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ON THE SI-N-BOND - XLV[1]. 2-AZA-ALLENIUM CATIONS: SYNTHESIS, MOLECULAR STRUCTURE AND ELECTROPHILIC RING CLOSURE TO 1H-ISOINDOLES

HARALD FREY, ACHIM MEHLHORN and KLAUS RÜHLMANN*

Sektion Chemie der Technischen Universität Dresden
Mommsenstr. 13, Dresden, DDR-8027

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Abstract - A new synthesis of 2-aza-allenium salts is described starting from N-trimethylsilylimines of aromatic ketones. Molecular structures and charge distributions of the linear allenoid and the angular allylic forms of monosubstituted 2-aza-allenium cations are calculated by the semiempirical MINDO/3 method. The u.v. spectra of tetraaryl-2-aza-allenium cations have been measured and interpreted by theoretical transition energies obtained from modified PPP investigations. The theoretical heats of formation suggest the linear allenoid structure of all of these cations to be favoured. Low energy differences between the linear and the angular geometries as well as the high positive charge at the carbon atoms of the C-N-C systems may explain the electrophilic ring closure to 1H-isoindoles found experimentally.

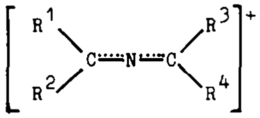
INTRODUCTION

In the last decade hetero-allenium cations of type 1 have attracted increasing attention as highly reactive synthons.[2]

$$\left[X \cdots N \cdots Y\right]^+ \quad (X,Y = BR,\ NR,\ CR_2,\ SR_2,\ PR_3)$$

1

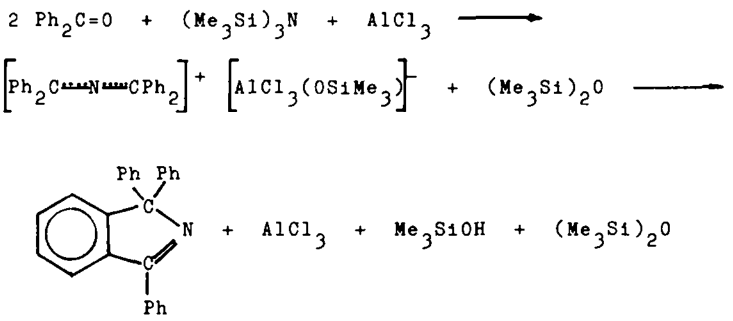
Among this class of compounds, 2-aza-allenium cations 2 are the most frequently investigated species.[3-20]


$$\left[\begin{matrix}R^1\\R^2\end{matrix}\!\!>C \cdots N \cdots C<\!\!\begin{matrix}R^3\\R^4\end{matrix}\right]^+$$

2

Cations of this type have been assumed in a variety of syntheses as reactive nonisolable intermediates,[9,13-15] but also made accessible in substance by unambiguous synthesis.[3-8,12,18] Moreover, the elementary and comparatively simple molecular structure of the 2-aza-allenium cations 2 challenged a series of theoretical investigations.[2,8,10,11,16,17,19,20]

2-Aza-allenium cations have also been postulated as intermediates in a new synthetic method to prepare 1H-isoindoles, described by us in a previous paper.[1]



(1)

In order to confirm our assumptions, 2-aza-allenium salts should be prepared by an unambiguous synthetical route, characterized spectroscopically and converted into 1H-isoindoles. Quantum chemical investigations should provide arguments concerning the molecular structure, the heats of formation, the charge distribution and the u.v.-vis. spectra of aza-allenium cations, and make it possible to propose a reasonable reaction profile for the ring closure of arylsubstituted 2 to 1H-isoindoles.

RESULTS AND DISCUSSION

Synthesis of the 2-aza-allenium salts

N-Diarylchloromethyl- and N-aryldichloromethylbenzophenone- or fluorenoneimines (table 1) could be obtained in yields up to 90% by reacting N-trimethylsilylbenzophenone- or fluorenoneimine with diaryldichloromethanes or trichlorophenylmethane in presence of HgI_2 at temperatures between 100 and 150°C, and further converted nearly quantitatively into 2-aza-allenium salts by Lewis acids (table 2).

