

1,3-Diaza-2-azoniaallene Salts as Novel N₃-Building Blocks: Preparation and Cycloadditions to Alkenes, Alkynes, Carbodiimides, and Cyanamides¹⁾

Wolfgang Wirschun

Konstanz, Fakultät für Chemie der Universität

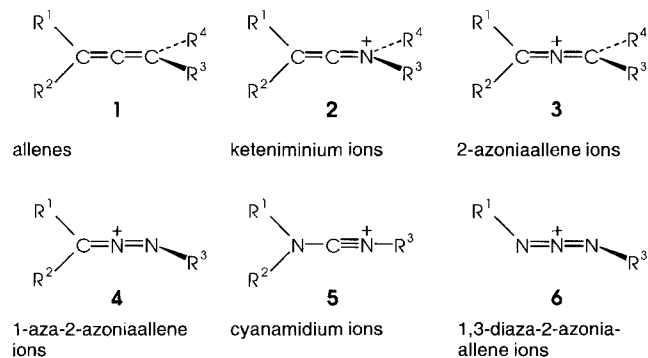
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Abstract. 1,3-Diaza-2-azoniaallene salts $R^1-N=N^+=N-R^2$ **6** represent a new functional group. 1,3-Disubstituted triazenes **8** are oxidized with *tert*-butyl hypochlorite to stable open-chain *N*-chlorotriazenes $R^1-N=N-NCl-R^2$ **9**, which at low temperatures with Lewis acids afford the reactive intermediates **6**. The salt **6a** is stable below -50 °C and was characterized by spectroscopic and analytical data. Heterocumulenes **6** behave as positively charged 1,3-dipoles undergoing cycloadditions to many different multiple bonds to furnish 1,2,3-triazolium and tetrazolium salts, *e.g.* to both electron-rich and electron-

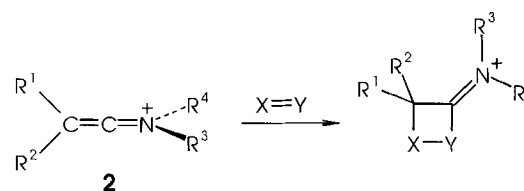
deficient alkenes, alkynes, to one or both double bonds of 1,3-butadienes, to carbodiimides, and cyanamides (1,3-dipolar cycloaddition with inverse electron demand). With an allene, a butatriene and a pentatetraene the 4,5-dihydro-1*H*-1,2,3-triazolium salts **17–19** were obtained. The constitutions of four of the products were secured by X-ray structural analyses. 4,5-Dihydro-1*H*-1,2,3-triazolium salts **11** and 1*H*-1,2,3-triazolium salts **20** are aza analogues of Arduengo's and Wanzlick's nucleophilic carbenes.

1 Introduction

Five classes of monocations **2–6** can be written by replacing one or more carbon atoms of allenes **1** by nitrogen atoms.



Only a few keteniminium salts **2** have been isolated. According to an X-ray crystallographic analysis they are isosteric to allenes [1] and react as strong electrophiles under [2+2]-cycloaddition with alkenes, alkynes, allenes and azomethines [2–4].



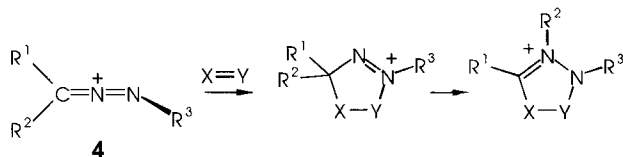
X = Y: alkenes, alkynes, allenes, azomethines

The $C=N^+=C$ unit of the remarkably stable 2-azoniaallene salts **3** is rather flexible [5, 6]. Depending on the substituents local symmetries of type D_{2d} (allene) [6], C_{2v} (allyl cation) [7, 8] or, most often, geometries in between these two extremes were found in the crystals [9, 10]. For certain compounds **3** reactions with alkenes, alkynes, isocyanates and carbodiimides have been reported [11–15].

Only recently, 1-aza-2-azoniaallene salts **4** have become known as reactive intermediates [16–21]. Semi empirical AM1 calculations suggest them to be geometrically related to ketenimines. Salts **4** are cationic three-center-four-electron components undergoing

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[3+2] cycloadditions to nitriles, alkenes, alkynes, carbodiimides, and isocyanates [16–21]. In most cases the primarily formed 3*H*-pyrazolium salts rearrange to the more stable 1*H* species.



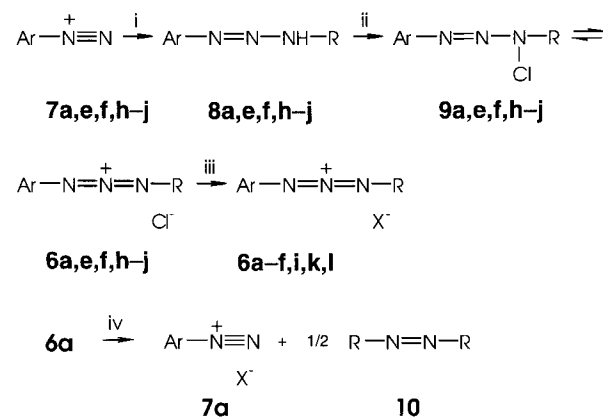
X = Y: nitriles, alkenes, alkynes, carbodiimides, isocyanates

For a cyanamidium salt **5** a linear NCN unit and bond lengths as expected for an aminonitrilium salt were found by X-ray crystallographic analysis [22].

Until recently 1,3-diaza-2-azoniaallene salts were unknown in the literature [23–25].

