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1,1-DIAMINOSUBSTITUTED 2-AZAALLENIUM SALTS: PREPARATION AND BARRIERS TO TOPOMERIZATION

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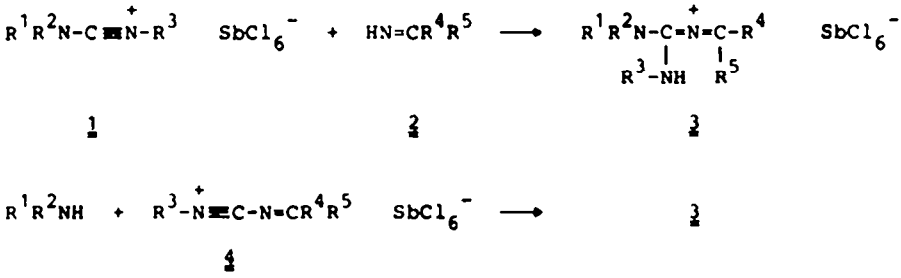
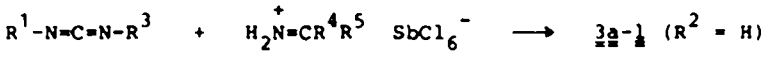
Abstract - Dialkylcarbodiimides, 5, react with iminium salts, 6, to afford the formal 1,1-diaminosubstituted 2-azaallenium salts 3. According to dynamic NMR measurements compounds 3 must be regarded as alkylidene-guanidinium salts A, undergoing a fast topomerization via a transition state B with allene geometry ($\Delta G^{\neq}_{265}$ = 45.9 ± 1 kJmol^{-1} for 3f) and a slower rotation around the peripheral C-N bonds (transition state C; $\Delta G^{\neq}_{290}$ = 58.0 ± 1 kJmol^{-1} for 3f).

2-Azaallenium salts form a relatively little known class of heterocumulenes [1], although recently some heterosubstituted 2-azaallenium compounds, e.g. Gold's salt [2], found interesting synthetic applications [3]. To our knowledge, only very few 1,1-diaminosubstituted formal 2-azaallenium salts, 3, have been described in the literature. An old example is the monoprotonated biguanide [4]. Gompper et al.[5] prepared several tri- and tetrasubstituted formal 1,1-diamino-2-azaallenium salts. Recently, we obtained some compounds 3 from reactions of cyanamidium salts 1 with imines 2 [6] and of alkylidene cyanamidium salts 4 with amines [7], respectively.



In this communication we describe a third new method for the preparation of 3 (R^2 = H) starting with dialkylcarbodiimides, 5, and iminium salts, 6, which are

readily accessible from α-chloroisocyanates [8,9]. Mixtures of 5 and 6 in dichloromethane are stirred for several hours at room temperature to afford compounds 3 directly, in pure form and in high yields.