Table 1

Preparation and properties of N-halogenomethylimines

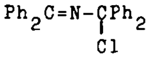
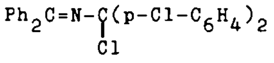
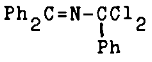
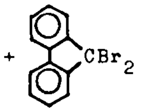
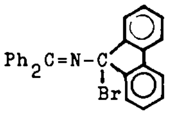
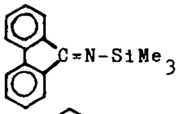
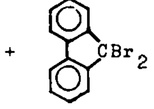
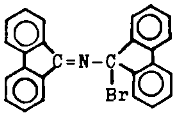
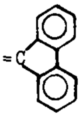
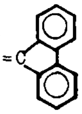
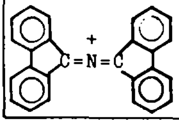
Educts	Products	m.p. (°C)	^{13}C-NMR (ppm)		i.r. (cm^{-1})	
			C=N	C-Hal	νC=N	νC-Hal
$Ph_2C=N-SiMe_3$ $+ Ph_2CCl_2$	 $Ph_2C=N-\underset{Cl}{\underset{\mid}{C}}Ph_2$	190 decomp.	180,5	79,3	1615s	690vs
$Ph_2C=N-SiMe_3$ $+ (p-Cl-C_6H_4)_2CCl_2$	 $Ph_2C=N-\underset{Cl}{\underset{\mid}{C}}(p-Cl-C_6H_4)_2$	210 decomp.	181,3	78,2	1620s	690vs
$Ph_2C=N-SiMe_3$ $+ PhCCl_3$	 $Ph_2C=N-\underset{Ph}{\underset{\mid}{C}}Cl_2$	156			1620s	720vs 670vs
$Ph_2C=N-SiMe_3$ 		150 decomp.			1620s	590vs
 		160 decomp.			1630s	580vs

Table 2

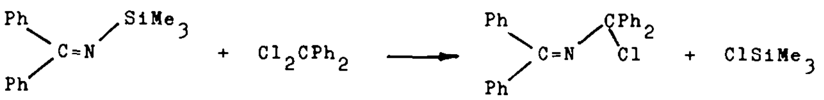
Properties of 2-aza-allenium salts

Compound[a]	Range of decomp. (°C)	Colour	i.r. (cm^{-1}) ν_{as} C=N=C	^{13}C-NMR δ(ppm)	u.v./E (nm)
$Ph_2C=\overset{+}{N}=CPh_2\ ZnCl_3^-$	160-170	orange	1860vs, 1610vs	157,6($>\overset{+}{\underline{C}}=N$) 127,6-136,7($\underline{C}_{ar}$)	295/4,66 306sh
$Ph_2C=\overset{+}{N}=CPh_2\ AlCl_4^-$	130-160[b]	brown[b]	1850vs, 1605vs[b]	157,8($>\overset{+}{\underline{C}}=N$) 127,9-137,0($\underline{C}_{ar}$)	295/4,68 305sh
$Ph_2C=\overset{+}{N}=CPh_2\ SnCl_5^-$	140-150	dark green	1855vs, 1600vs		293/4,62 308sh
$Ph_2C=\overset{+}{N}=C(p\text{-}Cl\text{-}C_6H_4)_2\ ZnCl_3^-$	170-180	red	1850vs, 1600vs		
$Ph_2C=\overset{+}{N}=C$  $ZnCl_3^-$	150-170	brown	1850vs, 1600vs		
$Ph_2C=\overset{+}{N}=C$  $SnCl_5^-$	130-150	dark blue	1845vs, 1605vs		
 $ZnCl_3^-$	150-170	reddish brown	1845vs, 1610vs		286/4,57 345/4,45