2 Preparation and Properties of 1,3-Diaza-2-azoniaallene Salts

Recently, we reported oxidation of triazenes **8** with *tert*-butyl hypochlorite to afford rather unstable open-chain *N*-chlorotriazenes **9**, a hitherto unreported class of compounds [23, 26] (Scheme 1). On the other hand, cyclic compounds such as 1-chlorobenzotriazole are well docu-



	Ar	R	X		Ar	R	X
a	a)	a)	SbCl ₆	g	c)	c)	Cl
b	a)	a)	AlCl ₄	h	d)	d)	Cl
c	a)	a)	½ TiCl ₆	i	e)	e)	SbCl ₆
d	a)	a)	ClO ₄	j	f)	Me	Cl
e	b)	b)	SbCl ₆	k	f)	Me	½ SnCl ₆
f	c)	c)	PF ₆	l	f)	Me	PF ₆

a) 2,4,6-Cl₃C₆H₂ b) 2,4,6-Br₃C₆H₂ c) 4-ClC₆H₄
d) 2,4,6-Me₃C₆H₂ e) 4-NO₂C₆H₄ f) 4-MeC₆H₄

Scheme 1 Reagents and conditions: i, H₂N-R; ii, *t*BuOCl, CH₂Cl₂, –20 °C, exclusion of light; iii, Lewis acid or KPF₆, CH₂Cl₂, –60 °C; iv, >–25 °C.

mented [27, 28]. While other *N*-chlorotriazenes **9** exploded on attempted isolation, compound **9a** proved to be moderately stable at room temperature [23]. However, for transformation into heterocumulenes **6** compounds **9** need not to be isolated [23–25]. In Scheme 1 some of the products **6**, **8**, **9** prepared are put together. On addition of antimony pentachloride to a cold (–60 °C) solution of **9a** a red-orange precipitate of the hexachloroantimonate **6a** was formed, which could be isolated at –50 °C. At –80 °C the salt is stable for months. The NMR-spectra (CD₃CN, –35 °C) show only signals for two equivalent aryl substituents [23].

Above –25 °C in solution (CD₃CN) compound **6a** decomposes quickly essentially into equal amounts of the diazonium salt **7a**, which remains in solution, and the azo compound **10**, which precipitates (Scheme 1). The IR spectrum (at –50 °C in acetonitrile) of **6a** is dominated by a very strong absorption at 2012 cm^{–1} assigned to the asymmetric stretching vibration of the –N=N⁺=N– unit. These data together with a correct elemental analysis are in accord with the proposed structure **6a**.

According to semiempirical calculations (AM1) the –N=N⁺=N– unit of **6a** is bent (155°) (Fig. 1). The planes through C15–N1–N2 and C4–N3–N2 are almost perpendicular with respect to each other as are the planes through the two aryl rings.

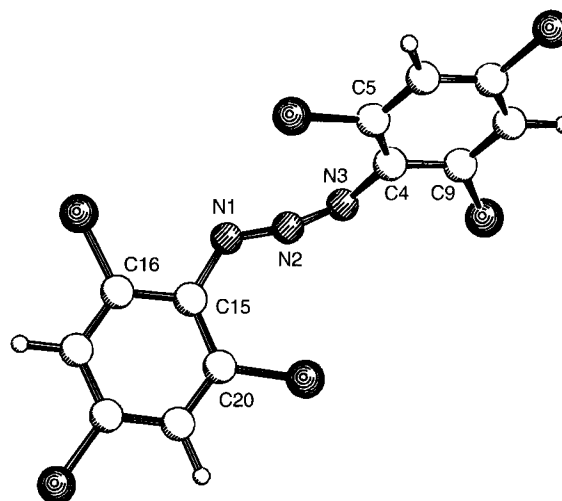


Fig. 1 AM1-calculated geometry of the cation **6a**

The bond distances (122 pm) between the nitrogen atoms are characteristic for N=N double bonds.

Cumulenes **6** can be regarded as N3 substituted azides. Schmidt showed, that alkylation and protonation of hydrazoic acid and alkyl azides give exclusively 1,1-disubstituted salts [29]. The structural proposal H₂N–N⁺≡N was confirmed by IR- and RAMAN spectroscopic studies [30]. According to ab initio calculations on the 3-21G-level of theory, an isolated cation

$\text{H}-\text{N}=\text{N}^+=\text{N}-\text{H}$ **A** is about 200 kJ mol^{-1} less stable than the tautomer $\text{H}_2\text{N}-\text{N}^+\equiv\text{N}$ **B** [31, 32] (Fig. 2). In Fig. 2 the differences in the calculated (AM1) geometries of a 1,3-diaza-2-azoniaallene salt **A** and an aminonitrilium salt **B** are shown. Recently, an X-ray structural analysis for $\text{H}_2\text{N}-\text{N}^+\equiv\text{N}$ SbF_6^- was reported [30].

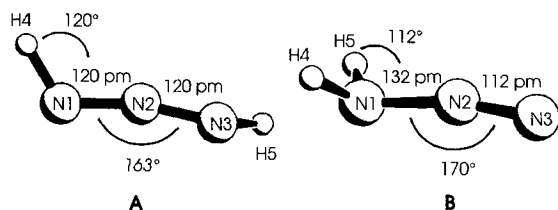


Fig. 2 Results of AM1 calculations

Heterocumulenes **6** with different aryl and alkyl substituents on N1 and N3 and with counterions such as SbCl_6^- , AlCl_4^- , SnCl_6^{2-} , TiCl_6^{2-} , PF_6^- , and ClO_4^- can be prepared (Scheme 1). Above -30°C all these salts decompose quickly.