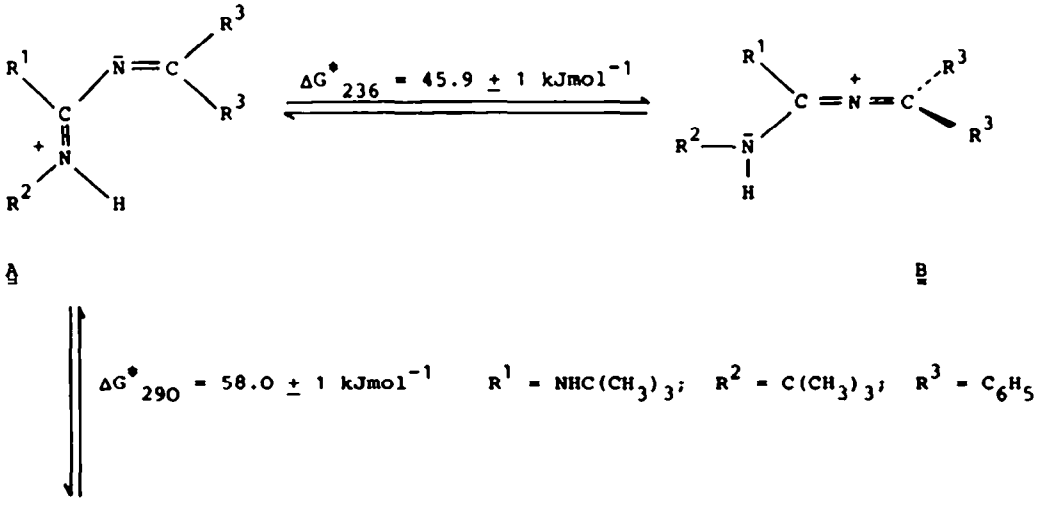
5 6

	R^1	R^3	R^4	R^5
a	$(CH_3)_2CH$	$(CH_3)_2CH$	$(CH_3)_3C$	C_6H_5
b	c-C_6H_{11}	c-C_6H_{11}	$(CH_3)_3C$	C_6H_5
c [7]	$(CH_3)_3C$	$(CH_3)_3C$	$(CH_3)_3C$	C_6H_5
d	$(CH_3)_2CH$	$(CH_3)_2CH$	C_6H_5	C_6H_5
e	c-C_6H_{11}	c-C_6H_{11}	C_6H_5	C_6H_5
f	$(CH_3)_3C$	$(CH_3)_3C$	C_6H_5	C_6H_5
g	$(CH_3)_2CH$	$(CH_3)_2CH$	α-$C_{10}H_7$	C_6H_5
h	c-C_6H_{11}	c-C_6H_{11}	α-$C_{10}H_7$	C_6H_5
i [7]	$(CH_3)_3C$	$(CH_3)_3C$	α-$C_{10}H_7$	C_6H_5
j	$(CH_3)_2CH$	$(CH_3)_2CH$	2-C_6H_4-C_6H_4-2'	
k	c-C_6H_{11}	c-C_6H_{11}	2-C_6H_4-C_6H_4-2'	
l	$(CH_3)_3C$	$(CH_3)_3C$	2-C_6H_4-C_6H_4-2'	

The NMR spectra of all compounds 3 are temperature dependent. For instance, below 230 K the ^{13}C NMR spectra of 3f show signals of equal intensities for two different tert-butyl groups und two unequal phenyl units. In the ^1H NMR spectra two lines (integrals 1:1) for the tert-butyl protons are observed. Equal intensities of the signals can hardly be explained by assuming intermolecular equilibria. Instead it would appear likely that the phenyl and tert-butyl groups within a molecule 3f unequal. Different chemical surroundings of the phenyl groups definitely rule out an allenium geometry B for 3f but are in agreement with several comformations of an alkylideneguanidinium cation, of which the conformer A f should be preferred for sterical reasons (for other compounds 3, e.g. 3l, equilibria between two conformations are observed). Above 240 K the exchange of the two phenyl groups, and above 310 K also the exchange of the tert-butyl groups was registered as fast on the NMR time scale. The barriers to activation were calculated as reported in the Scheme, viz. at the coalescence temperatures for the different pairs of ^{13}C respectively ^1H resonances. The spectra can be interpreted by assuming a fast stereomutation of A via a transition state B, accompanied by a slower topomerization passing over a transition state of a geometry C. Recent ab initio and MNDO calculations [10] predict that the unsubstituted 1,1-diamino-2-aza-

allenium ion **B** ($R^1 = NH_2$, $R^2 = R^3 = H$) should be less stable than the 2-azaallenium form **A** ($R^1 = NH_2$, $R^2 = R^3 = H$), while on the other hand, for the monoamino substituted formal 2-azaallenium salts the allenium form **B** ($R^1 = R^2 = R^3 = H$) is predicted to be more stable than **A** ($R^1 = R^2 = R^3 = H$). Both predictions have now been verified experimentally [6].

Scheme



A **B**

C **3f**

DNMR Parameters for **3f**

Nucleus	Coalescence Temperature T_c [K]	Shift Difference $\Delta\nu$ [Hz]	$\Delta G^*_{T_c}$ c) [kJmol^{-1}]
CH_3 a)	294	96	58.9
CH_3 b)	283	77	57.1
o- or p-phenyl b)	235	120	46.2
p- or o-phenyl b)	237	209	45.5

a) 250 MHz ^{1}H NMR in CD_3CN.

b) 63 MHz NMR in CD_3CN.

c) Calculated from the equation $\Delta G^*_{T_c} = 8.3144 \cdot 10^{-3} T(\ln T - \ln(\pi\Delta\nu)/\sqrt{2} + 23.7601)$.