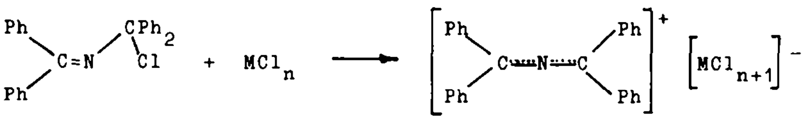
a Structure of anions uncertain

b Literature data:[3,4] decomp. at 135°C, brown, i.r. 1845cm^{-1}, 1600cm^{-1}

The following equations (2) and (3) refer to the synthesis of tetraphenyl-2-aza-allenium salts:



(2)



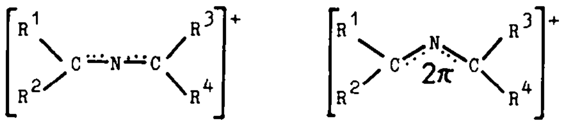
(3)

$MCl_n = ZnCl_2,\ AlCl_3,\ SnCl_4$

This two-step synthesis has the advantage of producing 2-aza-allenium salts with different anions in a pure form.

Structure of the 2-aza-allenium cations

Two structures can be suggested for 2-aza-allenium cations 2, a linear allenoid structure a and an angular planar allylic structure b.

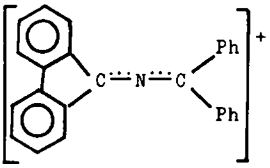


2

a b

The nature of the substituents at the C-N-C chain should mainly determine which structure is preferred.

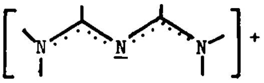
By means of MNDO and ab initio calculations using 3-21G and 6-31G* basis sets, Würthwein et al. established the preference of the allenoid structure 3a for the unsubstituted system 3 (2 with R^1 - R^4 = H).[8,19,20] These results were confirmed by X-ray analysis of a 4 salt; the C-N-C angle has been determined to be 163,1 degrees.[20]



4

Clear evidence for the allenoid structures of the 2-aza-allenium cations collected in table 2 comes from their i.r. spectra, which show two strong bands between 1850 and 1900 cm^{-1} such as is also characteristic for cumulenes.

The only structural exception expected is for 1,3-diamino-aza-allenium cations, which are predicted to prefer the angular allylic form.[8] This result is not surprising as these species can be considered as meso-aza-trimethinecyanines.



Despite the theoretical investigations mentioned above the conversion of substituted 2-aza-allenium cations from structure a into structure b has not been studied systematically in any detail.

Therefore MINDO/3 calculations[21] (program MOMIN 3[22]) have been carried out in order to estimate the optimal molecular geometry of monosubstituted 2-aza-allenium cations 3 and 5 - 9 (c.f. table 3).

The bond lengths and angles obtained are listed in table 3.

The introduction of donor and acceptor substituents changes the bond lengths of the C^1-N-bond only to a very small extent, whereas a pronounced bond lengthening of up to 0,036 Å results for the neighbouring C^2-N-bond.

The MINDO/3 bond lengths for 3a, 3b and 9a correspond closely to those obtained by MNDO and 3-21G calculations for 3a, 3b and 4.[20]

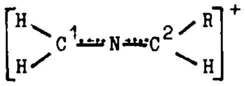
It is also possible to characterize the structure offered by analysis of the u.v.-vis. spectra of 10 (2, R^1 - R^4 = Ph), 11 (2, R^1-R^2, R^3-R^4 = fluorenyl), and 4 with different anions.

Fig. 1 shows the absorption curve of 4 with the anion $ZnCl_3^-$. Two strong bands can be observed within the u.v. range, followed by a weak inflection which extends up to the visible absorption range and causes the colour of the compound. Fig. 1 also contains the vertical transition energies, calculated by means of a modified PPP-method,[25] plotted below the spectral curve. The lengths of the lines are propor-

