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MESOIONIC TETRAZOLES – PROGRESS SINCE 1980

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Abstract – This article summarizes the findings made during the past decades with the traditional classes of mesoionic tetrazoles of type (**A**) and (**B**); it also deals with the 'abnormal' carbenes derived therefrom. – Emphasis is placed on preparative aspects.

INTRODUCTION

Mesoionic tetrazoles and their five-membered analogues (8π systems) belong to the extensive family of conjugated heterocyclic mesomeric betaines (HMBs) which occur in two types, generally known as **A** and **B** (Chart 1).[1a-c] The entire field has been reviewed repeatedly, covering the literature through 1980.[1d–f] The present report, however, focusses on the tetrazole derivatives as here substantial progress has been made, especially by contributions from the Araki group. It deals not only with a wide variety of type (**A**) and (**B**) systems like **A1–A5** and **B1**, **B2**, **B4**, **B5** (including **B1'**), but also features the corresponding mesoionic, 'abnormal' carbenes (**C**) and (**D**) as well as their metal complexes (**C'**) and (**D'**) – species of recent vintage.[2]

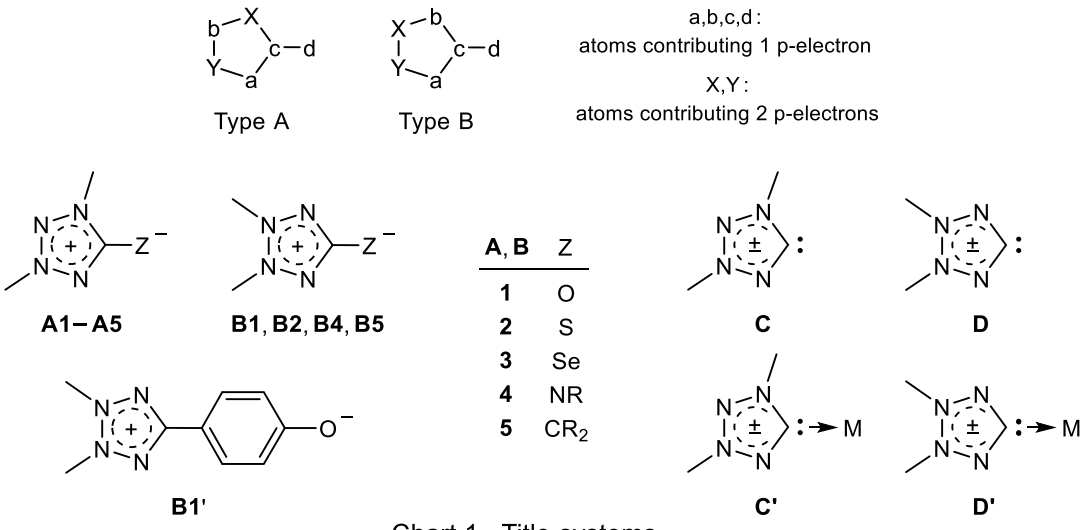
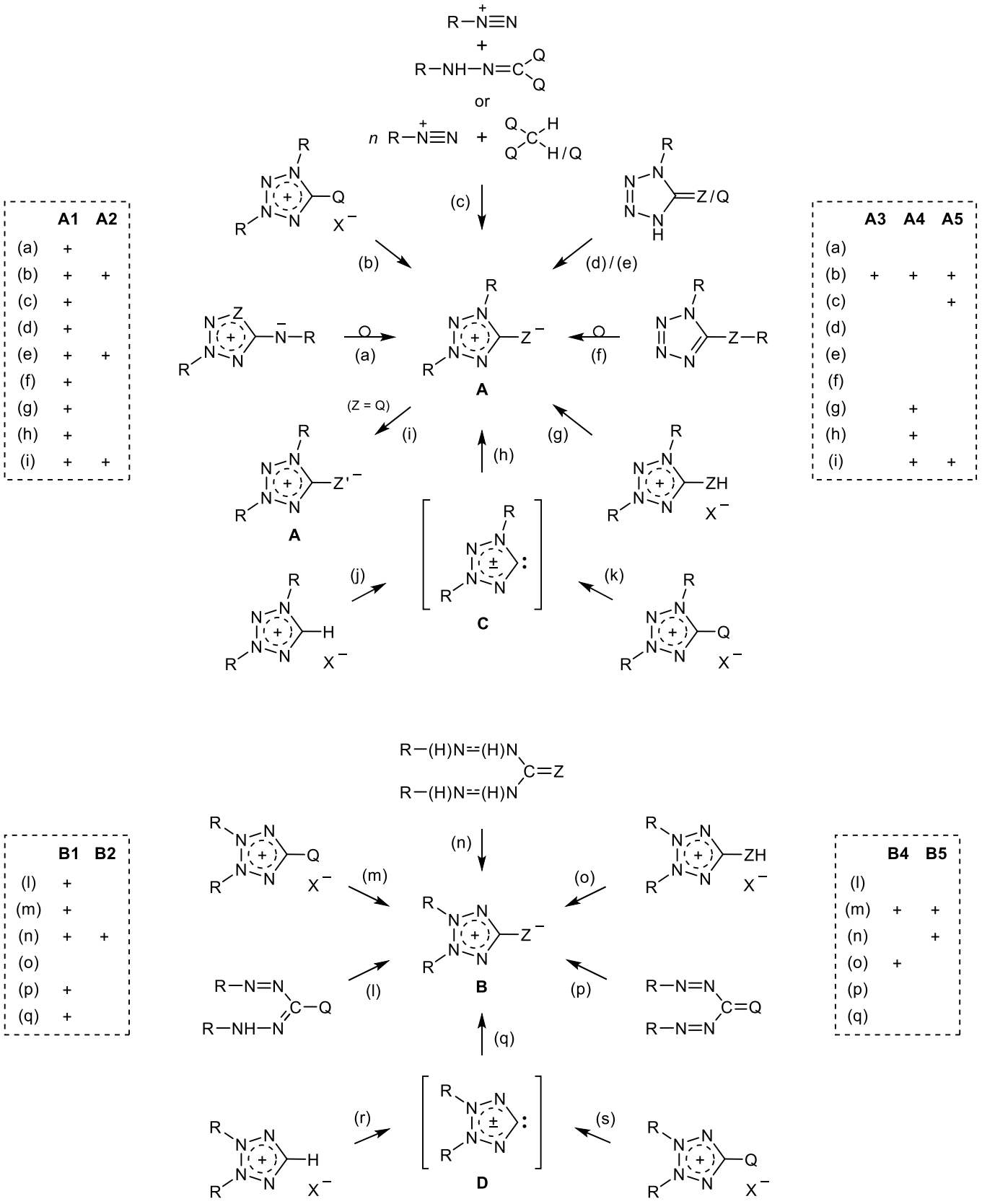


Chart 1. Title systems



Scheme 1. Synthetic principles for **A1**–**A5** and **B1**, **B2**, **B4**, **B5** (including **C** and **D**)
(for **1**–**5**, see Chart 1; Q = modifiable and/or leaving group)

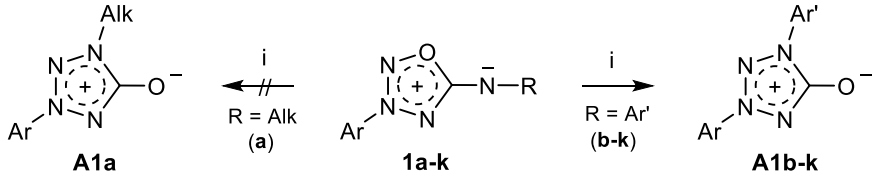
GENERAL

The main objective of this survey is the preparative chemistry, comprising synthesis and transformations. Scheme 1 gives a preview of the former, showing the general routes to **A–D**. To draw a full picture, material that has not been covered by the preceding reviewers,[1d–f] or dealt with too briefly, is considered as well. Selected physical data are provided in Sections (2) and (3). The traditional representation of **A** and **B** with a sextet in the ring has been retained, although type (**A**) mesoions do not show classical aromaticity.[1c,g]

1) MESOIONIC TETRAZOLES OF TYPE (A)

a) Tetrazolium-5-olates (A1)

Alkali-induced ring transformation of 1,2,3,4-oxatriazolium-5-aminides (**1**) constitutes the earliest access to tetrazolium-5-olates (**A1**) [Scheme 2; *cf.* route (a) in Scheme 1].[1d–f] Regarding the scope, the reaction works well with substrates having aryl-substituted aminide groups (such as **1b-k**),[3a–8] but the process failed with alkyl analogues (**1a**).[9a] *N*-Nitroso derivatives (**1**; R = NO) might be expected to afford the respective 1-nitrosotetrazolium-5-olates (**A1**; NO for Ar'), but an attempt with **1** (Ar = Ph, R = NO) showed that the compound is thermally unstable: it lost dinitrogen to give the corresponding 1,2,3,4-oxatriazolium-5-olate in high yield.[9b] Also the parent substrate (**1**; Ar = Ph, R = H) could not be induced to rearrange (*i.e.* into 2-phenyl-2*H*-tetrazol-5-ol), since it undergoes C–O bond breaking (instead of N–O cleavage).[9b]



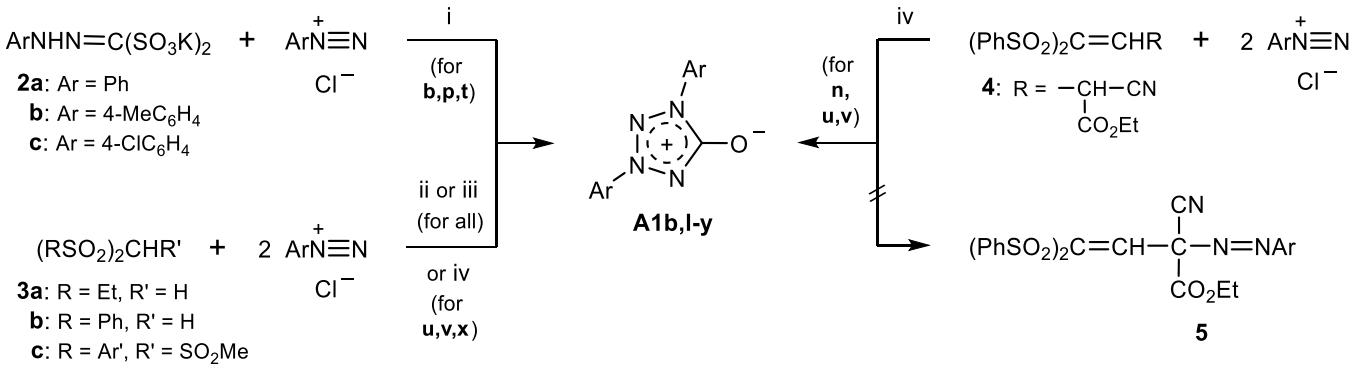
i: aq. NaOH, EtOH, Δ

1, A1 [a]	Ar	R, Ar'	yield (%)	mp (°C)	ref.
b	Ph	Ph	90	157	3a
c	Ph	4-MeC_6H_4	80	200	3a
d	Ph	4-ClC_6H_4	100	190	3a
e	4-MeC_6H_4	Ph	100	161	3a
f	4-ClC_6H_4	Ph	90	232	3a
g [b]/[c]	4-$MeOC_6H_4$	Ph	[d]/82	184–185 [e]	4/5
h [b]	Ph	4-$MeOC_6H_4$	[d]	[d]	6
i [b]	Ph	3,4-$Cl_2C_6H_3$	[d]	217	4
j [c]	Ph	2,4,6-$Me_3C_6H_2$	83	163–164	7
k	Ph	4-(*s*-Bu)C_6H_4	89	70–71	8

[a] Ar, Alk of **1a** and **A1a** unspecified. [b] Details of procedure (**1** → **A1**) not disclosed. [c] Substrates (**1g,j**) (prepared from the respective thiosemicarbazides) were reacted *in situ*. [d] Unreported. [e] Mp from ref.[4]

Scheme 2

Cyclization reactions using arenediazonium chlorides and (arylhydrazono)methanedisulfonate salts (**2**) or, alternatively, bis(alkyl/arylsulfonyl)methanes (**3a,b**) are also established entries to olates (**A1**) (Scheme 3; *cf.* route (c) in Scheme 1].[1d–f] The first mode may be viewed as likewise suited for products having different aryl substituents, but in practice ligand exchange occurs.[1e] In addition to the previously reviewed[1d,f] studies dealing with **A1b,q,s,u,v,y**,[3a,10] other early work is referred to for completion: it describes the preparation of **A1b,l-r,t-x**.[11,12] Of noticeable results, the higher yields of **A1b,q,u** obtained from **3a,b** deserve mention.[11a] A later variant of this procedure utilized the tris(sulfonyl)methane (**3c**): from the respective 4-substituted benzenediazonium salts, the derivatives (**A1u,v,x**) were obtained in yields up to 60% – besides a variety of linear coupling products.[12a] Also the propene (**4**) led to olates like **A1n,u,v** (in yields depending on the amount of the diazonium salt), but this was fairly surprising: in view of the behaviour of the acetyl analogue of **4** (COMe instead of CN), the coupling compound (**5**) had been expected actually.[12b]

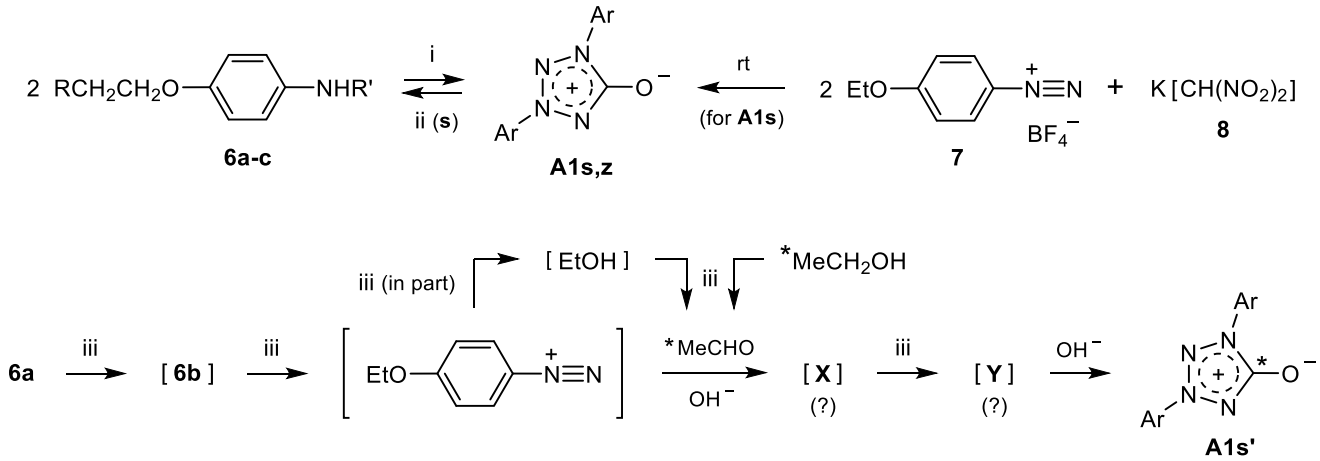


i: aq. KOH, Δ, then rt ii: using **3a**: aq. AcONa or NH_3, EtOH, rt
iii: using **3b**: aq. AcONa, EtOH, Me_2CO, 30–35 °C, then rt; or (for **A1s,u,v,y** only) aq. NaOH, rt
iv: aq. AcONa, EtOH, rt

A1	Ar	from	method	yield (%)	mp (°C)	ref.
b	Ph	**2a** / **3a**	i / ii	23 / 50	154–155 [a]	3a / 11a
l	3-ClC_6H_4	**3b**	iii	80	205–206	11b
m	3-IC_6H_4	**3b**	iii	93	230–231	11b
n	3-$NO_2C_6H_4$	**3a** / **3b** / **4**	ii / iii / iv	80 / 85 / [b]	212–213 [c]	11a / 11b / 12b
o	3-$CF_3C_6H_4$	**3a**	ii	70	142–143	11a
p	3-$(CO_2H)C_6H_4$	**3a**	ii	50	400	11a
q	4-MeC_6H_4	**2b** / **3a**	i / ii	39 / 60	192–193 [a]	3a / 11a
r	4-$MeOC_6H_4$	**3a**	ii	80	204–205	11a
s	4-$EtOC_6H_4$	**3b**	iii	61	185–186	10
t	4-FC_6H_4	**3b**	iii	88	216–217	11b
u	4-ClC_6H_4	**2c** / **3a** / **3b** / **3c** / **4**	i / ii / iii / iv / iv	26 / 60 / 59 / [b] / [b]	231–232 [d]	3a / 11a / 10 / 12a / 12b
v	4-BrC_6H_4	**3b** / **3c** / **4**	iii / iv / iv	43 / [b] / [b]	250–251 [d]	10 / 12a / 12b
w	4-IC_6H_4	**3b**	iii	90	291–292	11b
x	4-$NO_2C_6H_4$	**3b** / **3c**	iii / iv	70 / [b]	235–236 [e]	11b / 12a
y	4-$(CO_2H)C_6H_4$	**3b**	iii	52	> 400	10

[a] Product from **3a**. [b] See text. [c] Product from both **3a** and **3b**. [d] Product from **3b**. [e] Decomp.

Scheme 3



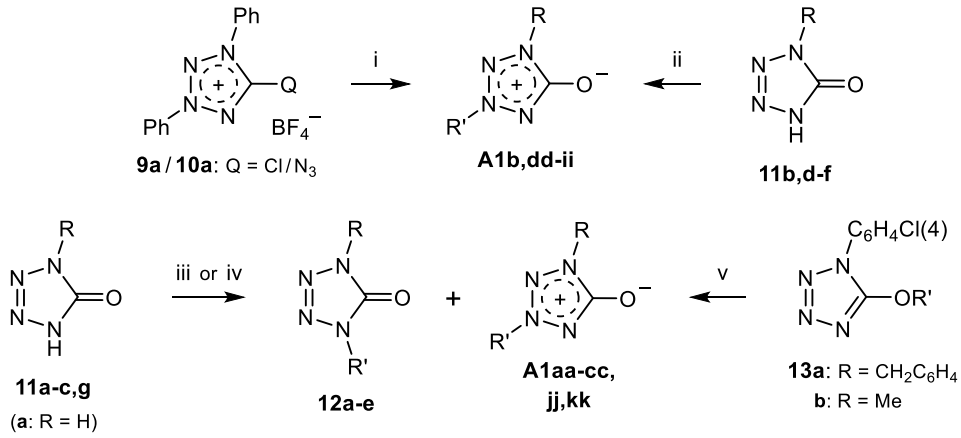
6	R	R'	A1	Ar	from	mp (°C)	ref.
a	H	$CONH_2$	**s**	4-$EtOC_6H_4$	**6a** or **6b**	183–184	13a-c
b	H	H	**z**	4-$(BrCH_2CH_2O)C_6H_4$	**6c**	167–168	13a,c
c	Br	H					

Scheme 4

As recorded only briefly in references,[1d,e] treatment of the sweetening agent dulcin (**6a**) with nitrous acid gives rise to the fluorescent olate (**A1s**) (Scheme 4); this constitutes the principle of a new fluorometric determination of that drug.[13a] The main findings are detailed below. Compound (**A1s**) reverted to **6a** on reduction with zinc and was identical to the material prepared from the diazonium salt (**7**) and potassium dinitromethanide (**8**) [the earlier synthesis of **A1s** (Scheme 3) was obviously not known to the authors].[13b] **A1s** was also formed from phenetidine (**6b**) and, for an X-ray study, the 2-bromoethoxy analogue (**A1z**) was made from **6c**.[13c] The mechanism of the process (**6a** → **A1s**) was clarified to the following extent: Nitrous acid converted **6a** to the cation of **7**, part of which was hydrolyzed to ethanol. The latter was oxidized to acetaldehyde which coupled with the diazonium ion at C(2); this was consistent with the fact that incorporation of C(2)-labelled ethanol gave the derivative (**A1s'**).[13d] The reaction proceeds *via* two species (**X**, **Y**) whose structures have not been elucidated; since both materials were isolable, it could be demonstrated that the step (**X** → **Y**) required nitrous acid, whereas alkali was needed for the conversion of **Y** into **A1s**. Evidence for the central role of acetaldehyde came also from the observation that addition of this component to the original reaction mixture intensified the fluorescence.[13e]

Nucleophilic displacement of functional groups at C(5) of appropriate tetrazolium salts is a straightforward access to olates (**A1**) [*cf.* route (b) in Scheme 1]. To date this method (formally hydrolysis) has been applied only occasionally, as exemplified by the reaction of the 5-chloro- and 5-azidotetrazolium salts (**9a**)[5] and (**10a**)[14] with alkali hydroxide; in both cases the product (**A1b**) was obtained in high yield (Scheme 5).