EXPERIMENTAL SECTION

IR spectra: Perkin-Elmer IR 299, always solutions in CH_2Cl_2. ^1H and ^{13}C NMR spectra: Bruker WM-250 spectrometer, δ-scale, internal reference tetramethylsilane, always solutions in CD_3CN at 303 K. The melting points are uncorrected.

General Procedure for the Preparation of 3a-l: To 2.00 mmol of the iminium salt 6 in anhydrous dichloromethane (20 ml) a solution of the carbodiimide 5 (2.06 mmol) in anhydrous dichloromethane (5 ml) was added. After stirring for three to eight hours at +22°C (till complete disappearance of the carbodiimide band in the IR spectrum) the product was precipitated by slow addition of ether (50 ml) (3d,i, j) or ether (50 ml)/pentane (20 ml). The stable salts 3 gave satisfactory elemental analyses without recrystallization. The compounds can be recrystallized from dichloromethane/ether.

N,N'-Diisopropyl-N"-(2,2-dimethyl-1-phenylpropylidene)guanidinium Hexachloroantimonate (3a): Yield 1.02 g (82%) of a colourless powder; m.p. 155-157°C (dec). IR: 1620, 1540, 3320, 3380 cm^{-1}. ^1H NMR: CH_3 δ = 0.89 (d, J = 7 Hz), 1.24 (d, J = 7 Hz), 1.28, CH 3.44 (m), 3.70 (m), NH 6.46 (d, J = 8 Hz), 6.62 (d, J = 8 Hz). ^{13}C NMR: CH_3 δ = 21.4, 22.3, 28.0, CH, C 42.5, 45.5, 48.0, C=N 160.6, 193.4, phenyl 126.7, 129.1, 130.5, 134.6. (Found: C, 34.90; H, 4.93; N, 6.68. Calc for $[C_{18}H_{30}N_3]SbCl_6$ (MW = 622.9): C, 34.70; H, 4.86; N, 6.75%).

N,N'-Dicyclohexyl-N"-(2,2-dimethyl-1-phenylpropylidene)guanidinium Hexachloroantimonate (3b): Yield 1.22 g (87%) of colourless crystals; m.p. 175-177°C (dec). IR: 1620, 1540, 3330, 3380 cm^{-1}. ^{13}C NMR: CH_3 δ = 28.2, CH_2 25.0, 25.5, 25.7, 32.0, 33.0, CH,C 42.5, 52.0, 66.1, C=N 160.5, 193.2, phenyl 126.6, 129.1, 130.6, 134.5. (Found: C, 41.20; H, 5.45; N, 5.92. Calc for $[C_{24}H_{38}N_3]SbCl_6$ (MW = 703.0): C, 41.00; H, 5.45; N 5.98%).

N,N'-Di-tert-butyl-N"-(2,2-dimethyl-1-phenylpropylidene)guanidinium Hexachloroantimonate (3c): Yield 1.11 g (85%) of colourless crystals; m.p. 155-157°C (dec) (Ref [7] 153-156°C). IR: 1600, 1620 (shoulder), 1540, 3400, 3430 cm^{-1}.

N,N'-Diisopropyl-N"-(diphenylmethylene)guanidinium Hexachloroantimonate (3d): Yield 1.04 g (81%) of a colourless powder; m.p. 167-169°C (dec). IR: 1620, 1580 (shoulder), 1540 (shoulder), 3340, 3380 (shoulder) cm^{-1}. ^1H NMR: CH_3 δ = 0.96 (d, J = 6 Hz), 1.27 (d, J = 6 Hz), CH 3.59 (m), 3.89 (m), NH 6.61 (d, J = 7 Hz), 6.73 (d, J = 8 Hz). ^{13}C NMR: CH_3 δ = 21.5, 22.4, CH 45.7, 48.1, C=N 160.5, 178.7, phenyl 129.6, 130.2, 133.5, 135.6. (Found: C, 37.53; H, 4.08; N, 6.46. Calc for $[C_{20}H_{26}N_3]SbCl_6$ (MW = 642.9): C, 37.36; H, 4.08; N, 6.54%).