Table 3

MINDO/3-optimized geometries of monosubstituted

2-aza-allenium cations



Compound	R	d_{C^1-N} (Å)	d_{N-C^2} (Å)	d_{C^2-R} (Å)	$<C^1-N-C^2$ (°)	$<N-C^2-R$ (°)
3a	H	1,248	1,248	1,108	179,2	121,9
3a[a]	H	1,239	1,239	1,074	180	120,1
3b	H	1,291	1,291	1,111	135,3	118,9
3b[a]	H	1,313	1,313		119,8	
5a	F	1,254	1,248	1,325	179,3	116,4
5b	F	1,276	1,291	1,291	135,0	111,9
6a	OH	1,245	1,275	1,289	179,5	117,3
6b	OH	1,264	1,343	1,253	134,3	113,7
7a	NH_2	1,241	1,284	1,312	179,5	123,3
7b	NH_2	1,262	1,358	1,283	132,5	117,9
8a	CHO	1,248	1,255	1,510	179,0	126,8
8b	CHO	1,294	1,301	1,511	135,3	122,3
9a	Ph	1,245	1,268	1,462	179,5	129,7
9b	Ph	1,258	1,329	1,425	146,2	136,7

a calculated by Würthwein with a 3-21G basis set[20]

tional to the oscillator strengths of the transitions. In the PPP-calculations, which provided promising results for the spectra of homologous cumulenes,[25] the two orthogonal π-systems were coupled by the electron repulsion integral $\gamma_{NC'}$ = 10,24 eV and the resonance integrals were set to β_{CN} =-2,898 eV. The other parameters correspond to previous PPP-studies.[26]

According to the calculations the form of the u.v. spectrum is mainly determined by intensive transitions resulting from a combination of $\pi\pi^*$- and $\pi'\pi'^*$-one-electron transitions of the two orthogonal chromophoric systems benzophenoneimine and fluorenoneimine. Transitions between the orthogonal π-systems $\pi\pi'^*$ or $\pi'\pi^*$ are electric dipole forbidden. They should be found at higher energies and are probably hidden under the intensive bands. The spectrum of 4 differs fundamentally in its structure from that of the non-substituted 2-aza-allenium cation 3. For this compound forbidden transitions were calculated at 250 nm whereas an intensive transition can be expected in the vacuum u.v. at about 160 nm. Though there is no experimental proof so far, this prediction corresponds closely

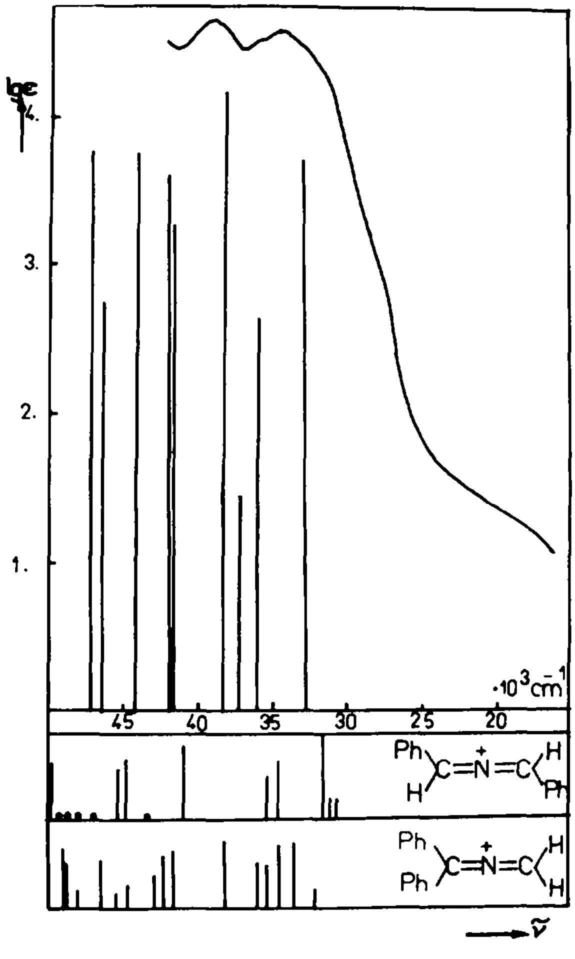


Fig. 1

Absorption curve of the 2-aza-allenium cation 4 and vertical transition energies calculated by means of a modified PPP-method to the experimental findings for the iso-π-electronic allene.[27] Similar results can be obtained by CNDO/S calculations, which have been carried out for the 1,1- and 1,3-diphenyl-aza-allenium cations. The results are given in the lower part of Fig. 1. According to both quantum chemical methods, no indication can be detected that 4 should absorb in the visible region. Therefore the origin of the weak band in the spectra of all investigated aza-allenium cations remains unclear. However, it is likely that this band does not correspond to a transition of the chromophoric system of the tetraaryl-2-aza-allenium cation. A more systematic study is necessary.