While the azido group of **10a** is also displaced by amines (see below Scheme 14), soft nucleophiles like cyanide and *p*-toluenesulfinate ion attack this group at the terminal nitrogen atom to give addition products, as will be shown in Scheme 16.[14]



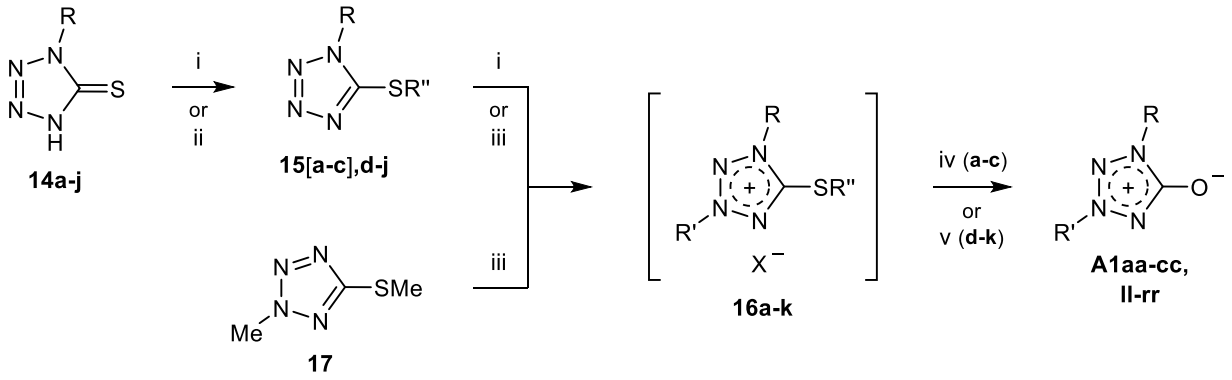
11	**12**	R	R'	**A1**	from	method	ratio **12** / **A1**	yield **A1** (%)	mp (°C)	ref.
b		Ph	Ph	**b**	**9a** / **10a**	i		92 / 87	(*cf.* Scheme 2)	5 / 14
	a	$[CH_2]_2OH$	$[CH_2]_2OH$	**aa**	**11a**	iii	65 / 35	32 [a]	[b]	15
c	**b**	Me	$[CH_2]_2OH$	**bb**	**11c**	iii	82 / 18	6 [a]	[b]	15
	c	Ph	$[CH_2]_2OH$	**cc**	**11b**	iii	87 / 13	10 [a]	[b]	15
		Ph	1-adamantyl	**dd**	**11b**	ii		74 / 75	179 – 181	16a / 16b
		Ph	*t*-Bu	**ee**	**11b**	ii		52	118 – 120	16a
d		Et	1-adamantyl	**ff**	**11d**	ii		71 / 60	110 – 112	16a / 16b
e		4-$(CO_2Me)C_6H_4$	1-adamantyl	**gg**	**11e**	ii		81	159 – 161	16a,b
f		4-$NO_2C_6H_4$	1-adamantyl	**hh**	**11f**	ii		73	212 – 214	16a
		4-$NO_2C_6H_4$	*t*-Bu	**ii**	**11f**	ii		41	149 – 151	16a
g	**d**	4-ClC_6H_4	CH_2Ph	**jj**	**13a**	v	[c]			17
				jj	**11g**	iv	91 / 9 [d]	5	119	17
	e	4-ClC_6H_4	Me	**kk**	**13b**	v	72 [e] / [f]			17
				kk	**11g**	iv	88 [e] / [f]			17

[a] From mixture of **12** / **A1**. [b] For data, see Scheme 6. [c] Mixture of **A1jj** (1.5%), **12d** (44%), and **12e** (54.5%) (according to NMR); besides traces of **11g**. [d] Ratio **12d** / **A1jj** after separation of small amounts of **11g** (NMR). [e] Isolated amount (%) of **12e**. [f] Possibly traces of **A1kk** (not isolated).

Scheme 5

Using non-quaternary tetrazoles as starting materials, three modes have been reported [*cf.* Scheme 1, routes (d) – (f)]. Alkylation of the tetrazolones (**11a-c**) with 2-chloroethanol afforded mixtures of **12** and **A1**, with the former predominating.[15] More importantly: when tetrazolones such as **11b,d-f** were treated with tertiary alcohols in conc. sulfuric acid, the attack occurred regioselectively at N(3) to give the derivatives (**A1dd-ii**) as the sole products.[16] Small amounts of olates (**A1**) were found as side products on heating tetrazolyl ethers like **13** in the presence of sodium iodide: **13a** rearranged into the tetrazolone (**12d**) and **A1jj**. This O → N

alkyl migration proceeded intermolecularly *via* the anion of **11**, as evidenced by addition of methyl iodide which produced – as a third component – substantial quantities of the congener (**12e**). Possibly, also the methyl ether (**13b**) gave some olate (**A1kk**), but the traces were not isolated, nor were they separated from a parallel run of **11g** with methyl iodide – in contrast to **A1jj** (made from **11g** and benzyl iodide).[17]



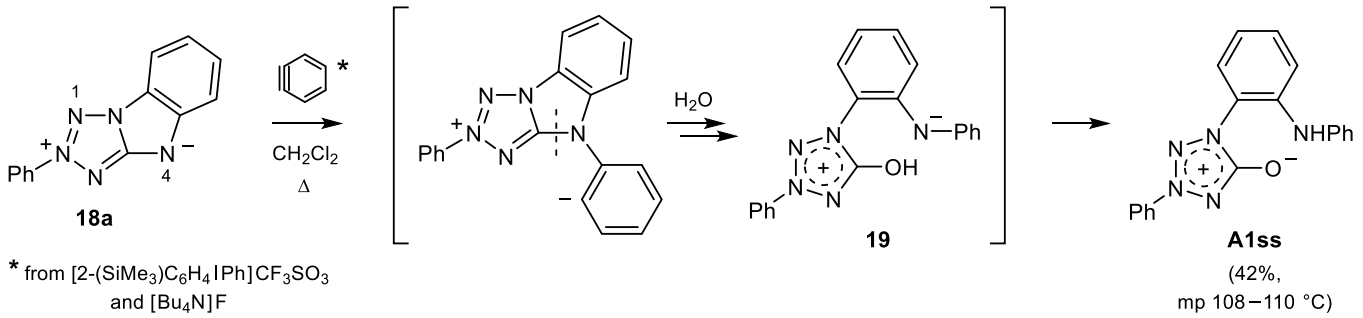
i: oxirane, AcOH, rt ii: BuBr, NaOMe, MeOH, Δ iii: $(MeO)_2SO_2$ (neat), Δ iv: AcOH, H_2O, rt v: aq. KOH, Δ

14–16	R	R'	R''	**A1**	from	steps to **16**	yield (%)	mp (°C)	ref.
a	$[CH_2]_2OH$	$[CH_2]_2OH$	$[CH_2]_2OH$	**aa**	**14a**	i, i	28	oil	15
b	Me	$[CH_2]_2OH$	$[CH_2]_2OH$	**bb**	**14b**	i, i	44	109–110	15
c	Ph	$[CH_2]_2OH$	$[CH_2]_2OH$	**cc**	**14c**	i, i	56	143–144	15
d	Et	Me	Bu	**ll**	**14d**	ii, iii	30	[a]	18
e	Bu	Me	Bu	**mm**	**14e**	ii, iii	44	[a]	18
f	C_6H_{13}	Me	Bu	**nn**	**14f**	ii, iii	37	[a]	18
g	Ph	Me	Bu	**oo**	**14g**	ii, iii	52	[a]	18
h	C_8H_{17}	Me	Bu	**pp**	**14h**	ii, iii	8	[a]	18
i	$C_{12}H_{25}$	Me	Bu	**qq**	**14i**	ii, iii	42	[a]	18
j	Me	Me	Bu	**rr**	**14b**	ii, iii	16 [b]	[c]	18
k	Me	Me	Me	**rr**	**17**	iii	60	[c]	19

[a] Ionic liquid. [b] Besides 34% **12** (R = R' = Me; Scheme 5); yields recalculated. [c] Unreported.

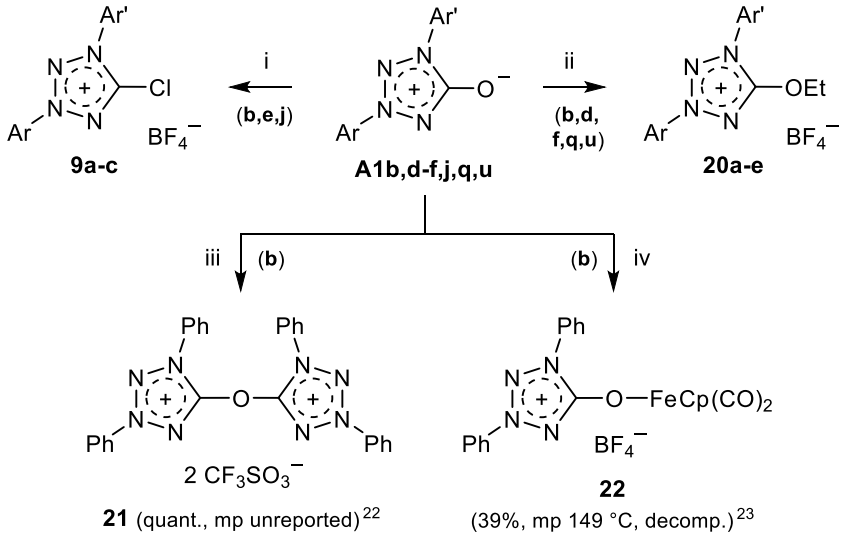
Scheme 6

An unexpected formation of olates (**A1**) was encountered on treatment of the tetrazolethiones (**14a-c**) with oxirane in acetic acid (Scheme 6) [*cf.* mode (e) of Scheme 1]. The reaction was recognized as proceeding *via* the thio ethers (**15a-c**); remarkably, these species underwent regioselective alkylation to give the salts (**16a-c**) which, during work-up, hydrolyzed to the olates (**A1aa-cc**).[15] Following the same sequence, olates like **A1ll-rr** (mostly ionic liquids) have been prepared; here the intermediary thio ethers (**15d-j**) were isolated (in contrast to **15a-c**), whereas the quaternary salts were hydrolyzed *in situ* by adding alkali hydroxide.[18] The latter step also finished an earlier synthesis of **A1rr** that started from the thio ether (**17**).[19]



Scheme 7

A peculiar olate-giving process constitutes the reaction of the heteropentalene mesomeric betaine (**18a**)[20] with benzyne (Scheme 7):[21] the product (**A1ss**) was assumed to arise from electrophilic attack at N(4), followed by sequential protonation of the phenyl group and ring opening through the residual hydroxide ion; this led to the species (**19**) which underwent proton transfer [*cf.* mode (g) of Scheme 1].



i: $POCl_3$ (neat), Δ, then aq. HBF_4 ii: $[Et_3O]BF_4$, CH_2Cl_2, rt iii: $(CF_3SO_2)_2O$, CH_2Cl_2, rt
iv: $[FeICp(CO)_2]$ / $AgBF_4$, CH_2Cl_2, rt

A1	Ar	Ar'	**9**	**20**	yield (%)	mp (°C)	ref.
b	Ph	Ph	**a**		90	185–188 [a,b]	14
	Ph	Ph		**a**	90	174	3a
d	Ph	4-ClC_6H_4		**b**	70	159	3a
e	Ph	4-MeC_6H_4	**b**		75	210 [a]	14
f	4-ClC_6H_4	Ph		**c**	95	180	3a
j	Ph	2,4,6-$Me_3C_6H_2$	**c**		82	186–188	7
q	4-MeC_6H_4	4-MeC_6H_4		**d**	100	138	3a
u	4-ClC_6H_4	4-ClC_6H_4		**e**	92	169	3a

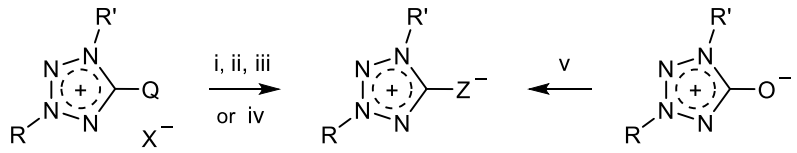
[a] Decomp. [b] Mp from ref.[5]

Scheme 8

Conversions of olates (**A1**) into a variety of tetrazolium salts are collected in Scheme 8. As a reversal of the reaction (**9a** → **A1b**) (Scheme 5), treatment of **A1b,e,j** with phosphoryl chloride and tetrafluoroboric acid gave the 5-chlorotetrazolium salts (**9a-c**) in good to excellent yield.[7, 14] Meerwein alkylation transformed the respective substrates (**A1**) into the 5-ethoxy salts (**20a-e**).[3a,c] Further reactions of the olate (**A1b**) include its conversion into the dicationic ether salt (**21**)[22] and the metal complex (**22**).[23]

b) Tetrazolium-5-thiolates (A2) and -5-selenolates (A3)

In contrast to the ring transformations of Scheme 2, attempts to rearrange thialogues of **1** (S instead of O) into thiolates (**A2**) failed.[3b] Thereupon, the authors successfully treated **20a** (and analogues) with sodium sulfide [Scheme 9; *cf.* mode (b) of Scheme 1]. Later, it was found that application of the 5-chloro salt (**9a**) improved the yield.[5] For preparing **A2a**, the methylthio function served as a leaving group,[19] as in the earlier synthesis of the 3-ethyl-1-phenyl congener.[1f] The selenolate (**A3a**) was also best made from **9a**, whereas employment of the iodo substrate (**9e**) was deteriorating.[5] A novel strategy for **A2** constitutes the conversion of olates (**A1**) by Lawesson's reagent [*cf.* route (i) of Scheme 1]. This method was first applied for the process (**A1b** → **A2b**).[24] Soon thereafter, the derivatives (**A2c,d**) were made in the same manner.[5]



9a,e; **20a**: X = BF_4
16k: X = $MeOSO_3$

A2a-d: Z = S
A3a: Z = Se

A1b,c,g

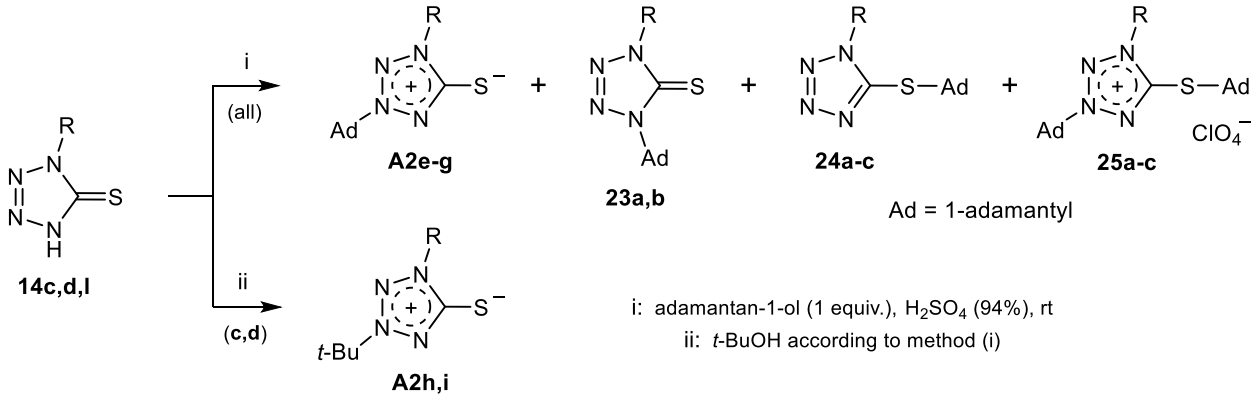
i: Na_2S (neat), Δ ii: Na_2S, DMF, Δ iii: NaHS, DMF, rt iv: NaHSe, EtOH, rt v: Lawesson's reagent, toluene, Δ

9	16	20	A1	Q	R	R'	A2	A3	from	method	yield (%)	mp (°C)	ref.
	k			SMe	Me	Me	**a**		**16k**	i	40	[a]	19
		a	**b**	OEt	Ph	Ph	**b**		**20a / 9a**	ii / iii	66 / 100	[a] / 155	3b / 5
a				Cl	Ph	Ph	**b**		**A1b**	v	93	[a]	24
e				I	Ph	Ph		**a**	**9a / 9e**	iv	100 / 77	158	5
			c		Ph	4-MeC_6H_4	**c**		**A1c**	v	94	132 – 134	5
			g		4-$MeOC_6H_4$	Ph	**d**		**A1g**	v	90	164 – 166	5

[a] Unreported.

Scheme 9

Another new synthesis of thiolates (**A2**) was found in the behaviour of tetrazolethiones (**14**) towards tertiary alcohols in sulfuric acid; established examples are the derivatives (**A2e-i**) (Scheme 10).[16a, 25] The reaction corresponds to mode (d) of Scheme 1 and resembles the process (**11** → **A1**) (Scheme 5). Whereas *tert*-butyl alcohol only yielded the thiolates (**A2h,i**), alkylation with adamantan-1-ol was not regioselective. The latter

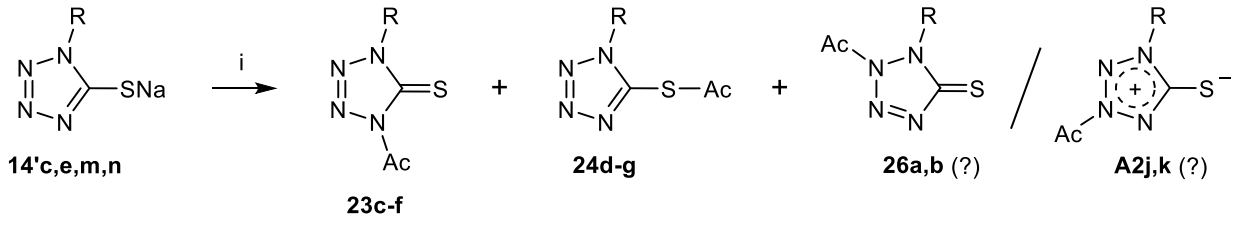


14	R	A2	23	24, 25	A2: yield (%)	mp (°C)	ratio A2 / 23 / 24	25: yield (%)	ref.
c	Ph	**e**		**a**	21	207		15 [a]	25
d	Et	**f**	**a**	**b**	19	144–146	77 / 4 / 19	26 [a]	16a
l	4-(CO_2Me)C_6H_4	**g**	**b**	**c**	25	157–159	82 / 4 / 14	17 [a,b]	16a
	Ph	**h**			15	168–170			16a
	Et	**i**			21	113–115			16a

[a] From the aqueous filtrate of **A2** / **23** / **24** by adding $HClO_4$. [b] Studied by X-ray diffraction.

Scheme 10

applies also to acetylation (Scheme 11),[26] but here it is questionable whether the third component obtained from **14'e,m** has structure (**26**), as thought by the authors.[26b] Tetrazoles with a 1,2-substitution pattern are not known, and a DFT study on acetyl derivatives having R = Me revealed that the respective compound (**26**) is higher in energy than the thiolate (**A2**).[26c] A similar relationship has recently been calculated for 1,2-dimethyltetrazol-5(2*H*)-one and the isomeric olate (**A1rr**).[1c]

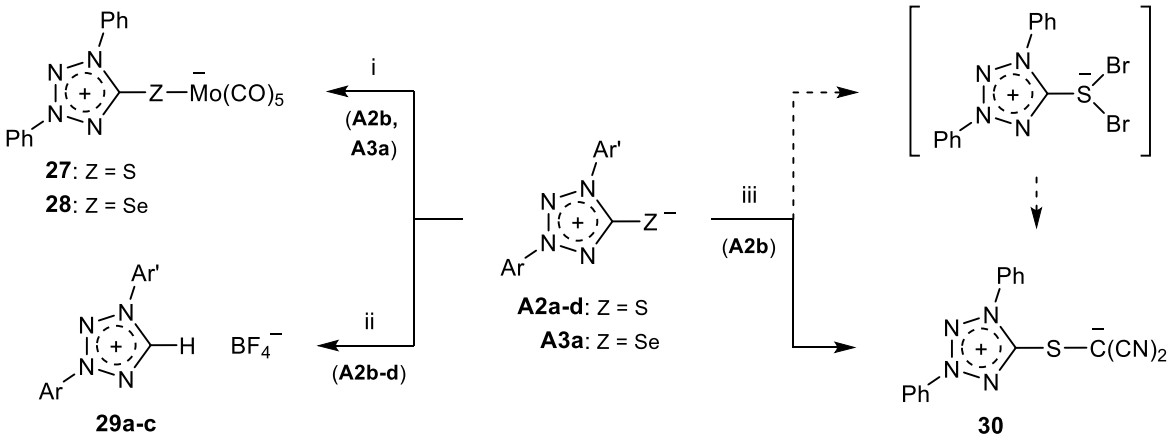


14'	R	23	24	26	ratio 23 / 24 / 26 [a]	ref.
c	Ph	**c**	**d**		50 / 50 / 0	26a
e	Bu	**d**	**e**	**a** [b]	52 / 25 / 23	26b
m	Pr	**e**	**f**	**b** [b]	37 / 35 / 28	26b
n	2,4,6-$Me_3C_6H_2$	**f**	**g**		30 / 70 / 0	26b

[a] Determined by ^{1}H NMR. [b] Possibly **A2j** and **A2k**, respectively.