3 Reactions of 1,3-Diaza-2-azoniaallene Salts with C-C-Multiple Bonds

3.1 Reactions of 1,3-Diaza-2-azoniaallene Salts with Alkenes, Cumulenes, and Butadienes

Between -60 and -30°C suspensions of the heteroallenes **6** react with the C-C-multiple bonds of alkenes [23], 1,3-butadienes, cumulenes (allenes, butatrienes, pentatetraenes) [23], and of alkynes [25] to afford 1,2,3-triazolium salts **11–20**. The cycloadducts are obtained in yields between 45 and 90%. Thus, between -60°C and -25°C the reactive intermediates **6** react with ethene and mono- to trisubstituted alkenes to give 4,5-dihydro-1,2,3-triazolium salts **11** (Scheme 2). No reaction occurred with tetrasubstituted alkenes [23].

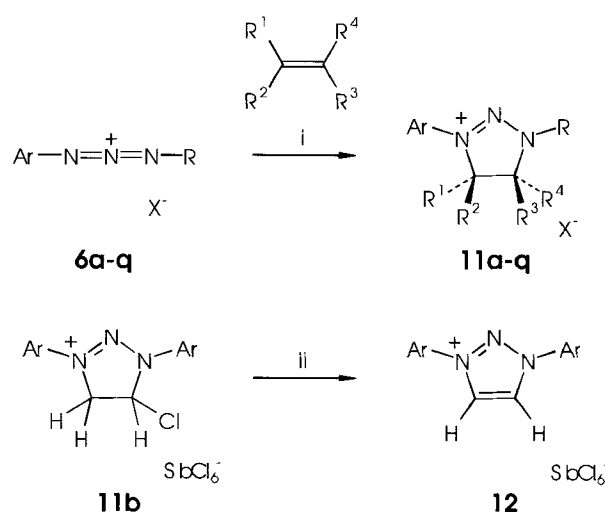
Electron-rich alkenes such as 2-methylbut-2-ene or vinyl acetate react equally well as do electron-deficient olefines like ethyl acrylate or *N*-phenylmaleimide.

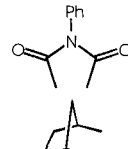

Spiro compounds (e.g. **11h**) as well as bicyclic 1,2,3-triazolium salts (e.g. **11f,g,o,p**) can be prepared. The reaction of **6a** with vinyl chloride furnished the triazolium salt **12** in 98% yield (Scheme 2). Obviously, the primary adduct **11b** loses HCl spontaneously.

Only very few 4,5-dihydro-1*H*-1,2,3-triazolium salts have been mentioned in the literature [33, 34].

The structural assignments of compounds **11** are based on the NMR and IR spectra. The structure of **11e** was confirmed by X-ray crystallographic analysis (Fig. 3).

No reaction could be achieved between 1-chlorobenzotriazole and alkenes in the presence of antimony pentachloride.



a)	Ar	R	R ¹	R ²	R ³	R ⁴
a	b)	b)	H	H	H	H
b	b)	b)	Cl	H	H	H
c	b)	b)	OAc	H	H	H
d	b)	b)	CO ₂ Et	H	H	H
e	b)	b)	Ph	Ph	H	H
f	b)	b)	H			H
g	b)	b)	H			H
h	b)	b)	H	H	-(CH ₂) ₄ -	
i	b)	b)	Et	H	H	Et
j	b)	b)	Et	H	Et	H
k	b)	b)	CO ₂ Bu	H	H	CO ₂ Bu
l	b)	b)	CO ₂ Bu	H	CO ₂ Bu	H
m	c)	c)	CO ₂ Bu	H	H	CO ₂ Bu
n	c)	c)	CO ₂ Bu	H	CO ₂ Bu	H
o	e)	d)	Me	H	-(CH ₂) ₃ -	H
p	b)	c)	H		-(CH ₂) ₃ -	H
q	b)	b)	Me	Me	Me	H

a) X: SbCl_6^- b) 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2$ c) 4- $\text{NO}_2\text{C}_6\text{H}_4$
d) 4- MeC_6H_4 e) X: Cl

Scheme 2 Reagents and conditions: i, CH_2Cl_2 , -60°C to 23°C , ca 2 h, 44–98%; ii, $-\text{HCl}$, 98%.

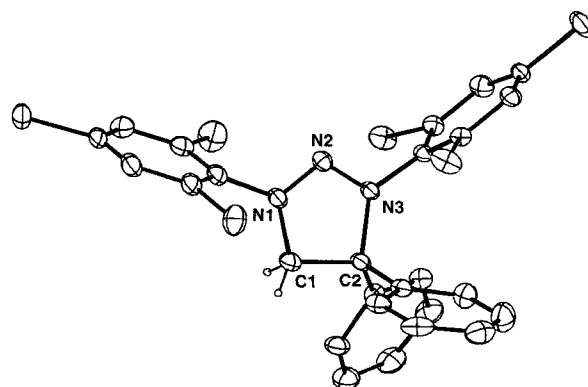
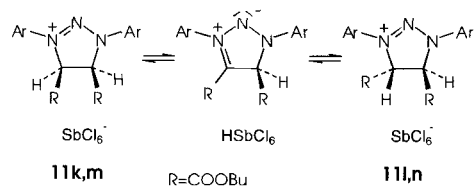
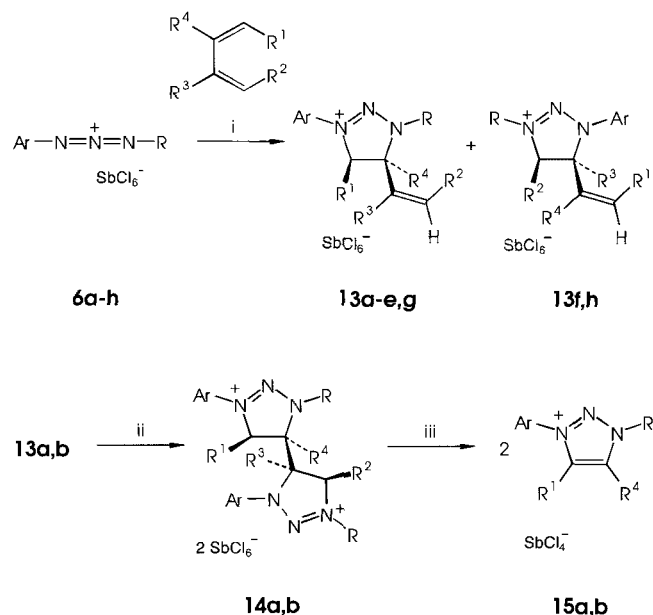