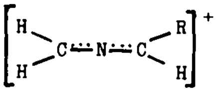
Formation energy of the angular form

The heats of formation (H_f), which we calculated by means of the MINDO/3 method,[21,22] show that the allenoid form is lower in energy for all monosubstituted 2-aza-allenium cations collected in table 4. The energy differences increase with acceptor substituents but decrease with donor substituents. The values determined by Würthwein were included into table 4. These data show the same pattern of variation at different absolute values.

Charge distribution

In the 1H-isoindol synthesis, besides the formation energy of the angular form we were interested in the charge distribution both in the allenoid and in the allylic form of 2-aza-allenium cations. Table 5 contains the total atomic charges, obtained by the MINDO/3 method.[21,22]

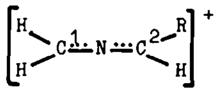
Table 4
Heats of formation (H_f) for allenoid and allylic forms of 2-aza-allenium cations



Compound	R	H_f (kJ mol^{-1})	$H_f(\underline{b}) - H_f(\underline{a})$ (kJ mol^{-1})		
		a	a	b	c
3a	H	814,17			
3b	H	986,33	172,16	174,9	98,3
5a	F	590,09			
5b	F	697,56	107,47	132,2	64,0
6a	OH	535,03			
6b	OH	626,39	91,36	95,8	52,3
7a	NH_2	668,72			
7b	NH_2	730.89	62,17	29,6	8,8
8a	CHO	661,56			
8b	CHO	840,00	178,44	-	-
9a	Ph	843,93			
9b	Ph	977,24	133,31	-	38,1

a calculated by the MINDO/3 method
b calculated by Würthwein with a 3-21G basis set[20]
c calculated by Würthwein by MNDO[20]

Table 5
Charge distribution in the allenoid and the allylic forms of 2-aza-allenium cations



Compound	R	MINDO/3 charge at			
		C^1	N	C^2	R
3a	H	0,1802	0,1656	0,1802	0,1185
3b	H	0,5161	-0,2014	0,5161	0,0070
5a	F	0,3196	-0,0516	0,6559	-0,2035
5b	F	0,4504	-0,2346	0,8683	-0,2182
6a	OH	0,2905	-0,0541	0,5826	-0,0093
6b	OH	0,4018	-0,2301	0,7470	0,0335
7a	NH_2	0,2671	-0,0703	0,3524	0,2629
7b	NH_2	0,3510	-0,2073	0,4001	0,3587
8a	CHO	0,1555	0,1819	0,0749	0,2338
8b	CHO	0,5159	-0,2154	0,3972	0,2255
9a	Ph	0,1787	0,0630	0,2690	0,2832
9b	Ph	0,4019	-0,2412	0,4578	0,3873
$CH_2=NH_2^+$		0,2433	0,1767		

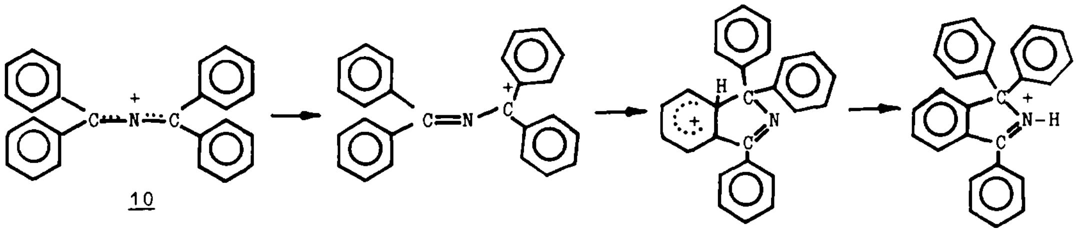
These values show that, even in the dominating allenoid forms a, a considerable portion of the positive charge is located at the C-atoms of the C-N-C-chain. This is further assisted by the lowfield-shift of the ^{13}C-NMR signals of the allenoidal C-atoms (up to nearly 158 ppm). Hence the C-atoms in the 2-aza-allenium cations are obviously more strongly deshielded than those of the cumulenes (signals at about 110 ppm) and of the polar isocyanates (at about 140 ppm; all values relative to the ^{13}C chemical shift of TMS).