Scheme 11

Specific reactions of **A2** and **A3** are shown in Scheme 12. Heating of the derivatives (**A2b**) and (**A3a**) with hexacarbonylmolybdenum(0) gave the complexes (**27**) and (**28**), the latter in low yield. Attempts to prepare the chromium analogue of **27** and the iron complex corresponding to **22** (Scheme 8) failed.[23] As expected, nitric acid smoothly desulfurized the thiolates (**A2b-d**) to the 5-unsubstituted tetrazolium salts (**29a-c**).[5] A remarkable product, the mesoionic thiocarbonyl ylide (**30**), arose on sequential treatment of **A2b** with bromine and sodium dicyanomethanide. The reaction was thought to proceed *via* a 1:1 bromine adduct that separated from the reaction mixture, but could not be fully characterized because of instability.[27]



i: $Mo(CO)_6$, benzene, Δ ii: HNO_3, Δ; then $NaBF_4$ iii: Br_2, CH_2Cl_2, rt; then $NaCH(CN)_2$

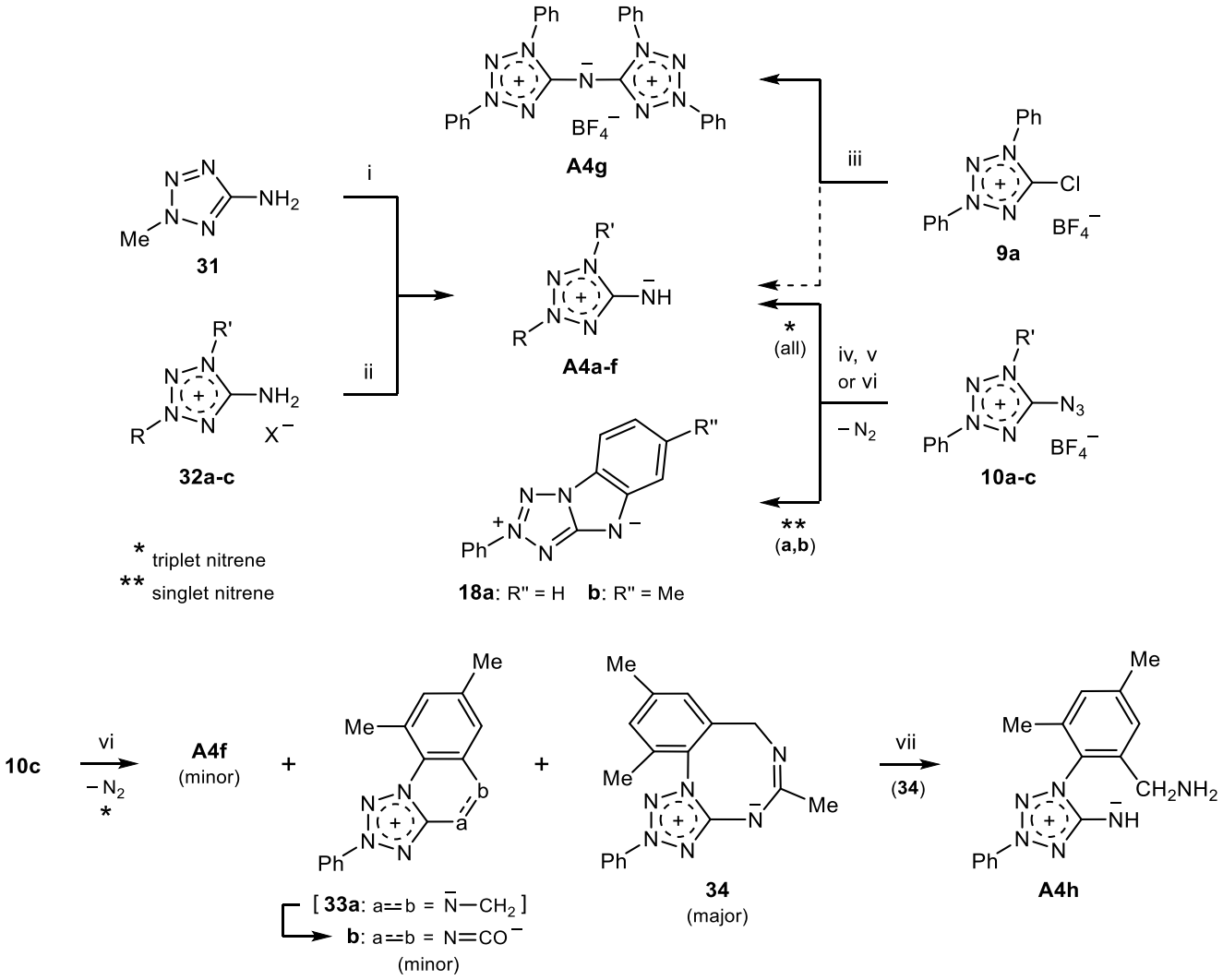
29	A2	A3	Ar	Ar'		yield (%)	mp (°C)	ref.		yield (%)	mp (°C)	ref.
a	**b**	**a**	Ph	Ph	**27**	98	114 [a]	23	**29a**	89	177–178	5
b	**c**		Ph	4-MeC_6H_4	**28**	10	120 [a]	23	**b**	61	186–188	5
c	**d**		4-$MeOC_6H_4$	Ph	**30**	36	120 [a]	27	**c**	66	172–175	5

[a] Decomp.

Scheme 12

c) Tetrazolium-5-aminides (A4)

The simplest aminide (**A4a**) has been generated in a frozen matrix by UV light-induced tautomerism of the tetrazole (**31**) (Scheme 13). Of all possible structures formed through proton migration, the *ap* conformer of **A4a** has been calculated to be lowest in energy (next to **31**).[28] Homologues of the earliest derivative (**A4b**)[29] were obtained from the salts (**9**), (**10**), and (**32**), *i.e.* after modes (b) and (g) of Scheme 1. Of these entries, deprotonation proved to be the most expeditious one (see **32b** → **A4c**,[30] **32c** → **A4d**[14]). Ammonolysis, exemplified with **9a**, mainly gave **A4g**, as the desired aminide (**A4d**) reacted further.[14] Photolysis of azides such as **10a,b** turned out to be complex, since both triplet and singlet nitrenes are involved; in general, the former lead to aminides (**A4**),[7,31] the latter to azapentalenes (**18**).[7] So, when **10a** was irradiated in methanol, **A4d** and **18a** were formed in equal quantities. However, on addition of the triplet sensitizer acetophenone,



i: Ar matrix, hν, 10 K ii: aq. NaOH (1 M), $CHCl_3$ or CH_2Cl_2, rt iii: aq. NH_3 (28%), MeCN, rt iv: hν, MeOH, then aq. NaOH, rt
v: method (iv), but using additives vi: hν, MeCN, then aq. NaOH, rt vii: HCl (conc.), Δ, then aq. NaOH (10 M)

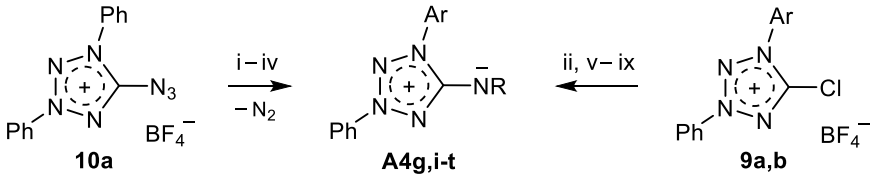
10	32	R	R'	X	A4	from	method	yield (%)	mp (°C)	ref.
		Me	H		**a**	**31**	i			28
	a	Me	Me	Cl	**b**	**32a**	ii	81	41–43	29
	b	*t*-Bu	*t*-Bu	ClO_4	**c**	**32b**	ii	91	69–70	30
a	**c**	Ph	Ph	BF_4	**d**	**32c** / **9a**	ii / iii	100 / 12 [a]	115–117	14
		Ph	Ph		**d**	**10a**	iv	23 [b]		7
		Ph	Ph		**d**	**10a**	v [c]	72 / 15 [d] / 26 [e]		7
b		Ph	4-MeC_6H_4		**e**	**10b**	[f]	[f]	132–134	7
c		Ph	2,4,6-$Me_3C_6H_2$		**f**	**10c**	iv / vi	56 / 10 [g]	100–101	7 / 31
					g	**9a**	iii	73	264–265	14
					h	**10c** *via* **34**	vi, vii	23 [h]	92–94	31

[a] Besides traces of **A1b** (Scheme 2) and 73% **A4g** (as listed below). [b] Besides 20% **18a** (mp 216–217 °C) as well as traces of **A1b** and **A4g.** [c] Additive: PhCOMe / pyrene / anthracene. [d] Besides 8% **18a**, 16% **A4g**, traces of **A1b**, and 7% **A4j** (Scheme 14). [e] Besides traces of **18a** and 13% **A4k** (Scheme 14). [f] Preparative details missing. [g] Besides 8% **33b** (mp > 300 °C, decomp.) and 29% **34** (mp 228–229 °C, decomp.; studied by X-ray diffraction). [h] Overall yield; unstable material.

Scheme 13

the formation of **18a** was suppressed. Singlet promotors like pyrene and anthracene should favour **18a**, but, surprisingly, these additives increased the yield of **A4d** (relative to **18a**) and gave *N*-substituted aminides (**A4j**) and (**A4k**) as side products (see Scheme 14).

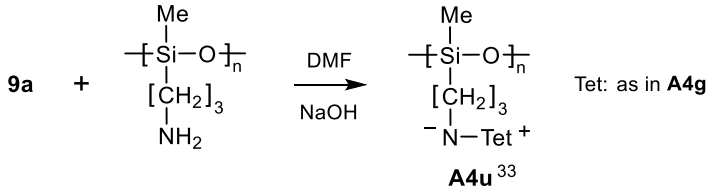
Another unexpected result was encountered with the mesityl derivative (**10c**): instead of benzylic hydrogen abstraction to give the tricycle (**33a**), the solvent was affected to afford **A4f** in good yield.[7] However, changing from methanol to acetonitrile, the amount of **A4f** was reduced and – as remarkable products – the tricycles (**33b**) and (**34**) were found, which obviously arose *via* **33a**.[31] Regarding irridiation of **10a,b** in acetonitrile, instead of the aminides (**A4d,e**) conspicuous amounts of acetanilide and *p*-acetotoluidide were formed (besides **18a,b**).[7] Finally, hydrolysis of the cyclic amidine function in the eight-membered ring of (**34**) led to another unsubstituted aminide (**A4h**).[31]



i: 1,3-diphenyltetrazolium-5-aminide (**A4d**), MeCN, rt ii: 1-phenyltetrazol-5-amine, DBU, CH_2Cl_2, rt
iii: hν, MeOH, pyrene; then aq. NaOH, rt iv: hν, MeOH, anthracene; then aq. NaOH, rt v: $[MeNH_3]Cl$, NEt_3, MeCN, Δ
vi: *s*-$BuNH_2$, MeCN, Δ vii: *c*-$C_6H_{11}NH_2$ or $PhC(Me)NH_2$ or 4-$MeOC_6H_4NH_2$ or 4-(*s*-Bu)$C_6H_4NH_2$, NEt_3, MeCN, Δ
viii: $PhNH_2$ or 4-$EtC_6H_4NH_2$ or L-alanine-*N*-propylamide, $CHCl_3$ or CH_2Cl_2, Δ or rt; then $NaHCO_3$, rt ix: 1-aminopyrene, MeCN, rt; then NaOH

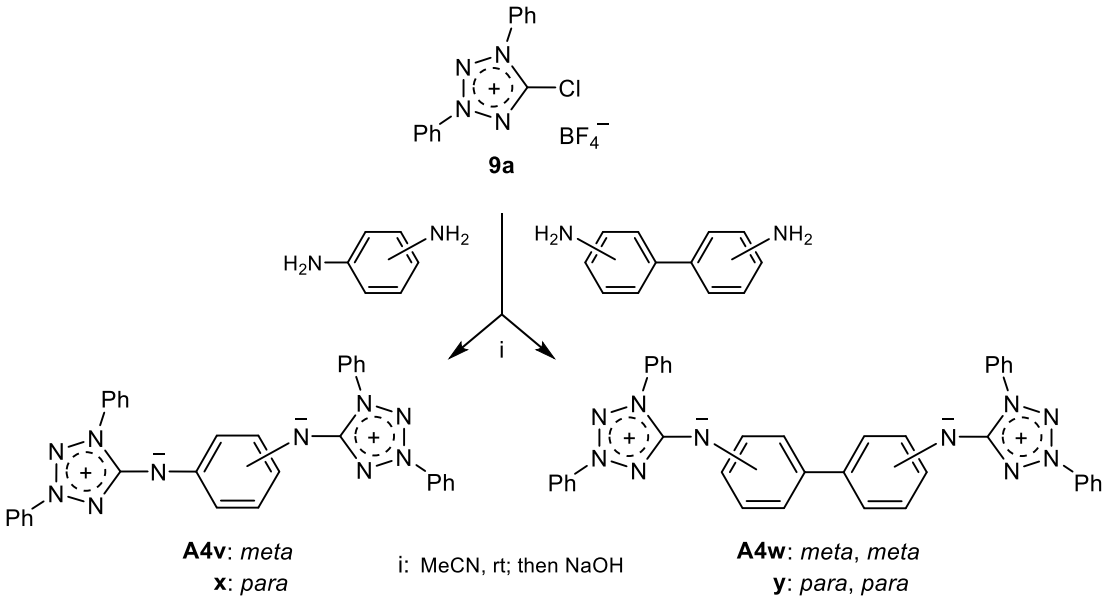
9	Ar	R	**A4**	from	method	yield (%)	mp (°C)	ref.
a	Ph	$Tet^+BF_4^-$ [a]	**g**	**10a**	i	87	(see Scheme 13)	14
	Ph	Tet [b]	**i**	**9a**/**10a**	ii / ii	45 [c] / 27 [d]	227–228	14
	Ph	pyren-1-yl	**j**	**9a**/**10a**	ix / iii	35/7 [e]	246–247	7/7
	Ph	9-anthryl	**k**	**10a**	iv	13 [f]	195–196	7
	Ph	Me	**l**	**9a**	v	72	[g]	32
	Ph	*s*-Bu	**m**	**9a**	vi	63	93–94	8
	Ph	*c*-C_6H_{11}	**n**	**9a**	vii	18	[g]	32
	Ph	CH(Me)Ph	**o**	**9a**	vii	45	92–102	8
	Ph	Ph	**p**	**9a**	viii	85	132	5
	Ph	4-$MeOC_6H_4$	**q**	**9a**	vii	28	[g]	32
	Ph	4-(*s*-Bu)C_6H_4	**r**	**9a**	vii	47	98–99	8
	Ph	C(Me)CONHPr	**s** [h]	**9a**	viii	[g]	[g]	33
b	4-MeC_6H_4	4-EtC_6H_4	**t**	**9b**	viii	69	86–88	21

[a] Tet^+ = 1,3-diphenyltetrazolium-5-yl. [b] Tet = 1-phenyltetrazol-5-yl. [c] Besides 25% **A1b** (Scheme 2). [d] Besides 43% **A1b.** [e] Besides 8% **18a** (Scheme 13), 16% **A4g**, and traces of **A1b.** [f] Besides traces of **18a.** [g] Unreported. [h] *S*-Isomer.



Scheme 14

N-Substituted aminides (**A4**) have been obtained from both the tetrazolium salts (**9**) and (**10**) (Scheme 14). Treatment of **10a** with the aminide (**A4d**) or 1-phenyltetrazol-5-amine furnished the derivatives (**A4g**) and (**A4i**), while photolysis in the presence of pyrene or anthracene produced small amounts of **A4j** and **A4k** (*cf.* preceding paragraph).[7, 14] But more frequently the salts (**9**) served as substrates, and their reactions with primary amines proceeded satisfactorily in most cases (→ **A4i,j,l-t**).[5, 7, 8, 14, 21, 32, 33] The procedure has also been applied to the synthesis of polymers of the type (**A4u**) which are useful for electrolytes of lithium batteries.[33] In the same fashion, certain bisaminides such as **A4v-y** have been provided for electrochemical investigations; these materials represent reversible four-stage redox systems (Scheme 15).[34]



A4	yield (%)	mp (°C)	ref.
v · 2 HBF_4	51	112−120	34
v	92 [a]	83 [b]	34
w	38	227 [c]	34
x · 2 HBF_4	70	260−262	34
x	100 [d]	284−286 [e]	34
y	79 [f]	> 300	34

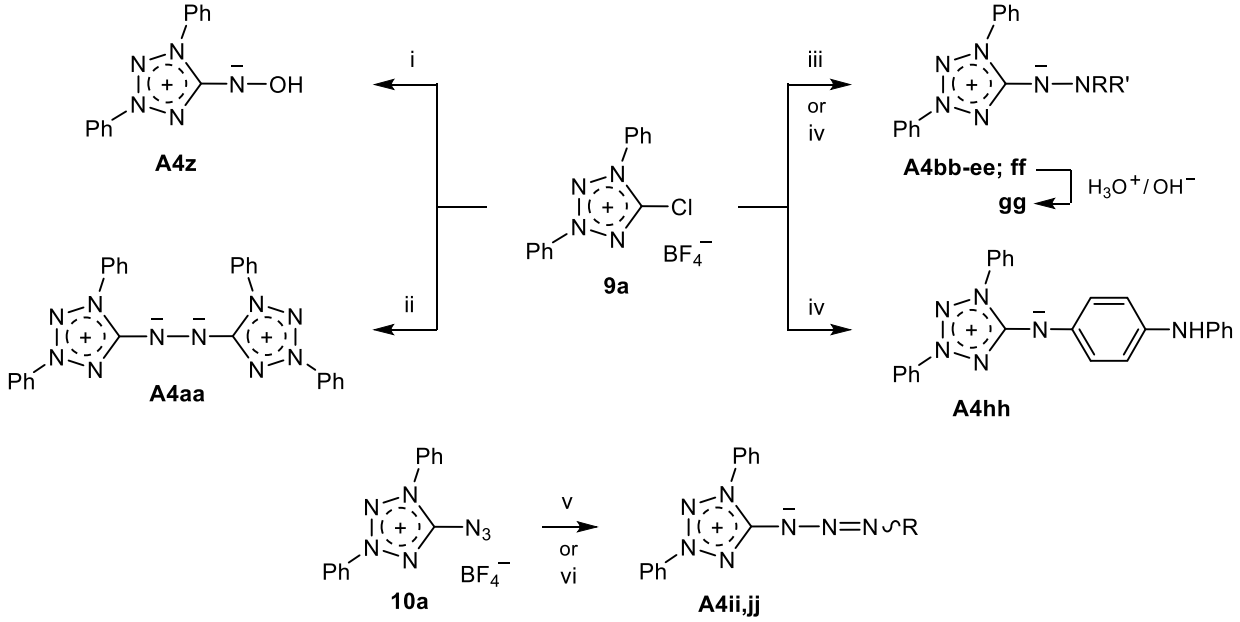
[a] Crude (based on **A4v** · 2 HBF_4); pure 27%. [b] Sesquihydrate. [c] Decomp. [d] Crude (based on **A4x** · 2 HBF_4). [e] Hemihydrate. [f] Crude; pure 55%.