N,N'-Dicyclohexyl-N"-(diphenylmethylene)guanidinium Hexachloroantimonate (3e): Yield 1.17 g (81%) of almost colourless crystals; m.p. 205-207°C (dec). IR: 1610, 1570 (shoulder), 1540 (shoulder), 3340, 3380 (shoulder). ^1H NMR: CH δ = 3.27 (m), 3.47 (m), NH 6.57 (d, J = 9 Hz), 6.72 (d, J = 9 Hz). ^{13}C NMR: CH_2 δ = 24.7, 25.4, 25.5, 25.6, 31.9, 33.1, CH 51.8, 54.7, C=N 160.3, 178.6, phenyl 129.5, 130.2, 133.3, 135.6. (Found: C, 43.21; H, 4.87; N, 5.88. Calc for $[C_{26}H_{34}N_3]SbCl_6$ (MW = 723.0): C, 43.19; H, 4.74; N, 5.81%).

N,N'-Di-tert-butyl-N"-(diphenylmethylene)guanidinium Hexachloroantimonate (3f): Yield 1.18 g (88%) of almost colourless prisms; m.p. 179-180°C (dec). IR: 1600, 1570 (shoulder), 1540 (shoulder), 3390, 3430 cm^{-1}. ^1H NMR: CH_3 δ = 1.34 (broad), NH 5.81 (broad), 6.19 (broad). ^{13}C NMR: CH_3 δ = 29.2 (broad), C 56.3 (broad), C=N 161.0, 178.1, phenyl 129.7, 130.9, 133.8, 135.6. (Found: C, 39.42; H, 4.80; N, 6.32. Calc for $[C_{22}H_{30}N_3]SbCl_6$ (MW = 671.0): C, 39.38; H, 4.51; N, 6.26%).

N,N'-Diisopropyl-N"-(α-naphthylphenylmethylene)guanidinium Hexachloroantimonate (3g): Yield 1.03 g (74%) of orange crystals; m.p. 167-169°C (dec). IR: 1610, 1570 (shoulder), 1540 (shoulder), 3330, 3390 cm^{-1}. ^1H NMR: CH_3 δ = 0.77 (broad), 1.12 (broad), CH 3.42 (m), 3.91 (m), NH 6.52 (broad). ^{13}C NMR: CH_3 δ = 21.4,

22.3, CH 45.6, 48.3, C=N 160.6, 179.4, aryl: 14 signals. (Found: C, 41.60; H, 4.08; N, 6.03. Calc for $[C_{24}H_{28}N_3]SbCl_6$ (MW = 693.0): C, 41.60; H, 4.07; N, 6.07%).

N,N'-Dicyclohexyl-N"-(α-naphthylphenylmethylene)guanidinium Hexachloroantimonate (3h): Yield 1.33 g (86%) of a yellow powder; m.p. 180-182°C (dec). IR: 1620, 1570, 1540 (shoulder), 3330, 3380 cm^{-1}. ^1H NMR: CH δ = 3.17 (m), 3.43 (m), NH 6.56 (broad). ^{13}C NMR: CH_2 δ = 24.7, 25.5, 31.9, 33.1, CH 51.9, 55.0, C=N 160.4, 179.1, aryl: 14 signals. (Found: C, 46.49; H, 4.97; N, 5.32. Calc for $[C_{30}H_{36}N_3]SbCl_6$ (MW = 773.1): C, 46.61; H, 4.69; N, 5.44%).

N,N'-Di-tert-butyl-N"-(α-naphthylphenylmethylene)guanidinium Hexachloroantimonate (3i): Yield 1.30 g (90%) of yellow prisms; m.p. 183-184°C(dec) (Ref [7] 185-187°C). IR: 1600, 1570, 3380, 3420 cm^{-1}. ^1H NMR: CH_3 δ = 0.89 (broad), 1.52 (broad), NH 5.70 (broad). ^{13}C NMR: CH_3 δ = 28.9 (broad), C ≈ 57 (broad), C=N 160.8, 179.1, aryl: 14 signals.