Fig. 3 ORTEP Plot of the Cation **11e**

The cycloadducts **11k,m** of dibutyl maleate (Ar = 2,4,6-Cl₃C₆H₂ and Ar = 4-NO₂C₆H₄) rearrange in solution (CD₃CN, 23 °C) into the *trans* isomers **11l,n** (half life of about 50 minutes, respectively 2500 min). The rearrangement is believed to proceed *via* an intermediate ylide.



1,3-Butadiene reacts with **6a** with formation of the vinyl derivative **13a** (Scheme 3). When a solution of **13a** in dichloromethane was treated with another equivalent of **6a** the pale yellow bistriazolium salt **14a** was formed in 67% yield showing that even the vinyl group of a cation is reactive enough to add another cation **6a**. Correspondingly, from 2,3-dimethyl-1,3-butadiene the vinyl triazolium salt **13b** (52%) and the bistriazolium salt **14b** (59%) were prepared [24].



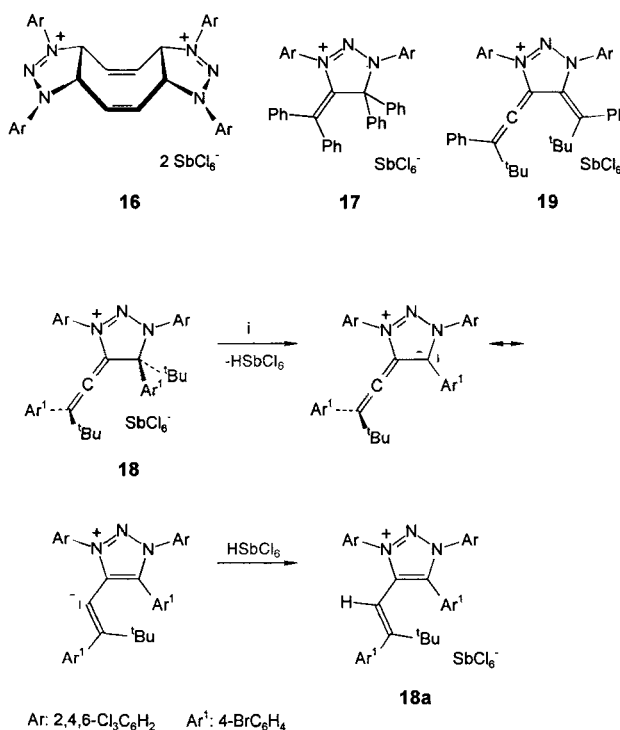
	Ar	R	R ¹	R ²	R ³	R ⁴
a	b)	b)	H	H	H	H
b	b)	b)	H	H	Me	Me
c	b)	b)	-(CH ₂) ₂ -		H	H
d e)	c)	c)	H	H	Me	Me
e,f	b)	b)	H	H	Me	H
g,h e)	d)	Me	H	H	Me	Me

a) X: SbCl₆⁻ b) 2,4,6-Cl₃C₆H₂ c) 4-ClC₆H₄
d) 4-MeC₆H₄ e) X: PF₆⁻

Scheme 3 Reagents and conditions: i, CH₂Cl₂, -60 °C to 23 °C, ca 2 h, 52–81%; ii, **6a**, CH₂Cl₂, -60 °C to 23 °C, ca. 2h; **a**: 67%; **b**: 59%; iii, CH₃CN, 24 h, reflux, 88%.

In acetonitrile the dihexachloroantimonates **14a,b** slowly decompose into two molecules of the triazolium tetrachloroantimonates **15a,b**. The mechanism could imply homolytic cleavage of the bond connecting the two rings of **14** followed by oxidation of the resulting radicals by antimony(V). The salts **13c,d** were prepared by reaction of equimolar mixtures of **6a,d** and the corresponding butadienes. Preparation of 2:1 adducts were not attempted. With isoprene an almost equimolar mixture of the regioisomers **13e,f** was obtained. With 2,3-dimethylbutadiene the unsymmetrically substituted heterocumulene **6g** afforded **13g,h** as a 1:5 mixture of the regioisomers in respect to the triazolium ring (Scheme 3). No reactions were observed between hexachloro-1,3-butadiene and cumulenes **6**.

In addition to 1,3-butadienes reactions of **6a** with cyclooctatetraene and a few cumulenes were studied. With cyclooctatetraene only the symmetric dication **16** could be prepared (Scheme 4). Large amounts of the diazonium salt **7a** were formed as side-product.



Scheme 4 Reagents and conditions: i, CH₃CN, 12 h reflux, loss of isobutene, 65%.

Tetraphenylallene afforded the triazolium salt **17** in 50% yield.

With (*E*)-1,4-bis(4-bromophenyl)-1,4-di-*tert*-butatrien [35] the allene **18** was isolated (73%). Recrystallization from acetonitrile resulted in loss of isobutene and quantitative formation of the triazolium salt **18a**, the constitution of which was secured by X-ray structural analysis (Fig. 4). AM1 calculations suggest

elimination of Me_3C^+ from the 4-position of **18** and protonation of the resulting ylide (Scheme 4).