During the transition to the angular and planar allylic forms b the positive charge and consequently the electrophilic character of the C-atoms of the C-N-C-chain are further increased considerably.

For a comparision of charge distribution between C and N, the protonated formaldehydeimine has been included into table 5. It can be seen that the charges at the C- and N-atoms of the linear allenoid forms a of the 2-aza-allenium cations correspond roughly with the charge distribution of $CH_2{=}NH_2^+$. The angular allylic forms, however, show a distinctly different charge distribution (but compare [19]).

Ring closure of aryl-2-aza-allenium salts to 1H-isoindoles

The positive charge at the C-atoms of the 2-aza-allenium cations makes these atoms likely to undergo electrophilic reactions. In the systems 4, 10 and 12 (2, R^1 and R^2 = Ph, R^3 and R^4 = p-Cl-C_6H_4), which are suitable for ring closure, the electrophilic C-atoms of the cumulated chain attack the C-atoms in o-position of the phenyl groups.


10

This intramolecular electrophilic substitution reaction to form the corresponding 1H-isoindoles has a plausible initial coordinate in the bending of the 2-aza-allenium cation accompanied by planarization of the molecule and an increase of the positive charge at the terminal C-atoms (transition from a to b).

Fig. 2 exhibits a rough reaction profile based on MINDO/3 calculations for the postulated intermediates. It becomes apparant that planarization, angle bending and electrophilic attack require energy whereas hydrogen migration to

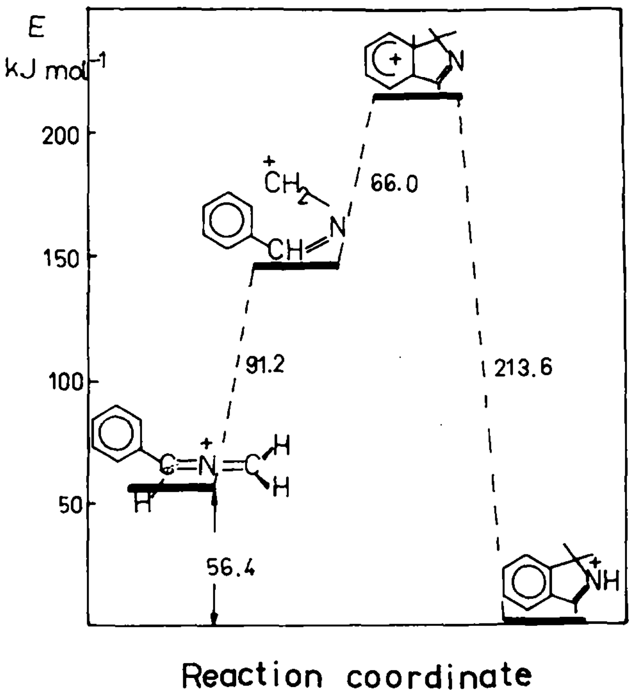


Fig. 2
Reaction profile for ring closure of 2-aza-allenium cations to 1H-isoindoles based on MINDO/3 calculations

the N-protonated 1H-isoindole is strongly exothermic. The protonated 1H-isoindole was calculated to be 56,4 kJ mol^{-1} more stable than the starting 1-phenyl-2-aza-allenium cation. Thus both experimental results and quantum chemical calculations of this study assist the mechanism we postulate.