Scheme 15

Following the above method, also derivatives bearing a heteroatom at the aminide function, such as **A4z** and **A4aa-ff**, have been prepared, *viz.* by reacting **9a** with hydroxylamine and the appropriate hydrazines (Scheme 16).[14, 34, 35] In the first case, part of the substrate underwent hydrolysis to give the olate (**A1b**). Using *N*,*N*-diphenylhydrazine, the expected hydrazinide (**A4ee**) was obtained in low yield only, because

rearrangement took place to afford the aminide (**A4hh**).[14] Since, as shown, hydrazine hydrate reacted twofold (→ **A4aa**), a hydrazinide having a free N–NH_2 function like **A4gg** had to be approached *via* the benzamido derivative (**A4ff**).[35]

A special class of heteroatom-substituted aminides, *viz.* the triazenides (**A4ii,jj**), was discovered by treating the salt (**10a**) with the soft anions cyanide and *p*-toluenesulfinate, which – in contrast to hard nucleophiles like hydroxide ion and amines (*cf.* Schemes 5 and 14) – do not displace the azido group. The same kind of addition was found with triphenylphosphine (another soft nucleophile).[14]



i: $[NH_3OH]Cl$, NEt_3, MeCN, rt ii: $H_2NNH_2 \cdot H_2O$, MeCN, rt iii: H_2NNRR', MeCN, rt, then aq. $NaHCO_3$ or NaOH
iv: H_2NNPh_2, MeCN, rt, then aq. $NaHCO_3$ v: NaCN, DMF, rt vi: 4-$MeC_6H_4SO_2Na$, DMF, rt

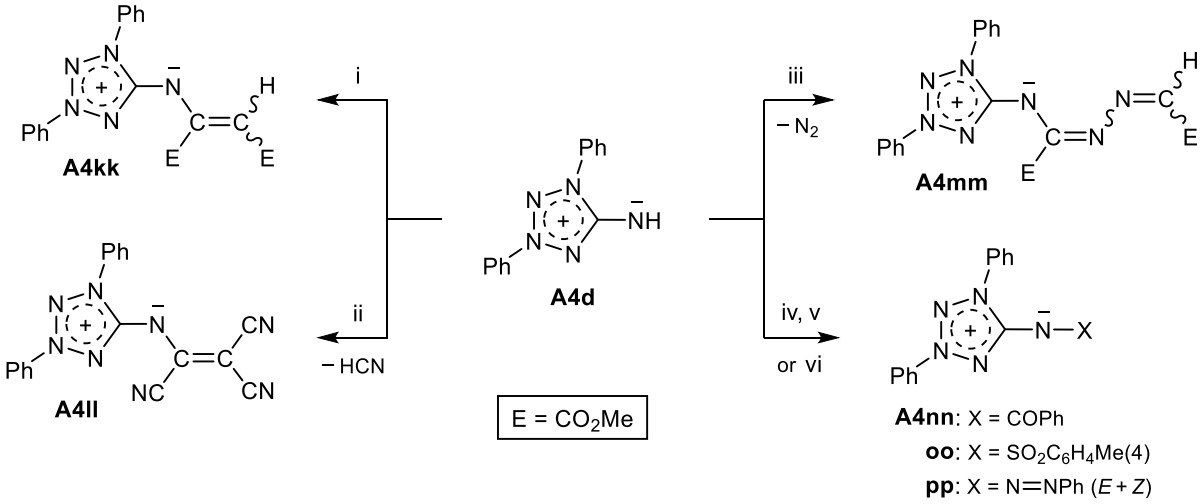
A4	R	R'	method	yield (%)	mp (°C)	ref.
z			i	62 [a]	151–154	14
aa			ii	72	> 300	34
bb	H	Ph	iii	67	127–130	14
cc	H	4-MeC_6H_4	iii	69	160–163	14
dd	Me	Ph	iii	37	145–148	14
ee	Ph	Ph	iii	18 [b]	218	14
ff	H	PhCO	iii	12	176–177 [c]	35
gg	H	H	[d]	84	107 [c]	35
hh			iv [e]	57	166–167	14
ii	CN		v	93 [f]	216–218	14
jj	$SO_2C_6H_4Me(4)$		vi	46	143–144	14

[a] Besides 22% **A1b** (Scheme 2) and 6% **A4g** (Scheme 13). [b] Besides 57% **A4hh** (as listed below). [c] Decomp. [d] From **A4ff** by acid hydrolysis and alkaline workup. [e] Alternatively, from **9a** and *N*-phenyl-*p*-phenylenediamine in 72% yield. [f] Mixture of geometrical isomers (ca. 4 : 1).

Scheme 16

Many aminides (**A4**) have been submitted to conversions, part of which led to further representatives of **A4** by simply modifying the functional group [*cf.* mode (i) of Scheme 1]. Thus, treatment of the unsubstituted aminide (**A4d**) with reagents having electron-deficient multiple bonds gave the addition products (**A4kk**) and (**A4mm**) (Scheme 17); using tetracyanoethene, the primary adduct extruded hydrogen cyanide to yield compound (**A4ll**).[21] As expected,[36] in no case did **A4d** react as a (masked) azimine dipole [see, however, the behaviour of the 1,2,3,4-oxatriazolium-5-aminide (**1b**) towards an isocyanate[3a]].

Substitution products, such as **A4nn-pp**, arose from treatment with acyl chlorides or a benzenediazonium salt;[31,35] the latter reaction implies an alternative (*i.e.* N–N forming) process giving a triazenide.



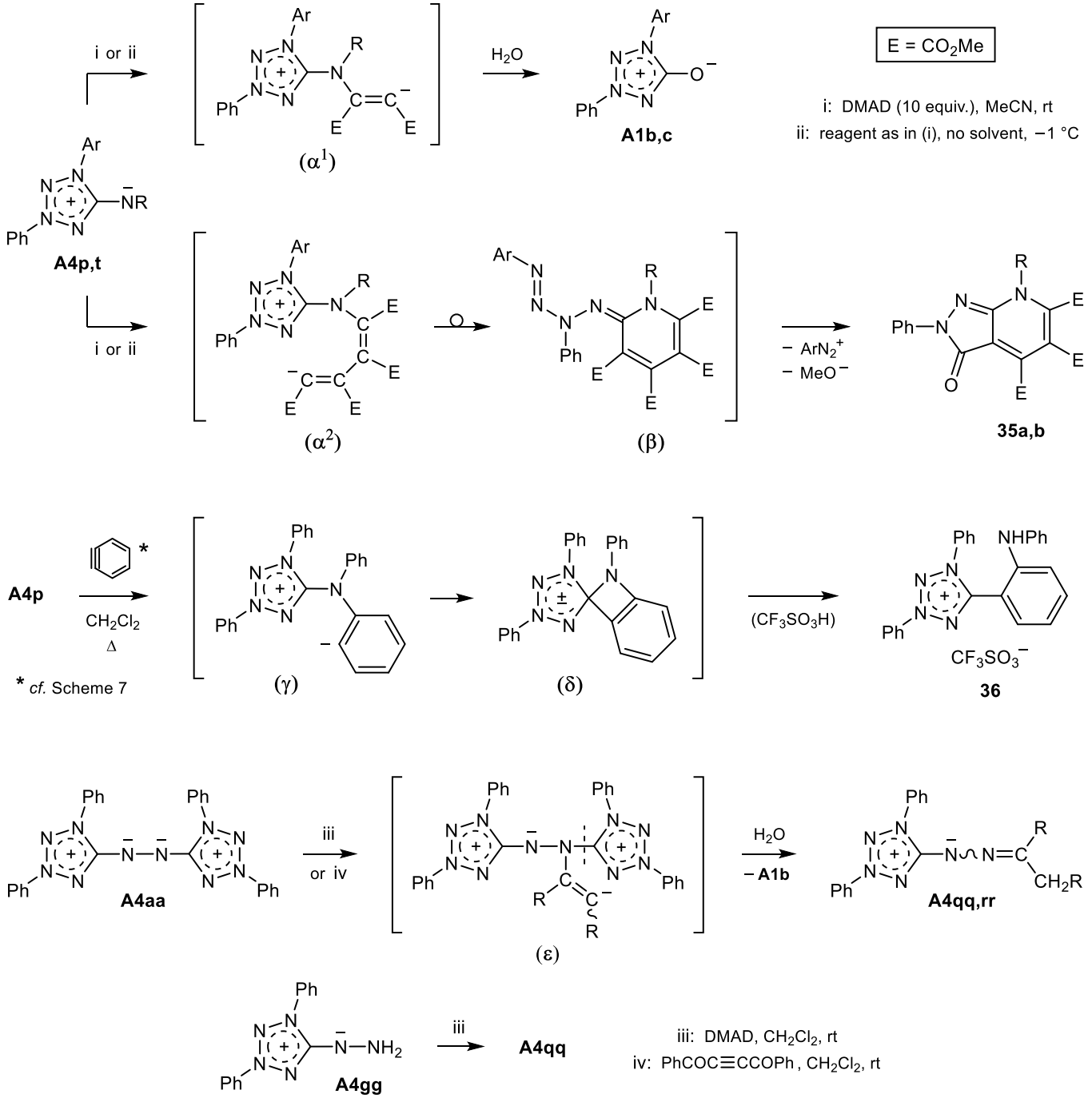
i: DMAD, toluene, rt ii: $(NC)_2C=C(CN)_2$, toluene, rt
iii: dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate, CH_2Cl_2, rt iv: PhCOCl, MeCN, rt; then aq. NaOH
v: 4-$MeC_6H_4SO_2Cl$, MeCN, rt vi: $[PhN_2]BF_4$, MeCN, 0 °C; then aq. NaOH

A4	yield (%)	mp (°C)	ref.
kk [a]	64 / 6	145–147 / 180–182	21
ll	78	240–241	21
mm	62 [b]	91–95	21
nn	84	228–229 [c]	31
oo	81	242 (*cf.* Scheme 20)	35
(*E*)-**pp**	41	204–206	35
(*Z*)-**pp**	11	140–142	35

[a] 2 geometrical isomers, structures not assigned. [b] Total yield of 3 geometrical isomers (ratio 59 : 29 : 12), not separated. [c] Decomp.

Scheme 17

Extending the above treatment with DMAD to *N*-aryl congeners, such as **A4p,t**, no addition products were obtained; rather, the respective Michael adducts (α^1) and (α^2) (concomitantly formed) underwent further conversions (Scheme 18): The first species hydrolyzed to the olates (**A1b,c**), whereas the second rearranged



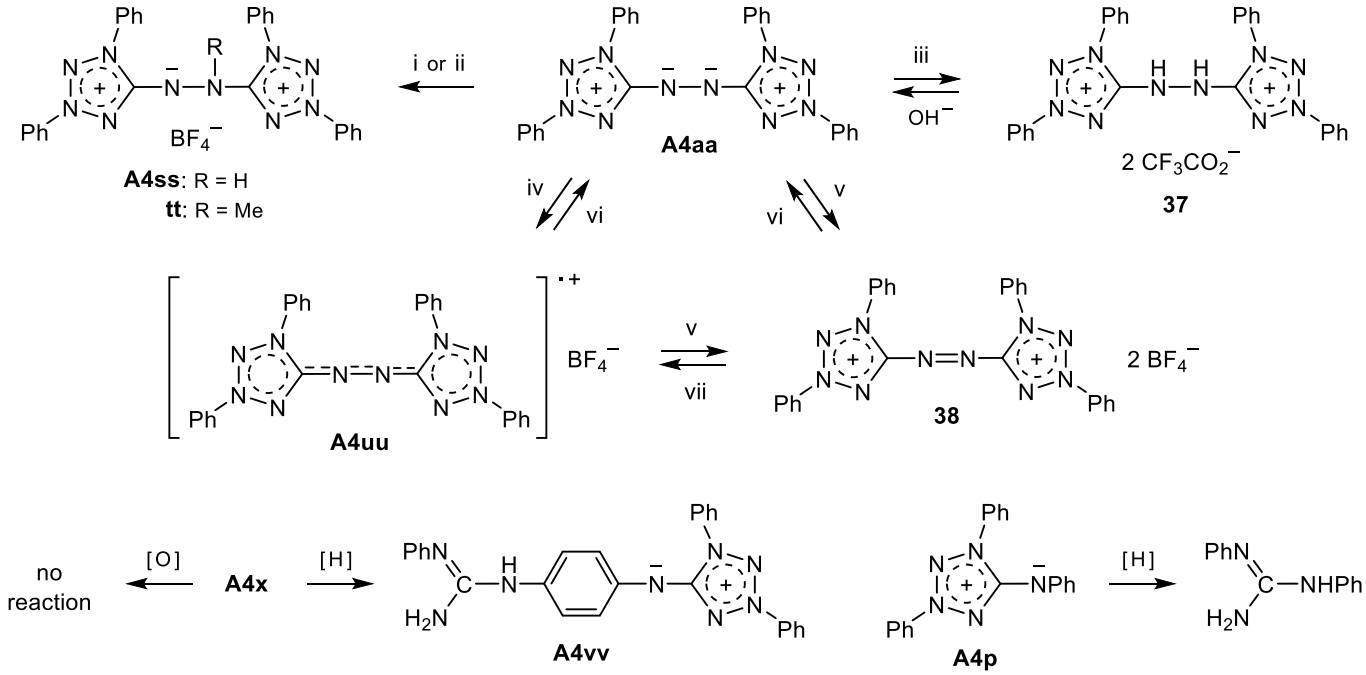
product	Ar	R	from	method	yield (%)	mp (°C)	ref.
A1b + **35a**	Ph	Ph	**A4p**	i	27 + 12 [a]	210−214 [b]	21
A1c + **35b**	4-MeC_6H_4	4-EtC_6H_4	**A4t**	ii	43 + 5 [c,d]	170−173 [b]	21
36					26	193−195	21
A4qq		CO_2Me	**A4aa**	iii	21 [e]	173−174	21
A4qq			**A4gg**	iii	91		21
A4rr		COPh		iv	14 [f]	162−165	21

[a] Besides 1% tetramethyl naphthalene-1,2,3,4-tetracarboxylate. [b] **35a** and **35b**, respectively. [c] Besides 2% dimethyl 2-(4-methylphenyl)maleate. [d] **35b** studied by X-ray diffraction. [e] Besides 21% **A1b** and 2% **A4kk** (Scheme 2 and 17, respectively). [f] Besides 46% **A1b.**

Scheme 18

to the tetrazene-substituted dihydropyridines (β) which, after extrusion of benzenediazonium ion, cyclized to the pyrazolo[3,4-*b*]pyridines (**35a,b**). A complementary experiment of **A4p** with benzyne afforded the tetrazolium salt (**36**); this compound arose through attack of the anionoid carbon of the adduct (γ) at C(5) of the tetrazolium moiety, followed by C–N bond cleavage of the four-membered ring of intermediate (δ).[21]

A unique reaction cascade started when the 'biaminide' (**A4aa**) was exposed to DMAD or dibenzoylethyne: The 1: 1 adduct (ε) was attacked at C(5) by the hydroxide ion (obviously from traces of moisture), with the consequence of expelling the adjacent tetrazole portion as olate (**A1b**); the residual enehydrazinic fragment underwent proton migration to afford the hydrazone derivatives (**A4qq**) and (**A4rr**) as final products. In a parallel run, compound (**A4qq**) was obtained in high yield from DMAD and the hydrazinide (**A4gg**).[21]



[O] = conc. HNO_3, PbO_2 or $K_3[Fe(CN)_6/OH^-$ [H] = Zn, CH_2Cl_2–HOAc, rt

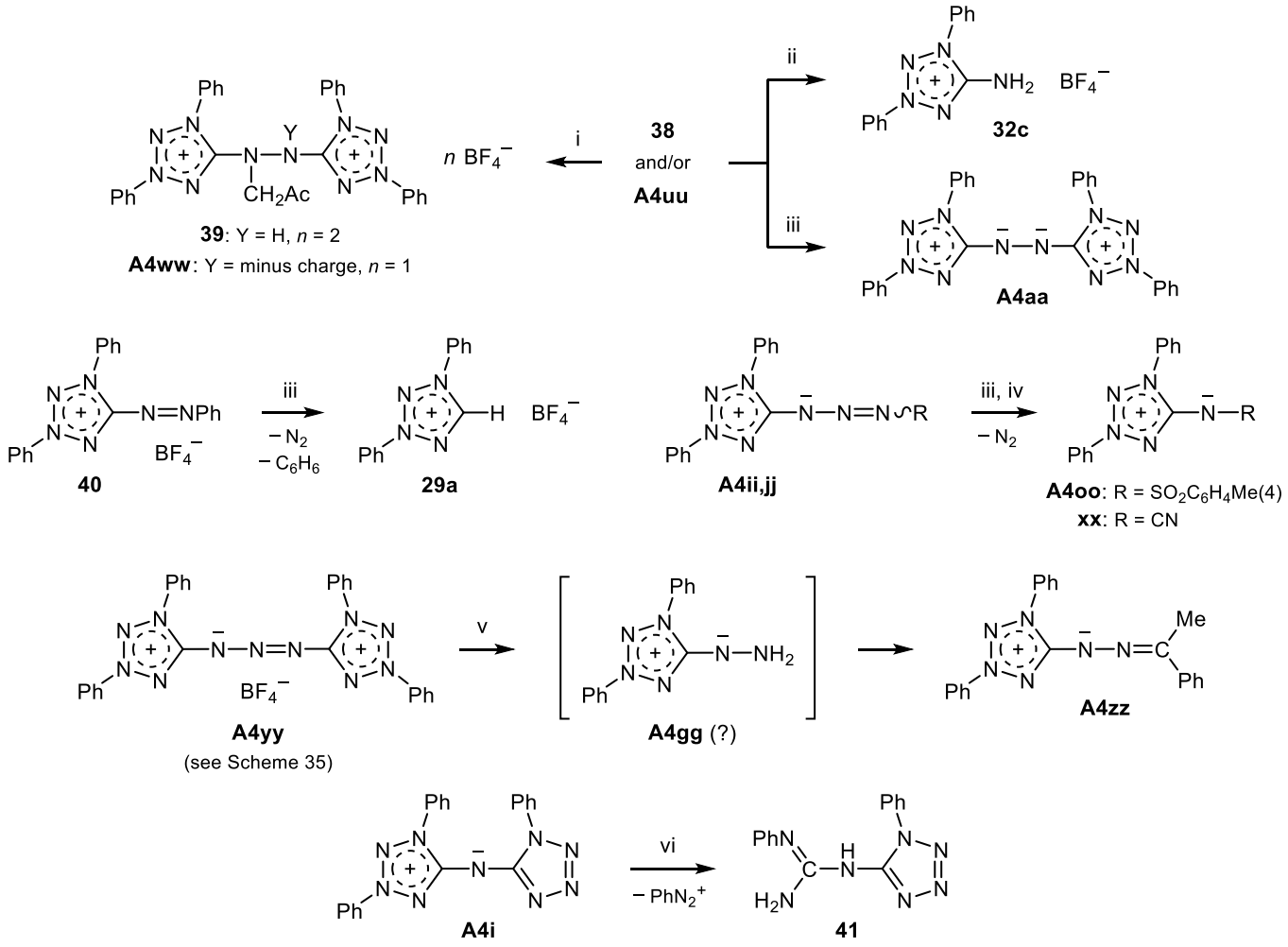
i: HOAc, CH_2Cl_2, then $NaBF_4$ ii: MeI, CH_2Cl_2, Δ, then $NaBF_4$ iii: CF_3CO_2H iv: $Pb(OAc)_4$, CH_2Cl_2, rt, then $NaBF_4$
v: conc. HNO_3, then $NaBF_4$ vi: Zn, MeCN, rt vii: Zn, EtOH, rt

product	method	yield (%)	mp (°C)	ref.
A4ss	i	85 [a]	130	34
A4tt	ii	56	221–222	34
37	iii	quant. [b]	[c]	34
A4uu	iv / vii	31	185–189	34
38	v	87	193–196	34
A4vv	viii	46	183–186	34

[a] Hemihydrate. [b] Crystals with 3 mol CF_3CO_2H. [c] Unreported.

Scheme 19

Further studies with the 'biaminide' (**A4aa**) comprise protonation, alkylation, and redox reactions (Scheme 19).[34] Using acetic and trifluoroacetic acid, **A4aa** could be selectively mono- and diprotonated to afford the



i: hν, Me_2CO ii: hν, EtCOEt iii: hν, MeOH; then aq. NaOH (in part) iv: hν, MeCN
v: hν, MeOH, PhCOMe (additive); then aq. NaOH vi: method (v) without alkaline work-up

product	from	method	yield (%)	mp (°C)	ref.
39 / **A4ww**	**38**	i	34 / 18 [a]	173–175 / 155–157	35
32c	**38**	ii	33	195 [b]	35
A4aa	**38**	iii	34 [c]	(see Scheme 16)	35
A4aa	**A4uu**	iii	54 [d]		35
A4oo	**A4jj**	iii / iv	1 [e] / 12 [f]	242 (*cf.* Scheme 17)	35
A4xx	**A4ii**	iii / iv	21 [g] / 34 [h]	211–212	35
A4zz	**A4yy**	v	13 [i,j]	178–179	35
41		vi	45	237–238	35

[a] Hemihydrate. [b] *Cf.* ref.[14] [c] Besides 18% **A1b** (Scheme 2), 3% **A4d** (Scheme 13), and 6% **A4g** (Scheme 13). [d] Besides 10% **A1b.** [e] Besides 53% **A4d** and 5% **18a** (Scheme 13). [f] Besides 32% **18a** and 12% acetanilide. [g] Besides 35% **A1b** and 6% **A4d.** [h] Besides 9% **18a.** [i] Besides 54% **A4d.** [j] 71% from authentic **A4gg** (Scheme 16) and PhCOMe.