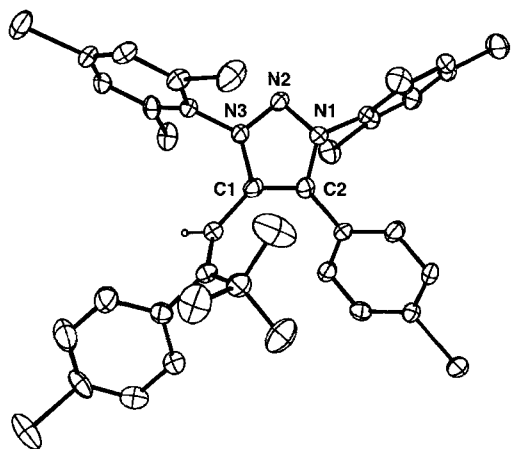


Fig. 4 ORTEP Plot of the Cation **18a**

In contrast to the butatriene, the central double bond of 1,5-di-*tert*-butyl-1,5-diphenylpentatetraene [36] was attacked by **6a** to afford the allene **19** (Scheme 4) the constitution of which was also secured by X-ray crystallographic analysis (Fig. 5).

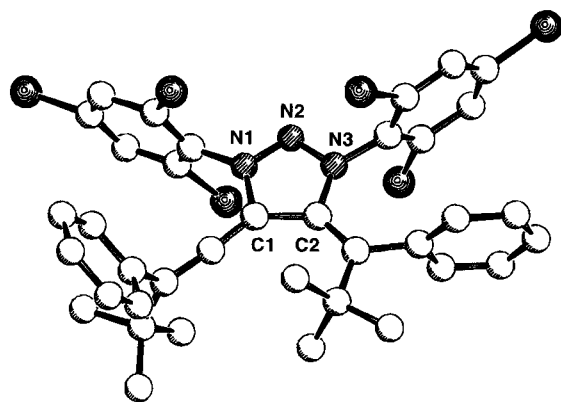
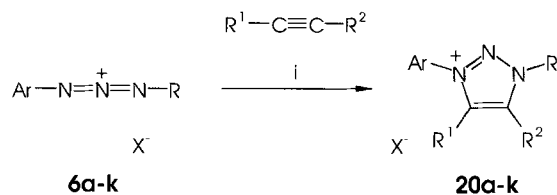


Fig. 5 SCHAKAL Plot of the Cation **19**

3.2 Reactions of 1,3-Diaza-2-azoniaallene Salts with Alkynes

Alkynes react with 1,3-diaza-2-azoniaallene salts **6** to afford 1*H*-1,2,3-triazolium compounds **20** (Scheme 5). For instance, from **6a** and acetylene the triazolium compound **20a** was isolated in 83% yield [25].

Alkyl-, aryl-, mono- and disubstituted acetylenes undergo cycloaddition to aryl and alkyl substituted cations **6**. The cations **6** react with electron-rich alkynes,



a)	Ar	R	R ¹	R ²
a	b)	b)	H	H
b	b)	b)	Bu	H
c	b)	b)	CH ₂ OH	H
d	b)	b)	Et	Et
e	b)	b)	CH ₂ Cl	CH ₂ Cl
f	b)	b)	Me	Ph
g	b)	b)	CO ₂ Me	CO ₂ Me
h ^{e)}	c)	c)	CH ₂ Cl	H
i ^{e)}	c)	c)	Et	Et
j ^{e)}	d)	Me	Et	Et
k ^{e)}	d)	Me	Ph	Ph

a) X: SbCl₆ b) 2,4,6-Cl₃C₆H₂ c) 4-ClC₆H₄
d) 4-MeC₆H₄ e) X: PF₆

Scheme 5 Reagents and conditions: i, CH₂Cl₂, -60 °C to 23 °C, ca 2 h; **a–j**: 49–83%; **k**: 27%.

such as 1- or 3-hexyne, as well as with the electron-deficient dimethyl acetylenedicarboxylate.

The constitution of **20d** obtained by reaction of **6a** with 3-hexyne was secured by X-ray crystallographic analysis (Figure 6).

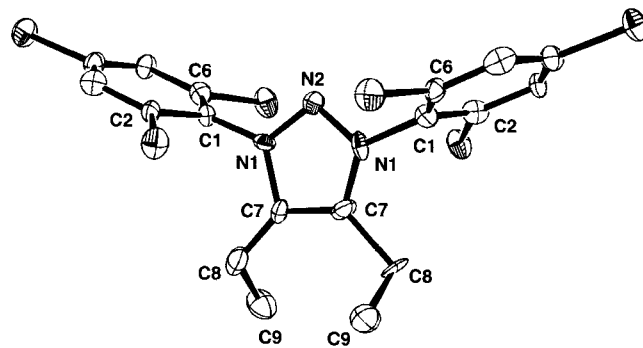
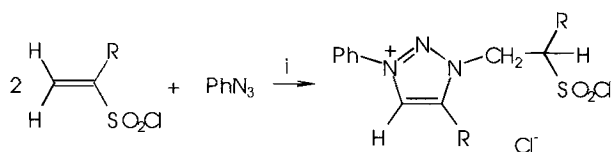


Fig. 6 Ortep Plot of the Cation **20d**

The cycloaddition to the triazolium salts **20** is not confined to the hexachloroantimonates **6**. Hexachlorostannates or hexachlorotitanates **6** also react with alkynes to give good yields of cycloadducts **20**. However, the products were obtained as brown oils, from which correct elemental analyses could not be obtained. A way around this difficulty was found by transformation of the oily salts into the hexafluorophosphates **20h–k** (Scheme 5).

Conventionally, 1,2,3-triazolium salts are prepared by alkylation of 1,2,3-triazoles [33, 37–44] or, for instance, by the following reaction sequence [45]:



Scheme 6 Reagents and conditions: i, benzene.