N"-(9-Fluorenylidene)-N,N'-diisopropylguanidinium Hexachloroantimonate (3j): Yield 0.99 g (77%) of orange prisms; m.p. 178-180°C (dec). IR: 1660, 1610, 1540, 3330 cm^{-1}. ^1H NMR: CH_3 δ = 1.24 (d, J = 6 Hz), 1.30 (d, J = 6 Hz), CH 3.85 (m), 3.94 (m), NH 7.00 (broad), 7.13 (broad). ^{13}C NMR: CH_3 δ = 21.7, 22.8, CH 46.0, 48.4, C=N 160.5, 171.3, aryl 122.4, 126.5, 130.2, 133.5, 136.2, 144.5. (Found: C, 37.56; H, 3.84; N, 6.54. Calc for $[C_{20}H_{24}N_3]SbCl_6$ (MW = 640.9): C, 37.48; H, 3.77; N, 6.56%).

N,N'-Dicyclohexyl-N"-(9-fluorenylidene)guanidinium Hexachloroantimonate (3k): Yield 1.24 g (86%) of a yellow powder; m.p. 205-206°C (dec). IR: 1660, 1610, 1540, 3330 cm^{-1}. ^1H NMR: CH δ = 3.46 (m), 3.74 (m), NH 7.01 (d, J = 8 Hz), 7.14 (d, J = 8 Hz). ^{13}C NMR: CH_2 δ = 23.6, 25.0, 25.5, 25.6, 32.1, 33.5, CH 52.3, 55.2, C=N 160.5, 171.3, aryl 122.3, 126.6, 130.1, 133.5, 136.2, 144.6. (Found: C, 43.25; H, 4.22; N, 5.76. Calc for $[C_{26}H_{32}N_3]SbCl_6$ (MW = 721.0): C, 43.31; H, 4.47; N, 5.83%).

N,N'-Di-tert-butyl-N"-(9-fluorenylidene)guanidinium Hexachloroantimonate (3l): Yield 1.15 g (86%) of orange crystals; m.p. 178-180°C (dec). IR: 1670, 1590, 1550 (shoulder), 3330 cm^{-1}. ^1H NMR: CH_3 δ = 1.38 (broad), NH 6.62 (broad). ^{13}C NMR: CH_3 δ = 29.4, C 56.5, C=N 162.1, 171.1, aryl 122.5, 127.0, 130.3, 133.4, 136.6, 144.7. (Found: C, 39.44; H, 4.04; N, 6.31. Calc for $[C_{22}H_{28}N_3]SbCl_6$ (MW = 668.9): C, 39.50; H, 4.22; N, 6.28%).

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REFERENCES

1 E.-U.Würthwein, Angew.Chem. 93, 110 (1981); Angew.Chem., Int.Ed.Engl. 20, 99 (1981).
2 H.Gold, Angew.Chem. 72, 956 (1960).
3 J.T.Gupton, M.J.Lizzi, and D.Polk, Synthet.Commun. 12, 939 (1982).
4 B.Rathke, Ber.Dtsch.Chem.Ges. 11, 967 (1878); 12, 776 (1879).
5 R.Gompper, and J.Schelble, Synthesis 1981, 647.
6 J.C.Jochims, R.Abu-El-Halawa, I.Jibril, and G.Huttner, Chem.Ber. 117, 1900 (1984).
7 J.C.Jochims, and M.A.Rahman, Chem.Ber. 117, 502 (1984).
8 M.Al-Talib, I.Jibril, J.C.Jochims, and G.Huttner, Chem.Ber., submitted for publication.
9 V.I.Gorbatenko, and L.I.Samarai, Synthesis 1980, 85.
10 M.Al-Talib, I.Jibril, E.-U.Würthwein, J.C.Jochims, and G.Huttner, Chem.Ber., submitted for publication.