Scheme 20

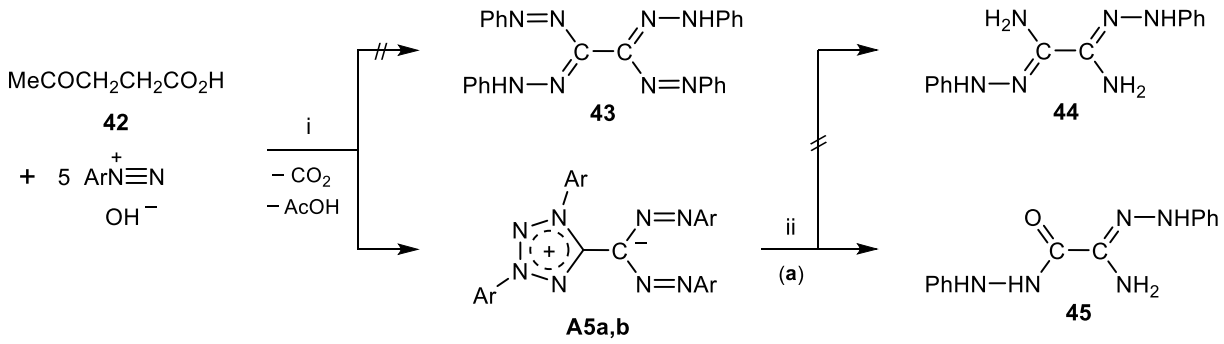
derivatives (**A4ss**) and (**37**). But methylation with methyl iodide (even used in excess) only allowed mono alkylation (**A4tt**). Treatment with lead tetraacetate and tetrafluoroborate ion gave the radical salt (**A4uu**), a remarkably stable compound, of which – for EPR and ENDOR spectra – also ^{15}N-labelled derivatives were made. Subsequent reaction with conc. nitric acid afforded the azo compound (**38**), while treatment of **A4uu** (and likewise **38**) with zinc powder restored the starting material. Further reduction did not give defined products, but voltammetric studies showed that **A4aa** is both oxidizable and reducible electrochemically, demonstrating that the compound is part of a reversible four-stage redox system. As for the 'phenylogue' (**A4x**) of Scheme 15, reduction with zinc proceeded readily (→ **A4vv**), *i.e.* after the pattern that converted **A4p** to *N*,*N*'-diphenylguanidine, but chemical oxidation failed – in contrast to the electrochemical methods, which were also effective with the congeners (**A4v,w,y**).[34]

Selected aminides (**A4**) including the azo salt (**38**) have been studied photochemically (Scheme 20).[35] The results were shown to depend on the solvent. Thus, when **38** was irradiated in acetone, the (CH-acidic) solvent added to the double bond, giving compound (**39**) besides its conjugate base (**A4ww**). Changing to diethyl ketone, no addition took place, but the N=N bond was cleaved to afford the aminotetrazolium salt (**32c**). Using methanol, **38** as well as the radical salt (**A4uu**) were reduced to **37** (BF_4 for CF_3CO_2) which on base treatment gave **A4aa**. Yet, considering that the phenylazo salt (**40**) releases dinitrogen and benzene to afford **29a**, the substrate (**38**) should have led to the 1,1',3,3'-tetraphenyl-5,5'-bitetrazolium ion.[35]

Also irradiation of the triazenides (**A4ii**) and (**A4jj**) gave product patterns that depend on the solvent. Using methanol, **A4jj** was mainly transformed into the *N*-unsubstituted aminide (**A4d**) and only negligibly into the tosyl derivative (**A4oo**), while in acetonitrile the yield of **A4oo** increased, although now, surprisingly, the azapentalene (**18a**) became the main product. Regarding **A4xx**, again a smaller quantity was found in methanol. Turning to the substrates (**A4yy**) and (**A4i**), both compounds reacted only in the presence of the sensitizer acetophenone. In the first reaction, a mixture of **A4d** (predominant material) and the hydrazone (**A4zz**) arose (the latter presumedly *via* transient **A4gg**); in the second case, ring cleavage occurred to give the guanidine (**41**).[35]

d) Tetrazolium-5-methanides (A5)

The material obtained in 1893 from **42** (or 4-oxoheptanedioic acid) and benzenediazonium hydroxide and at that time viewed as the biformazan (**43**)[37a] has later been recognized as the methanide (**A5a**)[38] (*cf.* ref.[1f]) (Scheme 21). The stepwise formation [which in part resembles route (c) of Scheme 1] was studied in detail, and it was shown that the fifth diazonium ion is required for dehydrogenation.[38] In order to complement ref.[1f], it might be added that an analogue (**A5b**) was prepared in the same way (low yield too) and, second, that the reduction of **A5a** following the procedure of ref.[37b] did not give the diamidrazone (**44**) as earlier described,[37a,b] but afforded the 'mixed' functionalized derivative (**45**).[38]

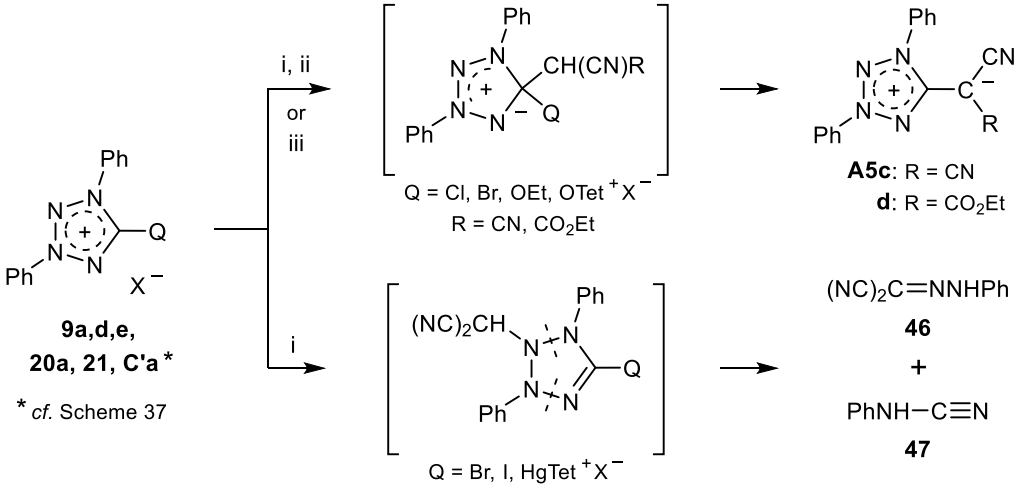


i: aq. KOH, −10 °C, then 1 N HCl, Δ, and aq. Na_2CO_3 ii: NH_3, H_2S, 0 °C, then H_2O

	Ar	mp (°C) [a]	ref.
A5a	Ph	224−226	38
b	4-MeC_6H_4	203−204	38
45		194−195	38

[a] Decomp.

Scheme 21



i: $CH_2(CN)_2$, DBU, CH_2Cl_2, rt ii: $CH_2(CN)_2$, Et_3N, CH_2Cl_2, −78 °C iii: $CH_2(CN)CO_2Et$, Et_3N, CH_2Cl_2, −78 °C

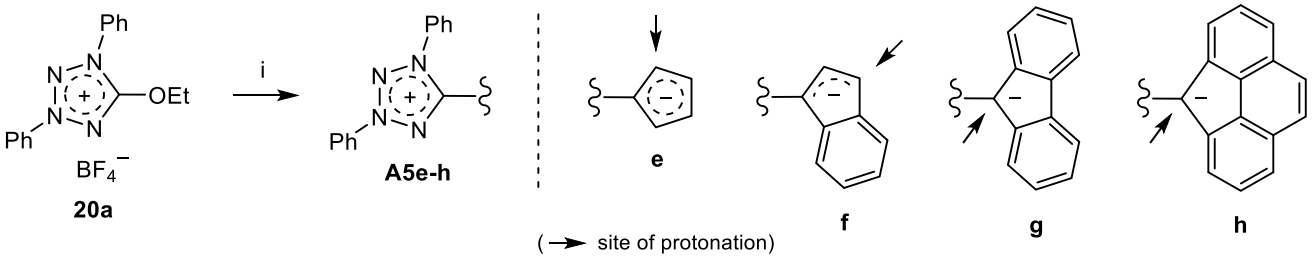
substrate	Q [a]	method		**A5c**	**A5d**	**46**	**47**	ref.
9a	Cl	i	yield (%)	94		<1	0	5
9d	Br	i		71		16	16	5
9e	I	i		0		54	63	5
20a	OEt	i		95 [b]		0	0	5
21	$OTet^+X^-$	ii		75 [c]		0	0	22
21	$OTet^+X^-$	iii			41 [d]	0	0	22
C'a	$HgTet^+X^-$	i		0		72	34	5

[a] Tet = 1,3-diphenyltetrazolium-5-yl; X = CF_3SO_3 (**21**), BF_4 (**C'a**). [b] 52% **A5c** in refluxing MeCN / Et_3N (same method: 26% di-*p*-tolyl analogue).[39] [c] Mp 227 °C. [d] Mp 207 °C.

Scheme 22

An expedient entry to derivatives of class (**A5**) consists in nucleophilic displacement with 5-functionalized tetrazolium salts [*cf.* route (b) of Scheme 1]. A systematic study has revealed that specific leaving groups are needed (Scheme 22):[5, 22] On action of the conjugate base of malononitrile, the desired product (**A5c**) was obtained from substrates having a chloro (**9a**), bromo (**9d**), ethoxy (**20a**) or tetrazoliumyloxy ligand (**21**). However, with electropositive substituents – as existing in **9e** and **C'a** – the carbanion preferentially attacked the ring at N(2) to give a transient dihydrotetrazole (with **9d** only in part); this species fragmented to eventually afford the hydrazone (**46**) and the cyanamide (**47**). The same reaction took place when 5-unsubstituted tetrazolium salts like **29b-d** (Scheme 12) were treated with malononitrile and base.[5]
Also the congener (**A5d**) was easily available.[22] But experiments with indane-1,3-dione failed: the salts (**9a**), (**20a**), and (**21**) all underwent hydrolysis to the olate (**A1b**) instead of being converted to the expected methanide (**A5**).[5]

A sesquifulvalene-type methanide (**A5e**) and some benzo-fused analogues, such as **A5f-h**, arose readily when the tetrazolium salt (**20a**) was treated with the sodium or lithium salts of the respective hydrocarbons (Scheme 23). The products are stable as crystals, but the solutions turned out to be air-sensitive. Protonation with trifluoroacetic acid occurred at the site indicated; the divergent position with **A5f** relative to **A5e** avoids a less stable *o*-quinonoid structure.[40]



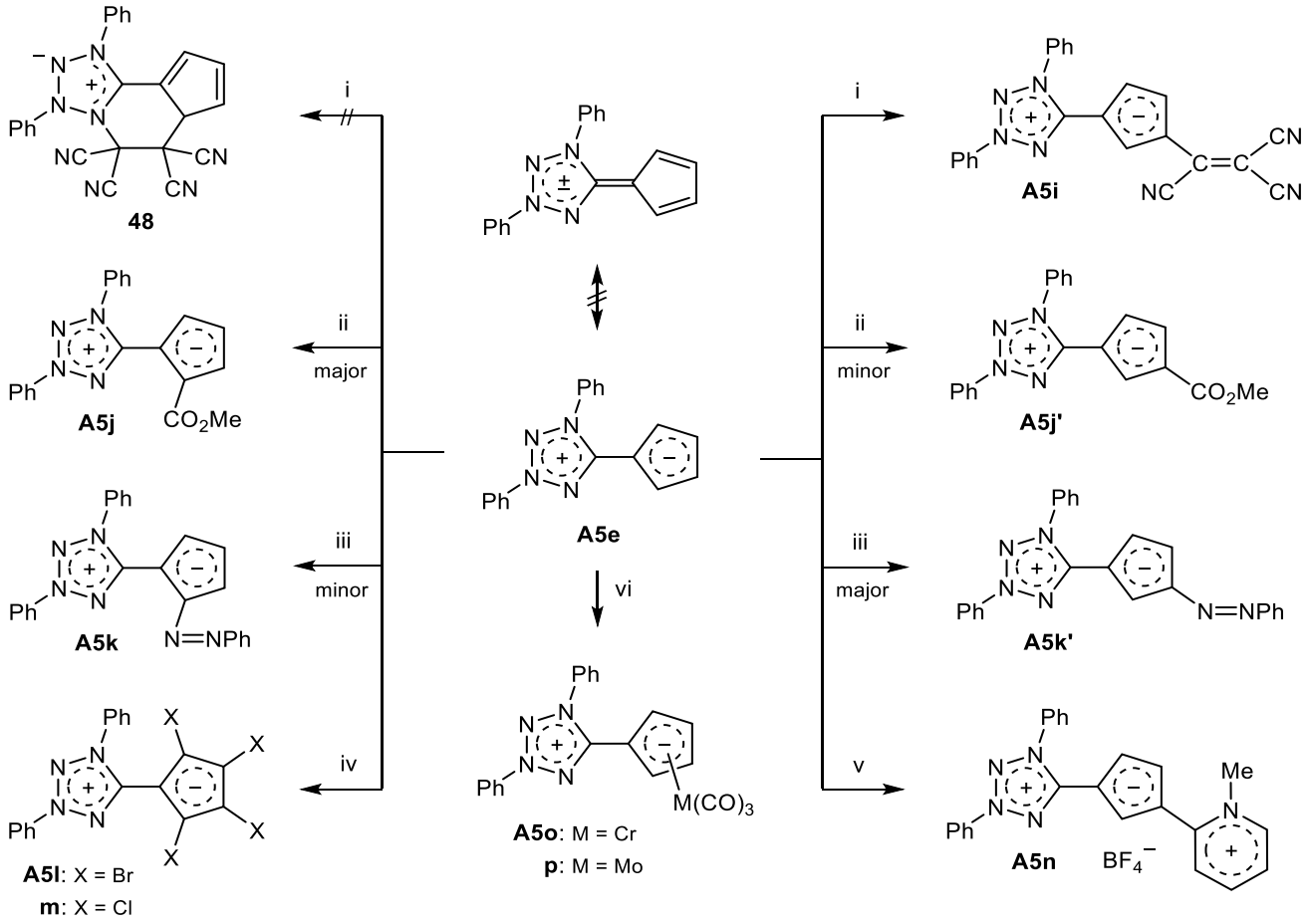
i: Sodium cyclopentadienide or lithium indenide/fluorenide/cyclopenta[*def*]phenanthrenide, THF, 0−20 °C

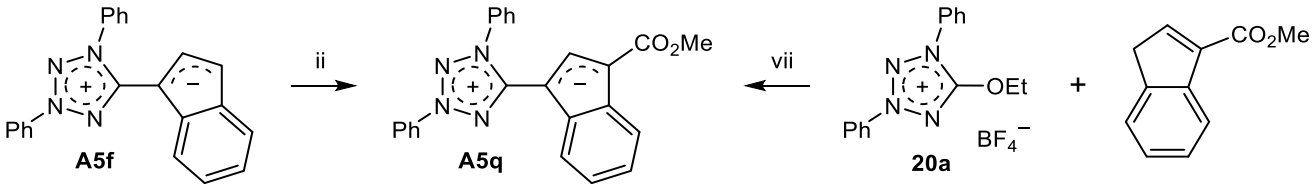
A5	yield (%)	mp (°C) [a]	ref.	**A5**	yield (%)	mp (°C) [a]	ref.
e	69	215	40a	**g**	76	229 [b]	40b
f	72	209	40b	**h**	52	245 [b]	40b

[a] Decomp. [b] Hemihydrate.

Scheme 23

Treatment of **A5e** with a dienophile such as tetracyanoethylene showed that the substrate has no olefinic but aromatic character (by virtue of the 5-substituent): instead of the cycloadduct (**48**), the substitution product (**A5i**) was formed (Scheme 24) [*cf.* route (i) of Scheme 1]. This property was confirmed by reactions with electrophiles like methyl chloroformate as well as the benzenediazonium and 2-bromo-1-methylpyridinium





A5	yield (%)	mp (°C)	ref.	A5	yield (%)	mp (°C)	ref.
i	8.2	276	41	**m**	88	197 [b]	41
j	41 [a]	85	41	**n**	70	206	41
j'		206	41	**o**	52	245 [b]	23
k	3	190 [b]	41	**p**	95 [c]	190 [b]	23
k'	35	220 [b]	41	**q**	42 [d]	273 [b]	40b
l	71	175 [b]	41	**q**	80 [e]		40b

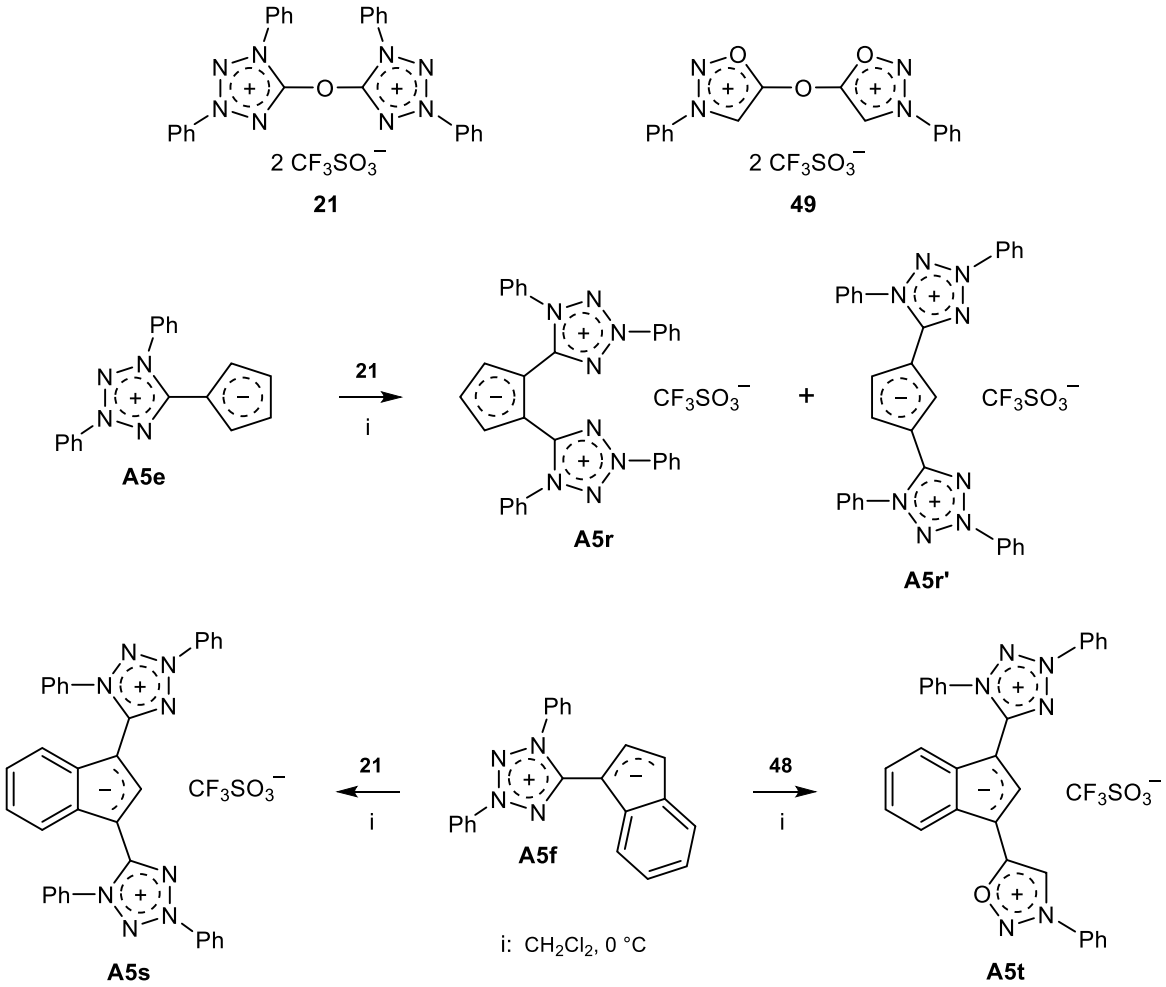
[a] Overall yield of **A5j** and **A5j'**, ratio 3:1. [b] Decomp. [c] Crude. [d] From **A5f.** [e] From **20a.**

Scheme 24

salts, which gave rise to the (monosubstituted) derivatives (**A5j** + **A5j'**), (**A5k** + **A5k'**), and (**A5n**). When using the more reactive *N*-halosuccinimides, full substitution took place (→ **A5l,m**).[41] Treatment of **A5e**

with the appropriate metal reagents produced the complexes (**A5o,p**); these materials are stable as solids, but their solutions rapidly released the free 'methanide' on exposure to air.[23] Also the indenide (**A5f**) proved capable of undergoing electrophilic substitution, as evidenced by formation of **A5q**; expectedly, the attack occurred regioselectively (in contrast to **A5e**); this was confirmed by the reaction of **20a** with methyl indene-3-carboxylate.[40b]

Finally, as interesting congeners of the tripolar compound (**A5n**), the derivatives (**A5r-t**) were formed on treatment of the 'methanides' (**A5e**) and (**A5f**) with the dicationic ether salts (**21**) and (**49**); both reagents showed comparable reactivity (Scheme 25). In the case of **A5f**, again substitution occurred exclusively at C(3) of the bicycle.[42]



A5	yield (%)	mp (°C)	ref.	A5	yield (%)	mp (°C)	ref.
r	53 [a]	177	42	**s**	42	293 [b]	42
r'		145	42	**t**	42	271 [b]	42

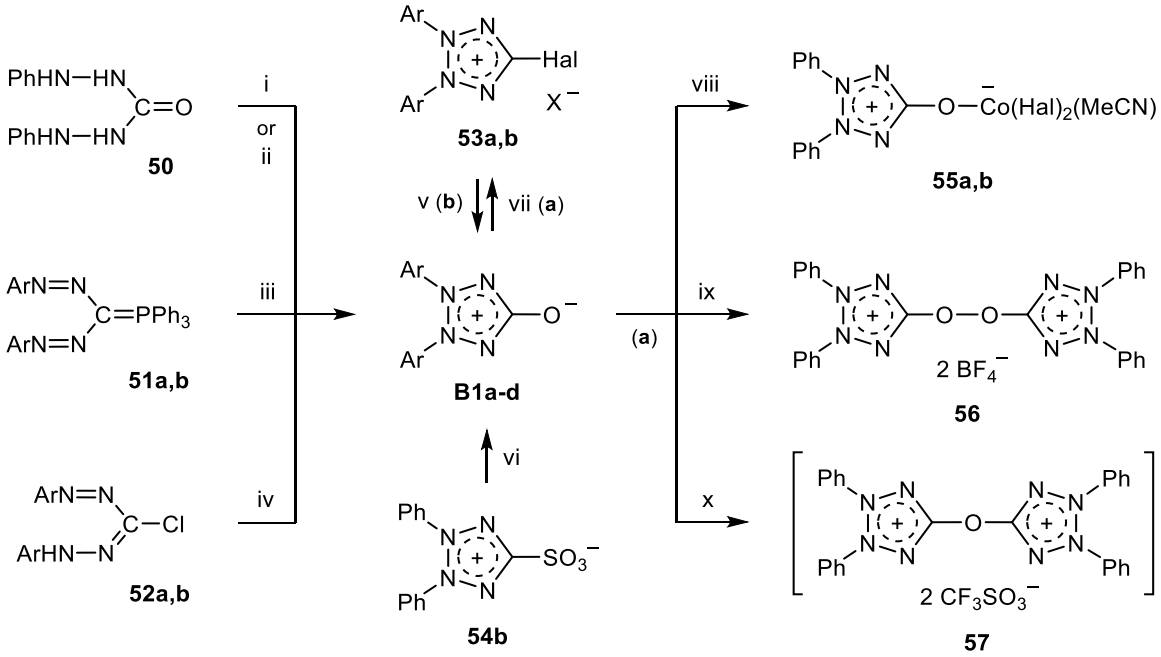
[a] Overall yield of **A5r** and **A5r'**, ratio 3:2. [b] Decomp.