3.3 Mechanism of the Reaction of 1,3-Diaza-2-azoniaallene Salts with C–C Multiple Bonds

The cycloaddition of 1,3-diaza-2-azoniaallene salts **6** to alkenes is completely stereoselective with respect to the configuration of the alkene double bond. Thus, from **6a** and (*E*)-3-hexene the *trans* adduct **11j** was obtained exclusively and (*Z*)-3-hexene afforded the pure *cis* form **11i**. Corresponding stereoselectivities were observed for cycloadditions of salts **6** to (*E*)- and (*Z*)-1,4-dichloro-2-butene, dibutyl fumarate, or dibutyl maleate. This points to a concerted [4 π + 2 π]-cycloaddition mechanism (1,3-dipolar cycloaddition with inverse electron demand) [20]. AM1 calculations for the cycloaddition of **6a** to ethene support this view (Scheme 7).

The cycloaddition was calculated to be exothermic by 167 kJmol⁻¹ with an activation enthalpy ΔH^\ddagger of 74 kJ mol⁻¹. In the transition structure the forming CN-bonds are of equal lengths (210 pm) in agreement with a synchronous reaction. The dominant orbital interaction is that of LUMO of **6a** (LUMO: -6.13 eV, HOMO: -13.14 eV) with HOMO of ethene (LUMO: +1.44 eV, HOMO: -10.55 eV) (Scheme 7).

The assumption of a concerted reaction is also supported by the structure of the cation **11d**, obtained by

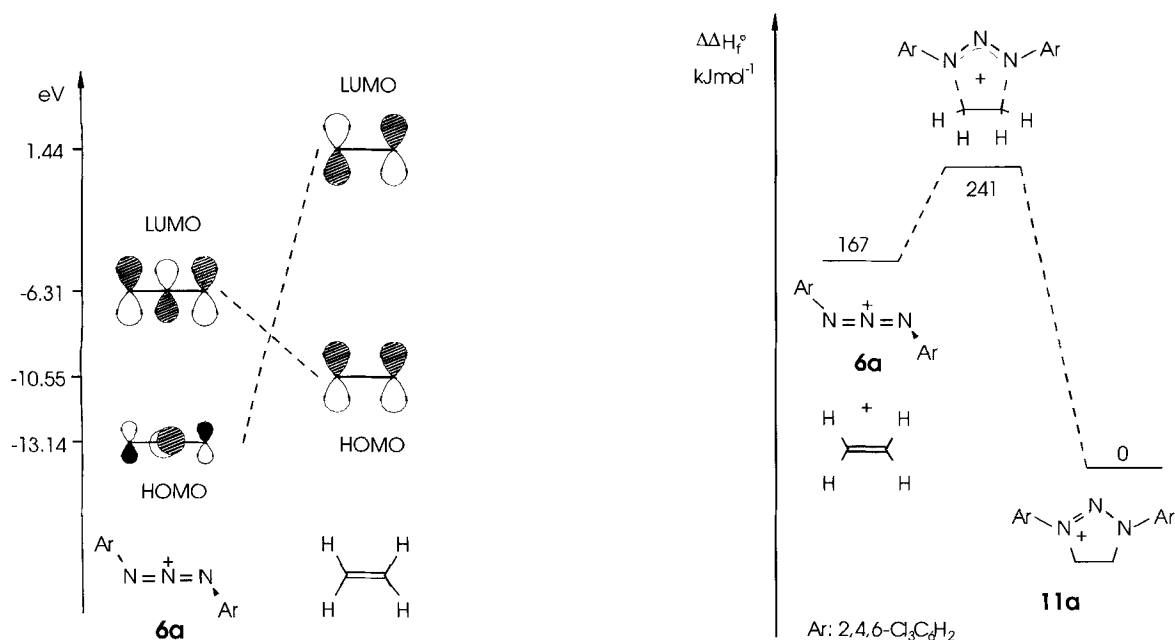
reaction of **6a** with norbornene. Mayr *et al.* have shown that addition of a carbenium ion R⁺ to the C=C double bond of norbornene gives a cation, which undergoes fast Wagner-Meerwein rearrangements and H shifts [46]. After quenching with a nucleophile X⁻, exclusively products with a rearranged norbornane skeleton are isolated. On the other hand, concerted cycloadditions, *e.g.* of chlorosulfonyl isocyanate [47–49] to the double bond of norbornene, yield *exo* products without rearrangement of the norbornane skeleton. Thus, norbornene can serve as a mechanistic probe to discriminate between concerted and stepwise mechanisms of cycloadditions of cations to norbornene (Scheme 8).

Similarly, for the reaction of **6a** with 2-butyne AM1 calculations suggest a concerted mechanism in the manner of a 1,3-dipolar cycloaddition with inverse electron demand.

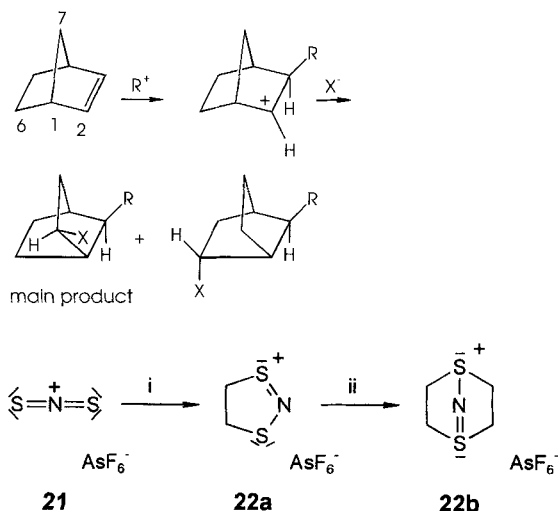
While 1,3-dipolar cycloadditions of electrically neutral 1,3-dipoles are widely used in preparative organic chemistry [50], reports on cycloadditions of cationic four-electron-three-center components to multiple bonds seem to be rare.

