. G. Schantl, A. Gieren, Th. Hübner, J. Wu, *Angew. Chem.* **1986**, *98*, 1111–1112; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1132–1133.
[11] J. G. Schantl, N. Lanznaster, H. Gstach, *Heterocycles* **1990**, *31*, 833–840.
[12] J. G. Schantl, N. Lanznaster, H. Gstach, *Heterocycles* **1990**, *31*, 825–832.
[13] H. Schildknecht, G. Hatzmann, *Angew. Chem.* **1969**, *81*, 469; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 456.
[14] H. Gstach, P. Seil, *Synthesis* **1990**, 803–808.
[15] H. Gstach, P. Seil, *Synthesis* **1990**, 808–815.
[16] H. Gstach, P. Seil, *Synthesis* **1990**, 1048–1053.
[17] M. W. Moon, *J. Org. Chem.* **1972**, *37*, 383–385.
[18] M. W. Moon, *J. Org. Chem.* **1972**, *37*, 386–390.
[19] M. W. Moon, *J. Org. Chem.* **1972**, *37*, 2005–2009.
[20] Cycloadditions of olefins to 1-aza-2-azoniaallene salts **3** will be reported in detail in a forthcoming paper.
[21] M. J. S. Dewar, C. Jie, J. Yu, *Tetrahedron* **1993**, *49*, 5003–5038.
[22] *MOPAC program*, version 6.0, J. P. Stewart, QCPE #455. The calculations were carried out with complete optimization of all bond lengths, bond angles, and dihedral angles.
[23] W. Warthmann, A. Schmidt, *Z. Anorg. Allg. Chem.* **1975**, *418*, 61–64.
[24] J. Lambrecht, L. Zsolnai, G. Huttner, J. C. Jochims, *Chem. Ber.* **1981**, *114*, 3655–3666.
[25] R. Abu-El-Halawa, J. C. Jochims, *Chem. Ber.* **1983**, *116*, 1834–1847.
[26] R. Sustmann, *Tetrahedron Lett.* **1971**, 2717–2720.
[27] S. Parsons, J. Passmore, M. J. Shriver, X. Sun, *Inorg. Chem.* **1991**, *30*, 3342–3348.
[28] N. Burford, J. P. Johnson, J. Passmore, M. J. Schriver, P. S. White, *J. Chem. Soc., Chem. Commun.* **1986**, 966–968.
[29] S. W. Liblong, R. T. Oakley, A. W. Cordes, M. C. Noble, *Can. J. Chem.* **1983**, *61*, 2062–2067.
[30] V. A. Koptyug, V. G. Shubin, *Zh. Org. Khim.* **1980**, *16*, 1977–2008.
[31] V. G. Shubin, *Top. Curr. Chem.* **1984**, *116/117*, 267–341.
[32] M. W. Majchrzak, E. Jefferson, J. Warkentin, *J. Am. Chem. Soc.* **1990**, *112*, 2449–2451.
[33] E. A. Jefferson, J. Warkentin, *J. Am. Chem. Soc.* **1992**, *114*, 6318–6325.

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