Scheme 25

2) MESOIONIC TETRAZOLES OF TYPE (B)

a) Tetrazolium-5-olates (B1)

Oxidative cyclizations of C-functionalized NNCNN chains constitute the traditional entry to olates (**B1**).[1d–f] Recent examples include oxidation of diphenylcarbazide (**50**) with lead tetraacetate[43] or *p*-benzoquinone[44] as well as ozonolysis of the ylides (**51a,b**)[43] (Scheme 26), *i.e.* reactions that follow the routes (n) and (p) of Scheme 1. The latter experiment aimed at detecting the open-chain valence isomers of **B1c,d**: compounds (**51**) having O instead of PPh_3, but these species were found to cyclize extremely rapidly once they were formed[43] [see, however, structure (**59**) in Scheme 27]. Regarding the use of chloroformazans [*cf.* route (l) of



i: $Pb(OAc)_4$, THF, then H_2O, rt ii: *p*-benzoquinone, benzene, Δ, then rt iii: O_3 (3%), CH_2Cl_2, −94 °C or −100 °C
iv: AcOH, *n*-$C_5H_{11}ONO$, Δ v: aq. Me_2CO, rt; or H_2O, Δ vi: KOH or LiOH, DME, rt vii: $POCl_3$ (neat), Δ, then aq. HBF_4
viii: $Co(Hal)_2$, MeOH, MeCN, rt ix: $NOBF_4$, $ClCH_2CH_2Cl$, rt, then Δ x: $(CF_3SO_2)_2O$, CH_2Cl_2, rt

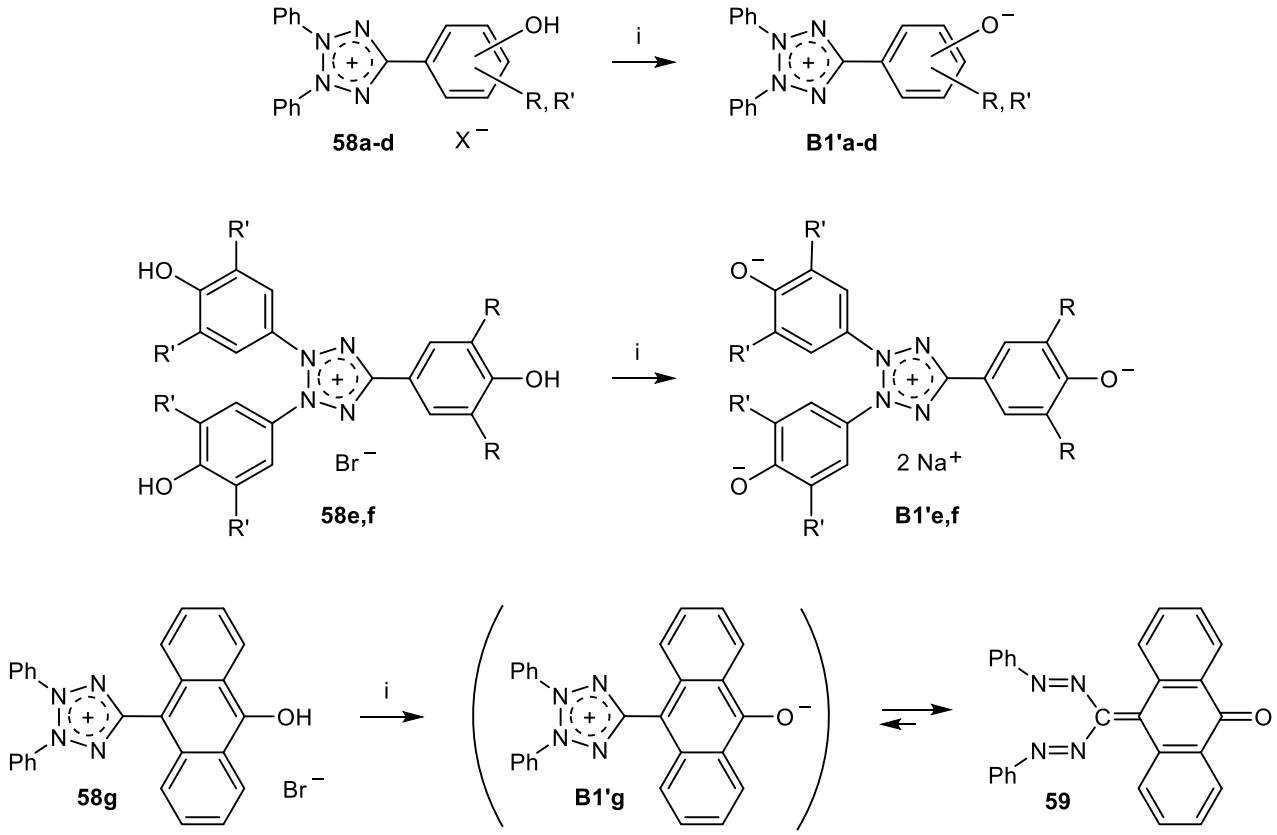
51	**52**	**53**	**55**	**B1** [a]	Ar	Hal	X	product [b]	from	yield (%)	mp (°C)	ref.
	a	**a**	**a**	**a**	Ph	Cl	BF_4	**B1a**	**50**	89 [c] / 36 [d]	174–182 [e]	43 / 44
			b			Br		**a**	**54b**	[f]	[f]	43, 45
								a	**52a**	ca. 70	176–177	47
	b			**b**	4-ClC_6H_4			**B1b**	**52b**	64	121–123	46
a		**b**		**c**	4-MeC_6H_4	F	Br	**B1c**	**51a**	30	[f]	43
								c	**53b**	[e]	[f]	45
b				**d**	4-$MeOC_6H_4$			**B1d**	**51b**	42	155–160 [e]	43
								53a	**B1a**	90	208–212	48
								56	**B1a**	67	[f]	43

[a] For rare examples (**B1**) having different substituents at N(2) and N(3), see review[1d] (namely ref.[239]). [b] **55a,b**: no yields and mps; studied by X-ray diffraction;[44] **57**: as intermediate only (see Scheme 34).[22] [c] Method (i). [d] Method (ii). [e] Decomp.[43] [f] Unreported.

Scheme 26

Scheme 1], the old process (**52b** → **B1b**)[46] (reviewed previously[1d,e]) may be complemented by the reaction of **52a**,[47] the more so since in that paper the modern representation of type (**B**) as a mesoion appears for the first time! New precursors to **B1** are the tetrazolium derivatives (**53b**) and (**54b**): submitted to hydrolysis, they yielded the olates (**B1c**) and (**B1a**), respectively [*cf.* route (m) of Scheme 1].[43,45]

Conversions include treatment of **B1a** with cobalt(II) halides to afford the complexes (**55a,b**)[44] as well as the reaction with the nitrosyl cation to yield the interesting peroxide (**56**),[43] while the products (**53a**)[48] and (**57**)[22] arose from methods already applied in the **A1** series [*cf.* Section (1a)].



i: aq. NaOH, rt

58 / **B1'**	function	R, R'	X	**B1'**: yield (%)	mp (°C)	ref.
a	2-OH / 2-O⁻	H, H	Br	95	140 [a]	49a,b
b	3-OH / 3-O⁻	H, H	Br	84	141 [b]	49a,b
c	4-OH / 4-O⁻	H, H	Br	68	154 [c]	49a,b
d	4-OH / 4-O⁻	3-*t*-Bu, 5-*t*-Bu	BF_4	quant.	209 [d]	49b
e		H, H		quant.	190 [e]	49b
f		Br, Br		88	235 [c]	49b
g				quant.	125 [c]	49b

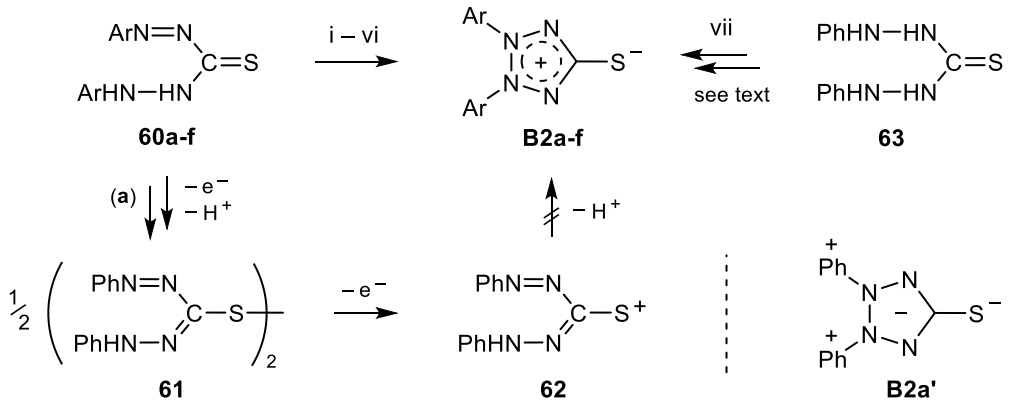
[a] Hemihydrate; decomp. [b] Hydrate; decomp. [c] Dihydrate; decomp. [d] Crystals with 0.25 mol H_2O. [e] Crystals with 4.5 mol H_2O; decomp.

Scheme 27

As formal congeners of olates (**B1**), quinonoid derivatives (**B1'**) have been made (Scheme 27). Compounds like **B1'a-f** were obtained from salts (**58a-f**) on treatment with base. As a consequence of the pronounced electron-withdrawal of the tetrazolium ring, these precursors are stronger acids than the parent phenol.[49] The material resulting from **58g** differed spectroscopically (UV, NMR) from the derivatives (**B1'a-f**) so as to point to the quinone methide (**59**) rather than the dipolar 'phenolate' (**B1'g**).[49b]

b) Tetrazolium-5-thiolates (B2)

The classical entry to these mesoions consists in oxidative cyclization of thiocarbazones (**60**) [*cf.* route (n) of Scheme 1], and several new preparations have been reported. Apart from manganese dioxide[39] and the traditional potassium hexacyanoferrate(III),[50–52] new oxidants like hydrogen peroxide[53,54] and air[54,55] have been used (Scheme 28). Electrochemical oxidation of **60a** by cyclic voltammetry (CV) generated a radical that dimerized to the disulfide (**61**) which gave the fully oxidized species (**62**) in turn; the latter should have cyclized chemically to **B2a**, but this did not occur on the CV time scale.[51] In a diluted ethanolic medium, manganese(II) chloride catalyzed the oxidation of the thiocarbazide (**63**) to **60a**, which disproportionated into **B2a** and **63**.[56] Theoretical studies on **B2** have been extensive; out of the various findings,[54,55,57] the new resonance hybride structure (**B2a'**) showing refined atomic charge distributions may be selected here.[54]



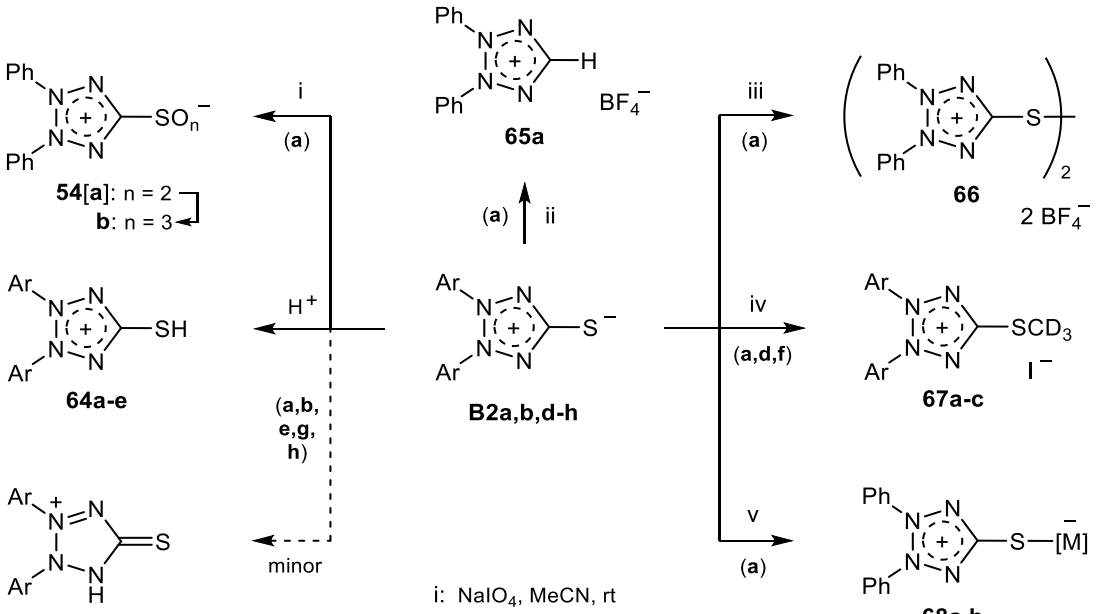
i: MnO_2, Me_2CO, Δ ii: aq. $K_3[Fe(CN)_6]$, aq. K_2CO_3, $CHCl_3$ (or similar), rt iii: H_2O_2, aq. NH_3, $CHCl_3$, rt
iv: H_2O_2, Me_2CO, Δ v: air, MeCN or $CHCl_3$, aq. NaOH, Δ vi: method (v) plus CS_2 vii: $MnCl_2$, EtOH, rt

60, B2	Ar	method	yield (%)	mp (°C)	ref.
a	Ph	i / ii / ii / iv / v [a]	75 / 65 / 52 / 98 / 96	[b]	39 / 50 / 51 / 54 / 54
b	3-ClC_6H_4	ii	[c]	[c]	52
c	4-ClC_6H_4	iv	95	202–203	54
d	2-MeC_6H_4	ii / iv	29 / 96	168–169 [d]	50 / 54
e	3-MeC_6H_4	ii	[c]	[c]	52
f	4-MeC_6H_4	ii / v / vi	34 / 95 / 88	170–171 [d]	50 / 54 / 55

[a] No yield with method (iii).[53] [b] Values from 167–169 to 180 °C (in part with decomp.). [c] Unreported. [d] Ref.[54]

Scheme 28

Conversions of thiolates (**B2**) are detailed below (Scheme 29). Oxidation of **B2a** with sodium periodate produced a mixture of the sulfonate (**54b**) and the disulfide (**66**) as main components, while with conc. nitric acid the 5-defunctionalized salt (**65a**) arose, obviously *via* sequential release of sulfur dioxide from the intermediary sulfinate (**54a**) and protonation of the transient carbene (**D**) (*cf.* Scheme 12: **A2** → **29**).[45] Protonation equilibria have been investigated with **B2a** and some analogues, showing that the substrates are Hammett bases; proton attack was assumed to occur mainly at the exocyclic sulfur atom (→ **64a-e**), but to a minor extent at nitrogen (→ **64'**) too,[52] a view that was verified later.[54] Reactions with other electrophiles concern the preparation of the deuterated 5-(alkylthio)tetrazolium salts (**67a-c**); these materials served as precursors to the respective formazans, which were sought for comparative purposes.[50] The sulfur atom is also attacked by metal ions; but because of the plethora of examples, the field can be covered appropriately only by a specialized review. Nevertheless, attention might be drawn to the tetrahedral complexes (**68a,b**):



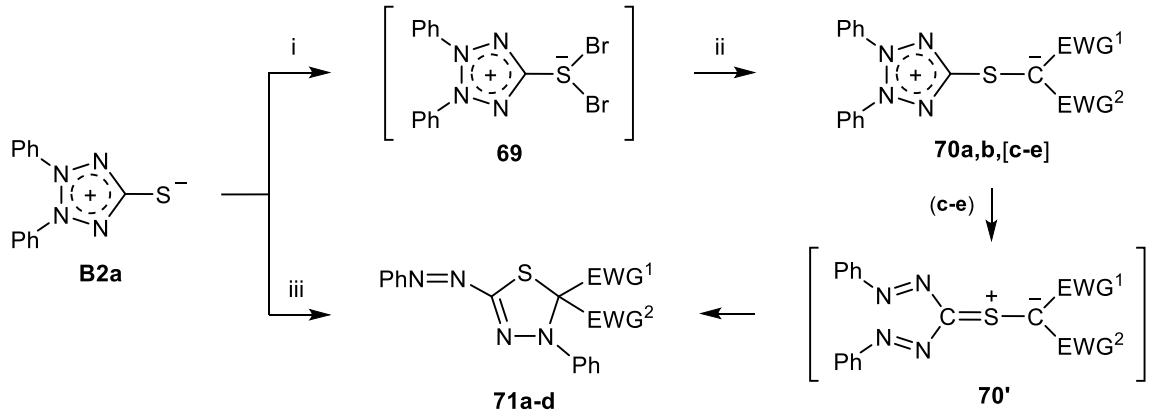
B2	64	67	Ar	68	[M]		−pK_a [a]	ref.		yield (%)	mp (°C)	ref.
a	**a**	**a**	Ph	**a**	$CoCl_2$(MeCN)	**64a**	1.73	52	**54b**	20 [b]	> 360 [c]	45
b	**b**		3-ClC_6H_4	**b**	$CoBr_2$(MeCN)	**b**	1.84	52	**65a**	95	217	45
d		**b**	2-MeC_6H_4			**c**	1.76	52	**66**	26	155–157	45
e	**c**		3-MeC_6H_4			**d**	1.80	52	**67a** [d]	89.5	[e]	50
f		**c**	4-MeC_6H_4			**e**	2.10	52	**68a** [f]	[e]	[e]	44
g	**d**		4-FC_6H_4						**b** [f]	[e]	[e]	44
h	**e**		2-ClC_6H_4									

[a] Determined spectrophotometrically in aq. $HClO_4$ at 25 °C. [b] Besides 26% **66** (as listed below); in addition: 8.5% **B1a** (Scheme 26) and 9.2% **104a** (Scheme 39), compounds formed *via* carbene (**Db**). [c] Explodes. [d] No yields and mps for **67b,c.**[50] [e] Unreported. [f] Studied by X-ray diffraction.