An interesting inorganic example for a cationic “1,3-dipole” are cycloadditions of S=N⁺=S AsF₆⁻ **21** prepared by Passmore *et al.* (Scheme 8) [51–53].

In contrast to the well-known nitronium ion O=N⁺=O, which reacts as an electrophile, *e.g.* effecting aromatic nitration, the ion S=N⁺=S acts as a four-electron component in cycloadditions to alkenes such as ethene to afford the 1,3,2-dithiazolium salt **22a**, which itself reacts as a four-electron component with another molecule of ethene to furnish the salt **22b**.

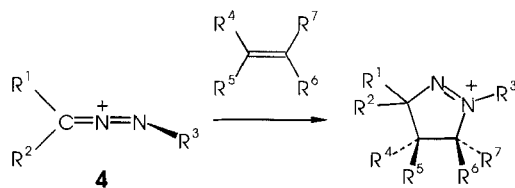


Scheme 7 AM1 calculation for the reaction of **6a** with ethene ($\Delta\Delta H_f^\ddagger$ relative to $\Delta H_f^\ddagger = 0$ kJmol⁻¹ for **11a**).



Scheme 8 Reagents and conditions: i, ethene, SO₂, 23 °C; ii, ethene.

Recently, we reported cycloadditions of 1-aza-2-azoniaallene cations **4** to nitriles, alkynes, carbodiimides, isocyanates, and alkenes [16–21]. It was shown that cations **4** behave as positively charged 1,3-dipoles against alkynes and alkenes undergoing cycloadditions to electron-rich olefins with complete conservation of the configuration of the alkene.

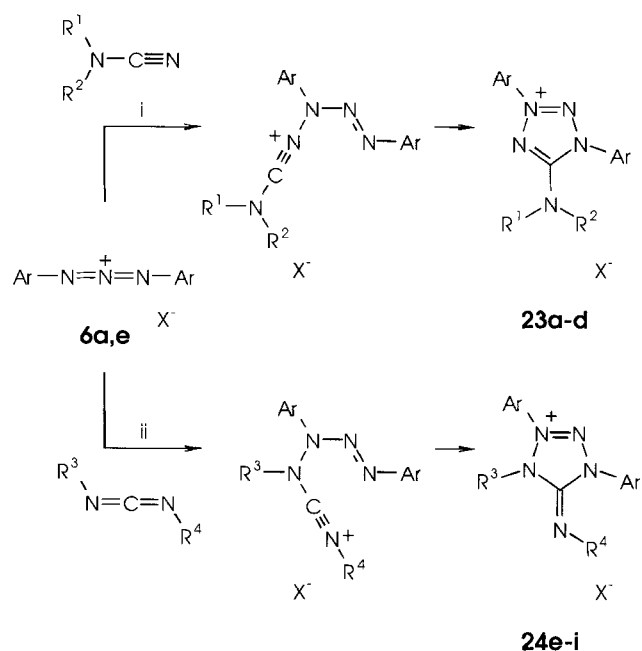


3.4 Reaction of 1,3-Diaza-2-azoniaallene Salts with Cyanamides and Carbodiimides

While 1-aza-2-azoniaallene salts undergo smooth reactions with simple nitriles, 1,3-diaza-2-azoniaallene cations **6** do not.

However, with cyanamides, *e.g.* dimethylcyanamide, and carbodiimides, *e.g.* diisopropylcarbodiimide, salts **6** react under formation of tetrazolium salts **23** and **24** (Scheme 9). AM1 calculations suggest a stepwise mechanism *via* nitrilium salts (Scheme 10) [25].

The formation of **23b** is calculated to be endothermic by 12 kJ mol⁻¹. The cyanamide reacts with an activation enthalpy of 71 kJ mol⁻¹ to give the nitrilium ion **25**, which is 9 kJ mol⁻¹ lower in energy than the sum of the formation enthalpies of the starting components. In the second step the nitrilium ion **25** cyclizes with an activation barrier of 84 kJ mol⁻¹ to the tetrazolium salt **23b**. Concerted formation of **23b** from **6a** and dimethylcyanamide would require an activation enthalpy of at least 200 kJ mol⁻¹.

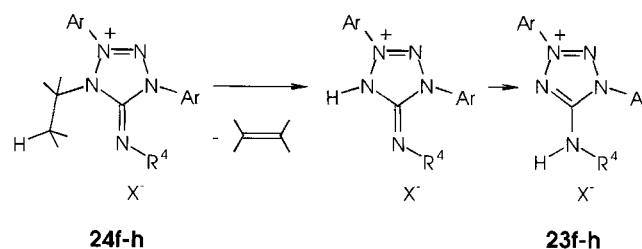


a)	Ar	R ¹	R ²	R ³	R ⁴
a	b)	H	<i>t</i> Bu	-	-
b	b)	Me	Me	-	-
c	b)	Me	<i>i</i> Pr	-	-
d	b)	<i>i</i> Pr	<i>i</i> Pr	-	-
e ^{d)}	c)	-	-	<i>i</i> Pr	<i>i</i> Pr
f ^{d)}	c)	-	-	C ₆ H ₁₁	C ₆ H ₁₁
g	b)	-	-	<i>t</i> Bu	<i>t</i> Bu
h	b)	-	-	<i>i</i> Pr	<i>i</i> Pr
i	b)	-	-	C ₆ H ₁₁	C ₆ H ₁₁