EXPERIMENTAL

Spectroscopic investigations: For recording u.v. and i.r. spectra, Specord instruments UV-VIS and IR-75 of VEB Carl Zeiss, Jena were used. NMR spectra were obtained with a WH-90 of Bruker Meßtechnik, GmbH, Karlsruhe.

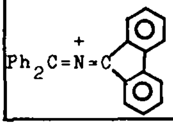
Quantum chemical calculations: The MINDO/3 MO-calculations were carried out on a BESM-6 computer using programme MOMIN 3.[28]

N-Halogenomethylimines 13: In a 25 ml-flask 5 mmol N-trimethylsilylketoneimine,[23,24] 5 mmol diaryldihalogenomethane and 1 mg HgI_2 were put together under dry nitrogen free of O_2. During heating on an oil bath an exothermic reaction starts at 100-150°C and the halogenotrimethylsilane forming distills off. The reaction product, solidifying on cooling, was recrystallized from benzene.
The results of the syntheses are summarized in table 1.

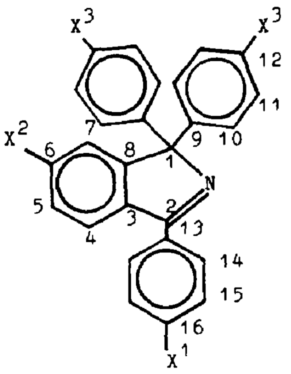
2-Aza-allenium salts 14: 1 mmol 13 was dissolved in 20 ml CH_2Cl_2 and 1 mmol Lewis acid was added. The reaction mixture became coloured immediately and within 30 min the Lewis acid dissolved. Solvent was stripped off under vacuum. The remaining solids were recrystallized from CH_2Cl_2.
The experimental results are given in table 2.

1H-isoindoles 15 - 19: 0,5 mmol 14 in a 25 ml-flask were heated on a metal bath to 200°C for 10 min under dry nitrogen. Then the reaction mixture was dissolved in boiling methanol. After cooling organic compounds are precipitated by addition of dilute aqueous HCl. The solids were recrystallized from benzene.
The experimental results are given in table 6.

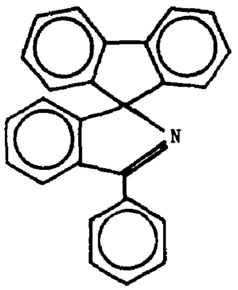
Table 6
Ring closure of aryl-2-aza-allenium salts to 1H-isoindoles

Educts	Products	Yield (%)	m.p. (°C)	i.r.(cm^{-1}) ν_{as}C=N	u.v./E λ(nm)/lgε
$Ph_2C=\overset{+}{N}=CPh_2\ ZnCl_3^-$	15	67	144	1550	220/4,4 250sh/4,2 265sh/3,9
$Ph_2C=\overset{+}{N}=CPh_2\ AlCl_4^-$	15	53	143		
$Ph_2C=\overset{+}{N}=C(p\text{-}Cl\text{-}C_6H_4)_2\ ZnCl_3^-$	15	11	156[a]		
	16	29	164	1555	223/4,45 255sh/4,2 265sh/4,0
	17	5			
	18	6			
 $ZnCl_3^-$	19	29	139	1555	

[a] mixture of 15 - 18



15: $X^1 = X^2 = X^3$ = H
16: $X^1 = X^2$ = H; X^3 = Cl
17: $X^1 = X^2$ = Cl; X^3 = H
18: $X^1 = X^2 = X^3$ = Cl



19

^{13}C-NMR shift values δ ppm

C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}a	C^{11}a	C^{12}	C^{13}	C^{14}b	C^{15}b	C^{16}
15:86,4	169,5	135,0	127,6	123,2	130,1	125,0	157,1	142,8	128,1	127,8	127,1	137,7	128,4	128,5	129,9
16:86,5	169,6	135,2	127,9	123,3	130,3	125,2	157,3	140,7	128,5	128,9	135,3	137,9	128,6	128,7	130,0
17:86,6	170,7	133,7	128,6	123,9	136,7	125,2	158,1	142,8	128,2	127,9	127,1	135,9	129,6	128,5	139,5

a,b assignment uncertain

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