Scheme 29

here, interestingly, the single ion magnetic anisotropy parameter (*D*), which was found positive in the case of the oxalogues (**55a,b**) (Scheme 26), switched to negative with a significant change in magnitude.[44]

Sequential treatment of **B2a** with bromine and the conjugate base of an active methylene compound gave mesoionic thiocarbonyl ylides like **70a,b** (Scheme 30). The reaction proceeded through a labile bromine adduct believed to be **69**.[27,58] However, using esters of malonic as well as cyano- and acetoacetic acid, the ylides (**70c-e**) eluded isolation, and the 1,3,4-thiadiazoles (**71a-c**) were obtained instead; these compounds apparently arose through 1,5-cyclization of the open-chain valence isomers (**70'**). Also **B2a** was found to ring-open, namely in the reaction with diazo compounds, which led to the derivatives (**71a,c,d**).[58]



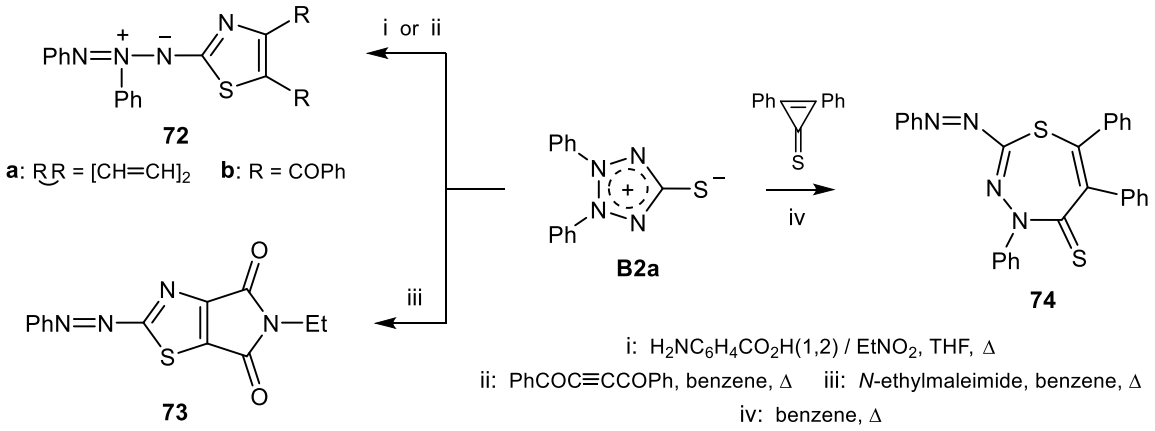
i: Br_2, CH_2Cl_2, rt ii: $Na[CH(EWG^1)EWG^2]$ iii: $N_2{=}C(EWG^1)EWG^2$, CH_2Cl_2, Δ

70	**71**	EWG^1	EWG^2		yield (%)	method	mp (°C)	ref.
a		CN	CN	**70a** [b]	[c]	i, ii	170 [d]	27
b		CO_2Et	$SO_2C_6H_4Me(4)$	**b**	89	i, ii	125	58
c	**a**	CO_2Et	CO_2Et	**71a**	96 / 47	i, ii / iii	91	58
d	**b**	CO_2Et	CN	**b**	62	i, ii	98	58
e	**c**	CO_2Et	COMe	**c**	94 / 5	i, ii / iii	72	58
	d	[a]	[a]	**d**	65	iii	286	58

[a] {EWG^1⌣EWG^2} = 10-oxo-9-anthrylidene. [b] Studied by X-ray diffraction.[59] [c] High yield (figure unreported). [d] Decomp.

Scheme 30

Resuming earlier reactions with unsaturated systems (*cf.* ref.[1f]), **B2a** was submitted to dibenzoylethyne, *N*-ethylmaleimide, diphenylcyclopropenethione, and, again, benzyne (Scheme 31).[60a] Since the latter was applied under milder conditions than originally, the azimine-functionalized benzothiazole (**72a**) could be isolated; an analogous product resulted from dibenzoylethyne (→ **72b**). However, the primary adduct with the maleimide underwent oxidation, followed by loss of phenylnitrene to afford the phenylazo-substituted pyrrolothiazole derivative (**73**). Finally, in the reaction with the cyclopropenethione, the thiadiazepine (**74**)



	yield (%)	mp (°C)	ref.		yield (%)	mp (°C)	ref.
72a [a]	39	178−179	60a	**73**	13	214−215	60a
b	77	163−164	60a	**74**	21	220 [b]	60a

[a] Studied by X-ray diffraction.[60b] [b] Decomp.

Scheme 31

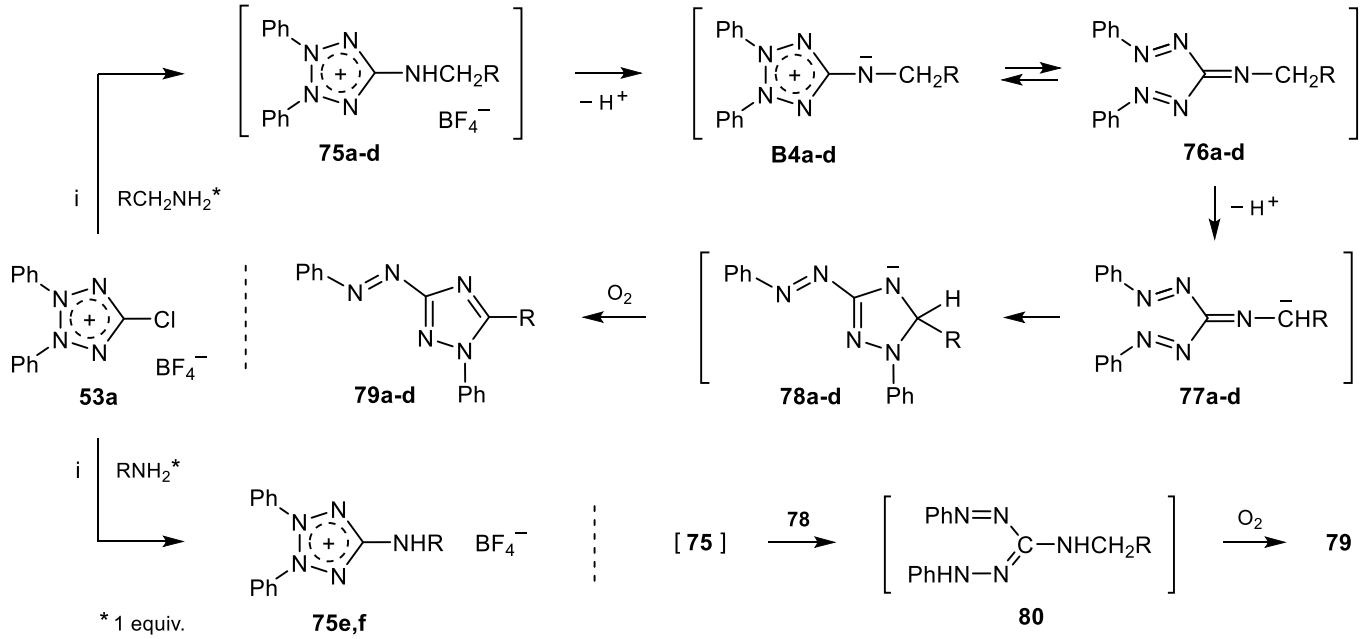
was formed; the isomeric structure having a 7-thioxo group could be excluded spectroscopically. All of the above conversions are understood as proceeding through the acyclic valence isomer of **B2a**.

c) Tetrazolium-5-aminides (B4)

Following the concept of aminolysis of 5-chlorotetrazolium salts, which had proved fruitful in the isomeric **A4** series [see Section (1c)], the substrate (**53a**) was treated with various primary amines in the presence of triethylamine [*cf.* routes (m) and (o) of Scheme 1].[48] However, using reagents with an α methylene group, neither the expected aminotetrazolium salts (**75a-d**) nor the corresponding aminides (**B4a-d**) were found; instead, the phenylazo-substituted triazoles (**79a-d**) were isolated (Scheme 32). Apparently, the aminides (**B4a-d**) once formed ring-opened to the valence isomers (**76**) which, after proton loss, gave the species (**77**); the latter cyclized to the dihydrotriazoles (**78**) which in turn were oxidized to **79**. A second pathway seems to involve an aminoformazan (**80**) which arose from **75** through reduction by the transient triazole (**78**): indeed, treatment of 3-chloro-1,5-diphenylformazan (**52a**; Scheme 26) with benzylamine led directly to **79a**, the respective formazan (**80**: R = Ph) being elusive.

While triethylamine induced a cascade reaction to afford **79**, the intermediary salts (**75**), such as **75a,b**, could be isolated when using an inorganic base. However, separate experiments with these salts have not been described.

In contrast to primary amines of the RCH_2NH_2 type, isopropyl- and *tert*-butylamine gave the expected salts (**75e,f**) even in the presence of triethylamine, but these substrates do not appear to have been checked for aminide formation.[48]



i: Et_3N, CH_2Cl_2 or MeCN, rt (in part Δ)

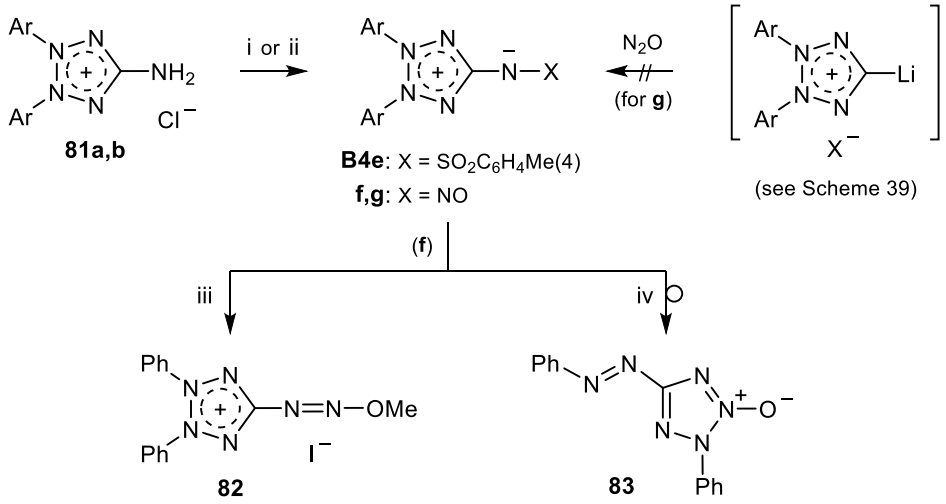
			75		79		
B4, 75–79	R	Et_3N (equiv.)	yield (%)	mp (°C) [a]	yield (%)	mp (°C) [a]	ref.
a	Ph	3	0 [b]		50 [c]	147–148	48
b	Pr	2	0 [d]		23	127.5–128.5	48
c	CH_2OH	3	2	[e]	50	144–148 [f]	48
d	CO_2Et	4 [g]	0		39	130–132	48
e	*i*-Pr	1	38 [h]	92–97			48
f	*t*-Bu	1 [i]	55	168–172			48

[a] Figures rounded. [b] 68 or 39% when using $NaHCO_3$ or Na_2CO_3 instead of Et_3N; mp 177–181 °C (hemihydrate); **79a** not obtained. [c] Obtained in refluxing CH_2Cl_2 (2.5 h), at rt (21 h) only 16%. [d] 34% when using $NaHCO_3$ instead of Et_3N; mp 158–159 °C; **79b** not obtained. [e] Unreported. [f] Containing ca. 0.3 mol EtOH. [g] Starting from hydrochloride salt of $EtOCOCH_2NH_2$. [h] Besides 3-(isopropylideneamino)-1,5-diphenylformazan as major product. [i] Reaction started from 1.4 equiv. *t*-$BuNH_2$.

Scheme 32

Aminides having acceptor groups like **B4e-g** were obtained by treating the aminotetrazolium salts (**81a,b**) with sulfonyl chloride[1d,61] and nitrous acid,[59,61–63] respectively (Scheme 33) [*cf.* route (m) of Scheme 1]. An attempt to get the derivative (**B4g**) by trapping the 5-lithiotetrazolium salt (**105c**; X = BPh_4) (Scheme 39) with dinitrogen oxide was unrewarding.[63]

Conversions of class (**B4**) members include methylation of **B4f** to afford the salt (**82**)[61] and, as reviewed earlier,[1d,e] ring transformation to the *N*-oxide (**83**) in hot ethanol or water[62] – a process that is comparable to the above sequence (**B4** → **76** / **77** → **78**). Whether also the nitroso analogue (**B4g**) is capable of undergoing this rearrangement, has not been investigated; only pyrolysis in the gas phase was studied, but this produced insignificant results.[43]



i: 4-$MeC_6H_4SO_2Cl$ (no details) ii: HNO_2, then $MeCO_2^-$ / H_2O, rt iii: MeI, MeCN, rt iv: aq. EtOH, Δ

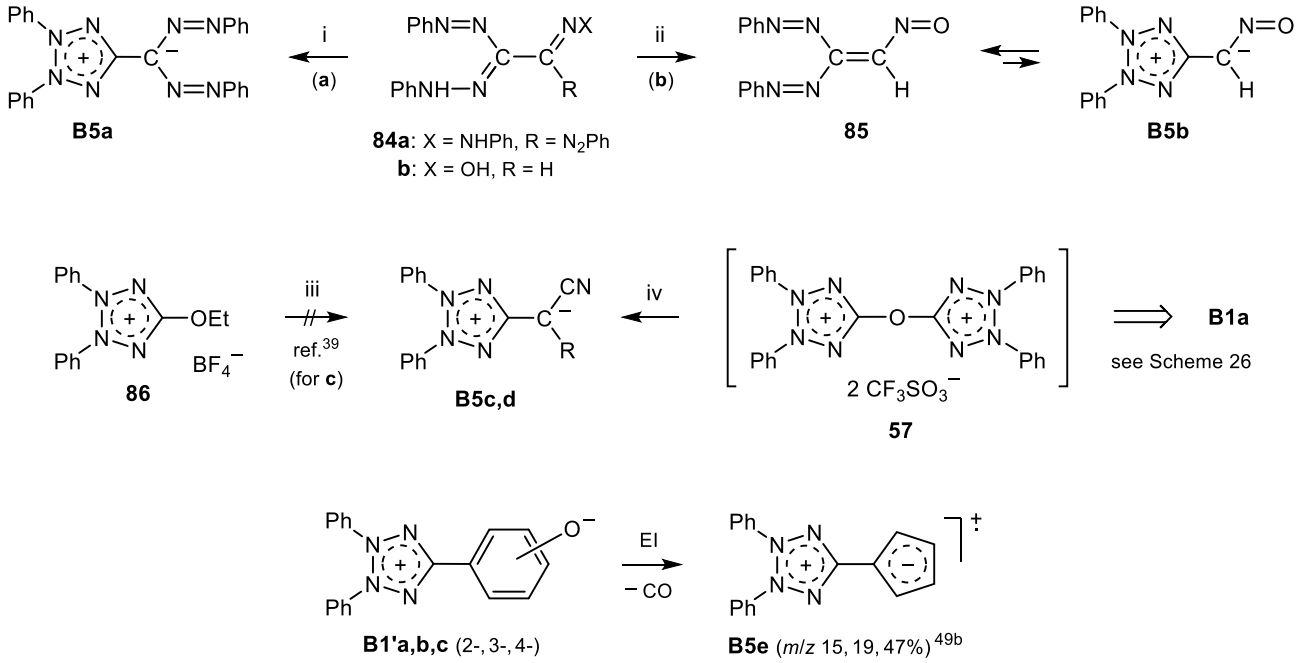
81	B4	Ar	product	yield (%)	mp (°C)	ref.
a	**e**	Ph	**B4e**	[a] / [b]	[a] / [b]	1d / 61
	f	Ph	**f**	58 / [b]	176 –177 / [b]	62 / 59, 61
b [c]	**g** [d]	4-$MeOC_6H_4$	**g** [e]	34 [f]	157 –165 [g]	63
			82 [h]	[a]	[b]	61
			83	94	154 –155 [g]	62

[a] First preparation obviously not published (see review,[1d] namely ref.[242]). [b] Unreported. [c] The triiodide salt as depicted in ref.[63] has not been submitted to the reaction (*cf.* ref.[43]). [d] This derivative has not been described in ref.[62] (incorrect citation[63]). [e] Containing 2 mol MeOH.[43] [f] Yield from ref.[43] [g] Decomp. [h] Studied by X-ray diffraction.[64]

Scheme 33

d) Tetrazolium-5-methanides (B5)

Applying principle (n) of Scheme 1, treatment of the formazans (**84a,b**) with either (an aminyl forming) tetraarylhydrazine or lead tetraacetate gave oxidation products that were presented as the methanide (**B5a**) and the nitrosoethylene (**85**), respectively (Scheme 34).[65] Since the latter, however, was reviewed to exist in the cyclic form (**B5b**),[1f] DFT calculations were conducted to show that the open-chain valence isomer (**85**) is energetically favoured.[66] Access to the cyano- and alkoxycarbonyl-substituted methanides (**B5c,d**) was achieved by nucleophilic displacement [*cf.* mode (m) of Scheme 1]. Treatment of the dicationic ether salt (**57**) with malononitrile in the presence of a base gave **B5c**,[22] after an earlier attempt of converting the substrate (**86**) had proved unrewarding.[39] Later, the analogue (**B5d**) was made accordingly,[59,67,68] but the authors did not provide details, except for referring to the procedure applied with **B5c**.[22] An unusual formation of a methanide (**B5**) occurred in the mass spectrometer under EI conditions: the quinonoid compounds (**B1'a-c**) fragmented to the cyclopentadienide (**B5e**).[49b] Thereupon, the authors undertook to synthesize the compound by flash vacuum thermolysis, but the results do not seem to have been disclosed.



i: $(4\text{-MeC}_6H_4)_2NN(C_6H_4Me\text{-}4)_2$, benzene, Δ ii: $Pb(AcO)_4$, CH_2Cl_2, rt
iii: $CH_2(CN)_2$, MeCN, Δ iv: RCH_2CN, CH_2Cl_2, Et_3N, rt (no details for **B5d**)

B5	R	yield (%)	mp (°C)	ref.
a		40	188−189 [a]	65
b		43 [b]	121−122	65
c [c]	CN	23	> 300	22
d	CO_2Et	[d]	[d]	59, 67, 68

[a] Decomp. [b] Besides 4% 2-phenyl-4-phenylazo-1,2,3-triazole.
[c] Containing 1 mol MeCN. [d] Unreported.

Scheme 34

Experimental Structural Methods

All derivatives (**A**) and (**B**) dealt with in Sections (1) and (2) have been characterized by physical methods. Literature data on bond lengths and angles are available for an increased number of systems (Table 1); the five-membered ring of the compounds listed is planar, and – also expectedly – in all cases the C–Z bond length was found intermediate between a double-bond and a single-bond distance.

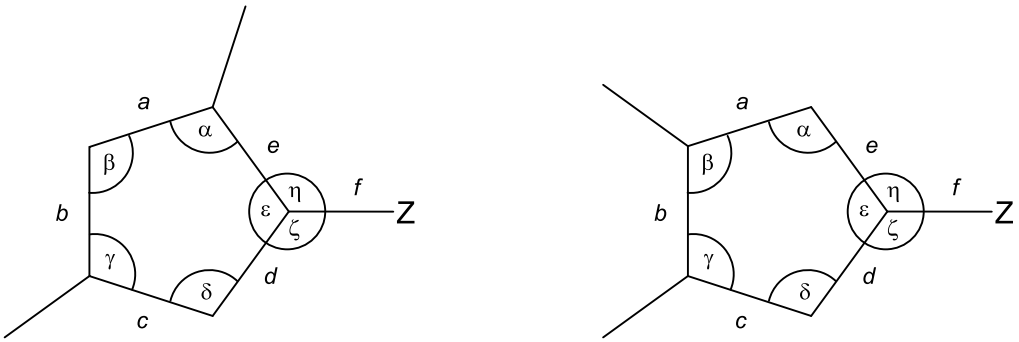
Spectral data have been determined in great number (for a selection, see Table 2). Outstanding systematic studies constitute the multinuclear NMR investigations conducted by the Jaźwiński group, and here also a range of other azolic mesoions of the type (**A**) were looked at; the majority of the findings have been reviewed.[71–73]

The collection of UV/Vis data shows that most derivatives are coloured materials; with lacking data, the compounds were described as such. A prominent feature is the pronounced negative solvatochromism which has been studied with several derivatives, *viz.* the methanides (**A5c,d**) and (**B5c**) (Schemes 22, 34),[22] the thiolates (**B2a,b,d–f**) [including analogues having Ar = 2-Cl/F/MeOC$_6$H$_4$ and 4-FC$_6$H$_4$] (Scheme 28),[53] the cyclopentadienide (**B5e**) and its benzo-fused congeners (**B5f-h**) (Scheme 23),[40a,b] and, finally, the phenolates (**B1'a-e,g**) (Scheme 27).[49a,b] A comparison of the isomers (**A5c**) and (**B5c**) shows that the solvatochromism is stronger with the latter derivative.[22]

From published MS spectra it is apparent that – under EI conditions – compounds of the **A** series are more stable: quite a number of derivatives gave parent ions of high intensity.

The radical cation (**A4uu**) (Scheme 19) and its bis- and tetra-^{15}N-labelled analogues were characterized by EPR spectroscopy (the labelled species also by ^{14}N and ^{15}N ENDOR spectroscopy which revealed that the largest N hyperfine coupling constants result from the central bridge).[34]

Table 1. Bond distances (Å) and angles (deg) of compounds (**A**) and (**B**) from X-ray diffraction



Compd (Scheme), ref. [a, b]	*a*	*b*	*c*	*d*	*e*	*f*	α	β	γ	δ	ε	ζ	η
A1bb (5), 15	1.324	1.276	1.320	1.350	1.365	1.231	111.1	102.8	116.7	103.5	105.9	128.9	125.3
A1dd (5), 16a	1.345	1.290	1.329	1.358	1.412	1.225	110.3	103.0	117.1	104.5	105.2	128.5	126.3
A2e (10), 25	1.340	1.292	1.337	1.346	1.387	1.678	111.2	102.6	116.1	104.6	105.5	127.2	127.3
B2a (28), 54 [c]	1.315	1.337			1.362	1.696	104.9	110.0			110.2		124.9
B4f (33), 59	1.320	1.337	1.308	1.354	1.345	1.368	103.8	109.8	110.4	103.8	112.2	126.6	121.2
B5c (34), 59	1.307	1.332	1.316	1.354	1.356	1.415	103.8	110.4	110.4	103.4	112.0	124.6	123.3
B5d (34), 59 [d]	1.316	1.332	1.311	1.360	1.368	1.426	103.4	110.7	110.4	104.0	111.5	123.1	125.4

[a] Also investigated by X-ray diffraction: **A1z** (4),[13a,c] **A5v** (36),[82] **B2f** (28),[54,55] **B2** (28; Ar = 2-MeOC$_6$H$_4$,[69] 3-FC$_6$H$_4$[70]). [b] For calculated parameters, see: (i) **A1rr** (6), **A2a** (9), and **A4** (13; NMe instead of NH, R = R' = Me) (bond lengths),[1i] (ii) **B2a** (28) (bond lengths, angles),[57b] (iii) **B2f** (28) (bond lengths, angles, dihedral angles).[55] [c] See also ref.[56] [d] Selected from two molecules.