a) X: SbCl₆ b) 2,4,6-Cl₃C₆H₂
c) 4-ClC₆H₄ d) X: PF₆

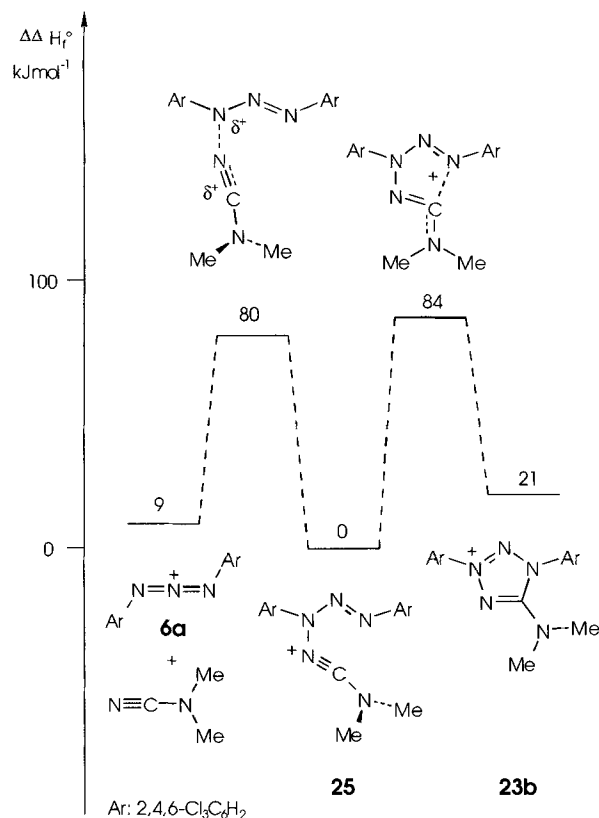
Scheme 9 Reagents and conditions: i, CH₂Cl₂, -60 to -20 °C, ca 2 h; **23a**: 36%; **23b-d**: 61–71%; ii, CH₂Cl₂, -60 to -30 °C, ca 2 h, **24e-i**: 50–77%.

The reaction products of salts **6** with carbodiimides with R³ = CC-H underwent eliminations of alkenes to furnish tetrazolium salts **23f-h**. A mechanistic proposal for this reaction is given [25]:



4 Are 1,2,3-Triazolium Salts Stable Nitrenium Salts?

Recent investigations of Arduengo and others on stable so-called nucleophilic carbenes **26** and **27** attracted

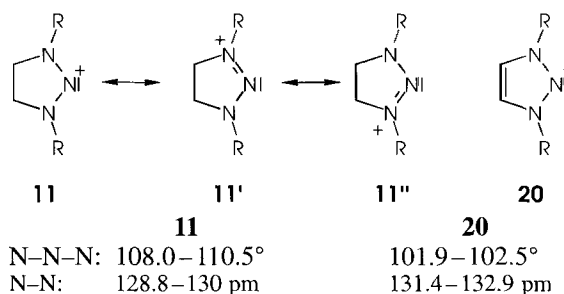
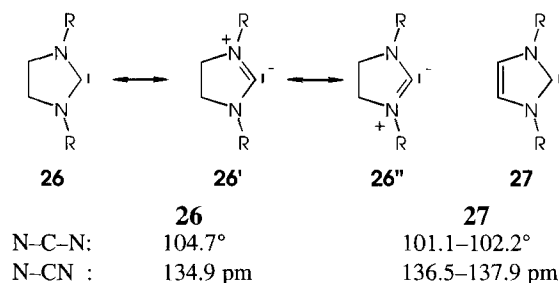


Scheme 10 AM1 calculated heats of formation (kJ mol⁻¹) for the reaction of **6a** with dimethylcyanamide relative to $\Delta H_f^\circ=0$ kJmol⁻¹ of **25**.

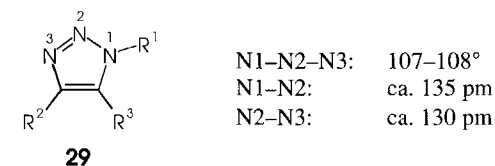
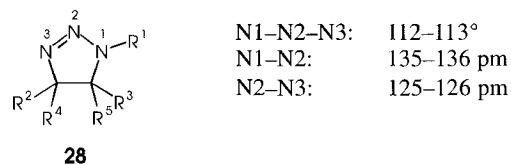
much attention [54–59,72–77]. The work is based on earlier observations of Wanzlick who postulated carbene character for **26** and **27** but did not isolate such compounds [60–64].

1,2,3-Triazolium cations **11** and **20** are isoelectronic to cations **26**, **27**. Arguments put forward in favor of the singlet carbene character of **26**, **27** and against important ylidic contributions **26'**, **26''** are small bond angles N–C–N of ca 105° (**26**) and 102° (**27**), and long single bonds between nitrogen and the carbene carbon (132–137 ppm).

Rather short bond angles were also found by X-ray crystallographic analyses for the 1,2,3-triazolium salts **18a**, **20c** [N1–N2–N3: 102.5(4), respectively 101.9(2)] and the 4,5-dihydrotriazolium salt **11c** [N1–N2–N3: 110.5(3)] (Fig. 3, 4, 6).



These angles and the N–N bond distances may be compared with those of 1-substituted 4,5-dihydro-1,2,3-triazoles **28** [N1–N2–N3: 112–113°; N1–N2: 135–136 pm; N2=N3: 125–126 pm [65–67]], and 1-substituted 1,2,3-triazoles **29** [N1–N2–N3: 106–108°; N1–N2: ca 135 pm; N2=N3: ca 130 pm [68–70]].



Thus, while allylic conjugation (**11'**, **11''** etc) is certainly important in compounds **11** and **20**, the small N–N–N-bond angles may suggest some singlet nitrenium character for these compounds [24, 71].

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Address for correspondence:

Dr. W. Wirschun

Universität Konstanz, Fakultät für Chemie

Postfach 78457

D-78434 Konstanz

E-mail: ww1@chclu.chemie.uni-konstanz.de