Table 2. Selected spectral data of compounds (**A**) and (**B**) [a]

^{13}C and ^{15}N NMR: Tetrazolium ring atoms and α atom of Z group							UV/Vis: Longest wavelength maxima MS: Relative intensities of parent ions		
Compd (Scheme), ref. [b]	N(1)	N(2)	N(3)	N(4)	C(5)	Z(α)	Compd (Scheme), ref.	nm	%
A1b (2), *6*, *74* [c]	–163.1	–52.4	–108.9	–121.4	158.8		**A1s** (4), 13a,b	348 [r]	72
A1k (2), 8 [d]	–163.2	–53.8	–109.9	–122.1	159.5		**A4d** (13), 14	396	100
A1rr (6), *19*	–178.4	–39.3	–117.7	–113.5	161.1		**A4i** (14), 14	373	23
A2a (9), *19*	–148.2	–26.6	–107.9	–74.8	173.9		**A4j** (14), 7	409	100
A2b (9), *69*	–135.8	–34.9	–99.2	–83.9	173.7		**A4t** (14), 21	445.5	100
A4a' (13), *76* [e]	–204.2	–9.8	–103.3	–141.3	159.6	–286.5	**A4x** (15), 34	443 sh [s]	100
A4b (13), *19*	–178.5	–43.3	–117.6	–116.5	162.5	–271.2	**A4z** (16), 14	455	15
A4d (13), *6*, *32* [f]	–178.5	–56.8	–106.0	–121.7	162.1	–258.5	**A4aa** (16), 34	542 [t]	100
A4g (13), *6* [f]	–156.8	–42.0	–102.2	–107.4	156.9	[i]	**A4bb** (16), 14	517	100
A4m (14), 8	–181.2	–61.2	–106.6	–127.6	154.8	–217.3	**A4ff** (16), 35	434	10
A4p (14), *32* [g]	–172.0	–55.6	–106.0	–124.7	154.3	–227.3	**A4gg** (16), 35	486	56
A4r (14), 8 [h]	–173.7	–57.7	–106.4	–125.0	154.3	–227.2	**A4ii** (16), 14	330 [u]	0.9
A4z (16), *32* [f]	–191.6	–60.2	–103.6	–128.9	159.8	–154.8	**A4ll** (17), 21	377	100
A5a (21), *77*	–130.5	–27.5	–91.3	–73.2	[j]	[j]	(*E*)-**A4pp** (17), 35	370	37
A5c (22), *74* [k, l]	–161.4	–34.7	–97.9	–104.6	160.9	24.8	**A5a** (21), 38	470 [v]	[w]
A5d (22), *74* [k, l]	–158.1	–37.0	–97.5	–97.5	159.9	47.6	**A5c** (22), 22	413 [t, x]	100
A5e (23), *6* [m]	–165.6	–40.8	–98.9	–104.7	158.3	96.9	**A5d** (22), 22	413 [t, x]	100
A5g (23), *6* [m]	–169.1	–44.9	–96.8	–102.2	153.6	83.3	**A5e** (23), 40a,b	565 [x, y]	100
B1a (26), *78* [n, o]	–97.9	–119.5			169.7		**B2a** (28), 79a	465 [s, z]	
B2a (28), *78* [n, p]	–64.5	–108.5			181.4		**B1'c** (27), 49a,b	513 [x]	47 [aa]
B4e (33), *61*	–89.0	–109.9			165.3	–233.7	**B1'd** (27), 49b	605 [x]	100
B4f (33), *61*	–90.0	–108.2			174.1	–241.7	**B1'g** (27), 49b	509 [x]	45
B5a (34), *77* [q]	–66.2	–101.0			161.2	131.2	**B5a** (34), 65	477 [v]	
B5c (34), *67* [m]	–89.0	–106.8			169.2	22.6	**B5b** (34), 65	425 [v]	[w]
B5d (34), *67* [m]	–84.0	–108.4			168.3	47.8	**B5c** (34), 22	504 [t, x, bb]	19

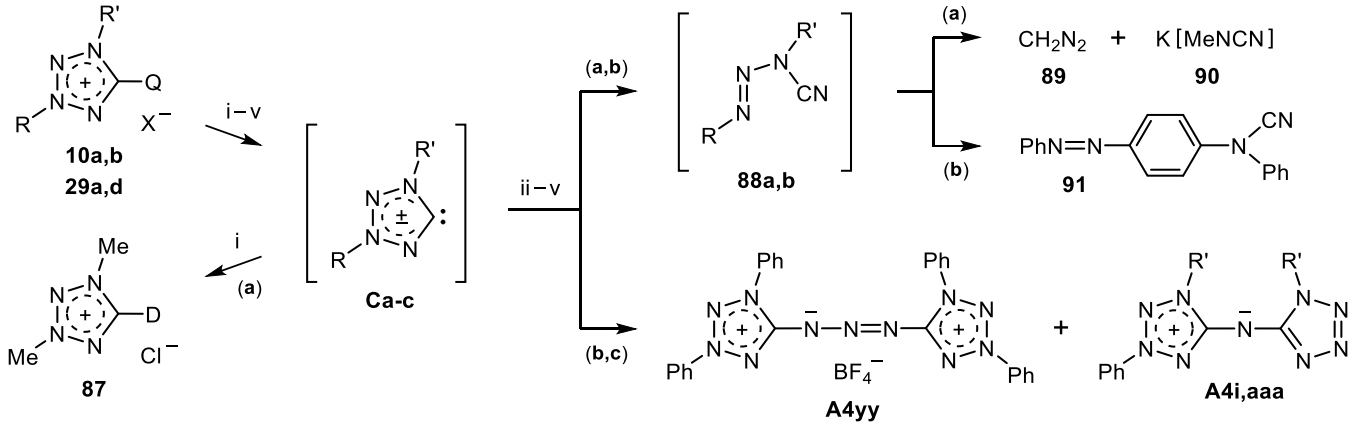
[a] NMR: DMSO-d_6 (unless otherwise stated), shift values (δ, ppm) relative to $SiMe_4$ and $MeNO_2$, respectively; half-width of ^{14}N signals omitted; UV/Vis: MeCN (unless otherwise stated); MS: EI. [b] In case of *italicized* references, see also reviews.[71–73] [c] For a comparison with calculated values, see ref.[75] [d] Acetone-d_6. [e] **A4a'** (R = R' = H): calculated values for *ap* conformer. [f] $\delta_{C(5)}$ from ref.[14] (**A4d**: $CDCl_3$, **A4g**: DMSO-d_6). [g] $\delta_{C(5)}$ ($CDCl_3$) from ref.[5] [h] $CDCl_3$ for $\delta_{C(5)}$. [i] Not observed. [j] No assignment because of large number of peaks. [k] For $\delta_{C(5)}$ and $\delta_{Z(\alpha)}$, see also ref.[22] [l] For $^1J_{(13C–13C)}$, see ref.[65] [m] $\delta_{C(5)}$ and $\delta_{Z(\alpha)}$ ($CDCl_3$) from ref.[40b] [n] See also refs.[61,67] [o] For $\delta_{C(5)}$, see also refs.[22,43] [p] For $\delta_{C(5)}$, see also refs.[43,54] [q] **B5a** · HCl. [r] $CDCl_3$; fluorescence: emission 446 (excitation 354). [s] $CHCl_3$. [t] CH_2Cl_2. [u] DMSO. [v] EtOH. [w] Parent ion observed, intensity unreported. [x] Solvatochromism studied. [y] CCl_4. [z] Calculated ππ*-chromophore 440;[80] for comparison, **B1a** (26): observed 350,[79b] calculated 355.[80] [aa] M–CO (*cf.* Scheme 34). [bb] Calculation of ππ*-chromophores not extended to **B5c**.[80]

3) MESOIONIC TETRAZOLYLIDENES OF TYPE (C)

It is with these species that the general term 'mesoionic carbene' has been introduced into the literature.[5,81] There are two procedures of generation (Scheme 35): (i) Deprotonation of 5-unsubstituted tetrazolium salts (**29**) and (ii) treatment of the 5-azido congeners (**10**) with azide ion [*cf.* routes (j) and (k) of Scheme 1].

(i) The carbene (**Ca**) was postulated as intermediate in an H/D exchange experiment with **29d** to give the deuterated salt (**87**) (even below pH 7), whereas potassium hydroxide (50% in water) was shown to split the substrate into diazomethane (**89**) and potassium methylcyanamide (**90**). These compounds originated from the cyanotriazene (**88a**) which arose through ring cleavage of **Ca**.[82] But also milder conditions caused ring opening, as observed on treatment of **29a** with DBU in dichloromethane; the isolated material, first viewed as **88b**,[5,14] was later revised to be the azo compound (**91**).[83]

(ii) Treatment of the salt (**10a**) with sodium azide not only afforded **91** but also aminides like **A4yy** and **A4i** [*cf.* route (h) of Scheme 1], whereas the congener (**10b**) gave **A4aaa** exclusively. With reference to Balli's 'azidinium' salts and their carbene-based formation,[84] these aminides were thought to arise *via* **Cb** and **Cc**, respectively.[14] The behaviour of **10a** has been reviewed elsewhere,[2c] but without realizing the correction in ref.[83] where the putative triazene (**88b**) was discarded.



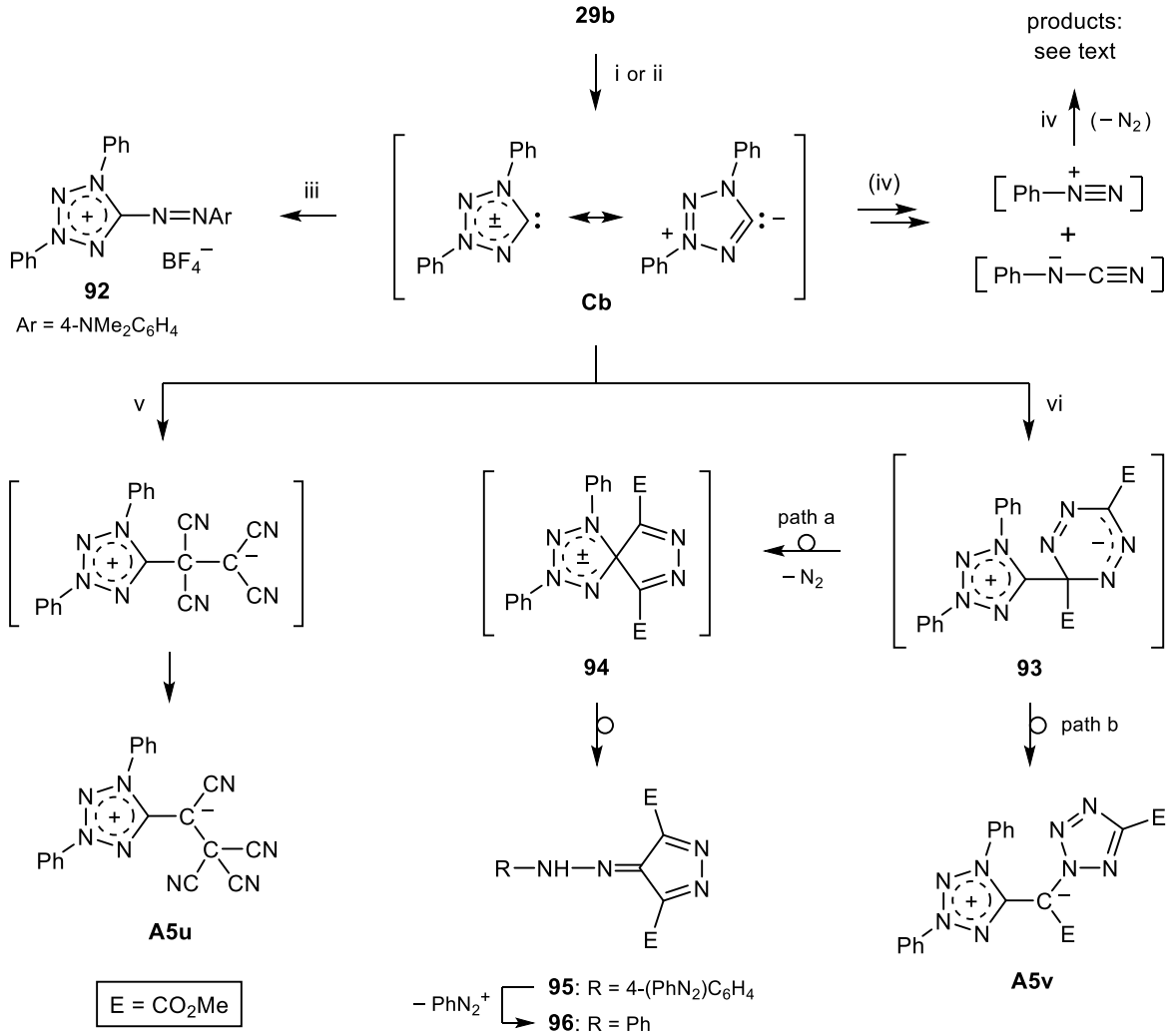
i: phthalate buffer (D_2O, pD 4.40), rt ii: aq. KOH (50%), rt iii: DBU, CH_2Cl_2, rt iv: NaN_3, DMF, −50 °C → rt v: method (iv), rt

	R	R'	Q	X	product	from	method	yield (%)	mp (°C)	ref.
10a	Ph	Ph	N_3	BF_4	**89**	**29d**	ii			82
10b	Ph	4-MeC_6H_4	N_3	BF_4	**90**	**29d**	ii			82
29a	Ph	Ph	H	BF_4	**91** [a]	**29a** / **10a**	iii / iv	62 / 12 [b]	146 – 147 [c]	5 / 14
29d	Me	Me	H	Cl	**A4i**	**10a**	iv	51 [d]	(see Scheme 14)	14
Ca, 88a	Me	Me			**A4i**	**10a**	v	87 [e]		14
Cb, 88b, A4i	Ph	Ph			**A4yy**	**10a**	iv / v	7 [d] / traces	242 – 243 [f]	14
Cc, A4aaa	Ph	4-MeC_6H_4			**A4aaa**	**10b**	iv or v [g]	[h]	273 – 276 [f]	14

[a] Erroneously reported as **88b**; for revision, see ref.[83] [b] Besides 4% olate (**A1b**) [possibly through action of O_2 on **Cb**; *cf.* mode (h) of Scheme 1], 51% **A4i**, and 7% **A4yy** (both as listed below). [c] Hemihydrate. [d] For side products, see [b]. [e] Besides PhN_3 (quant.) and traces of **A4yy** (as listed below). [f] Decomp. [g] Unspecified. [h] Almost quant., side products not observed.

Scheme 35

The nucleophilic nature of the carbene (**Cb**) – more properly expressed by the mesomeric ylide structure – was also demonstrated by trapping with a diazonium salt (→ **92**) (Scheme 36).[5] Interception was likewise successful with tetracyanoethene or an electronegatively substituted 1,2,4,5-tetrazine, giving the methanide (**A5u**) or a mixture of two 4*H*-pyrazoles (**95**, **96**) and the methanide (**A5v**).[83] The latter materials arose *via*



i: DBU, MeCN, – 30 °C ii: DBU, DMF, – 60 °C iii: $[4\text{-}NMe_2C_6H_4N_2]BF_4$, ➔ rt iv: *N*-phenylmaleimide, fumaronitrile or DMAD, ➔ rt
v: $(NC)_2C{=}C(CN)_2$, ➔ rt vi: dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate, ➔ rt

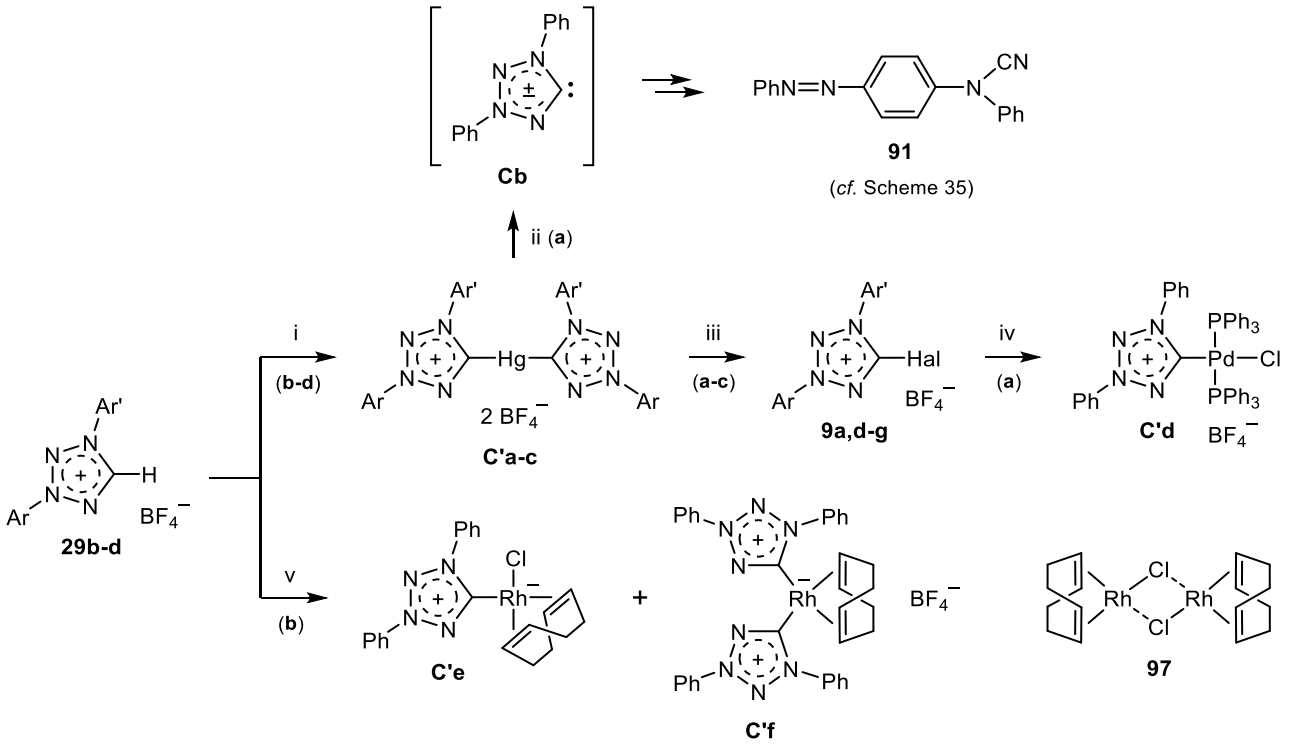
product	yield (%)	method	mp (°C)	ref.
92 [a]	69	i, iii	186	5
95	4 [b]	ii, vi	191 – 192.5	83
96	22 [b]	ii, vi	159.5 – 162	83
A5u	9 [c]	ii, v	153 – 157	83
A5v	15 [b]	ii, vi	179 – 184	83

[a] Containing 0.5 mol EtOH. [b] Determined by ^{1}H NMR. [b] Besides 25% **A1b** (Scheme 2).

Scheme 36

the joint intermediate (**93**) showing dichotomous behaviour: extrusion of dinitrogen led to the spirane (**94**) which was stabilized by tetrazole ring opening, whereas contraction of the tetrazine moiety gave **A5v**. The interesting route to this compound provides a new direct access to 2*H*-tetrazoles by ring transformation.[85] However, on attempts to trap **Cb** with weaker electrophiles (*N*-phenylmaleimide, fumaronitrile, DMAD), the tetrazole ring did not survive: only fragments of it were incorporated to yield phenylated maleimides, fumaronitriles, and cyanamido-substituted *N*-phenylsuccinimide and DMAD.[83] Attempted interceptions of **Cb** with alkyl halides and carbonyl compounds were unrewarding too.

Metal complexes of **C** have been made in considerable number (Schemes 37, 38). The first examples were the derivatives (**C'a-c**), obtained by mercuration of the salts (**29b-d**). Studying the stability of the C–Hg bond, it was found that heating with conc. hydrochloric acid returned the starting compounds (**29**), whereas action of base released the ligand (**Cb**); moreover, treatment with halogens produced the tetrazolium salts



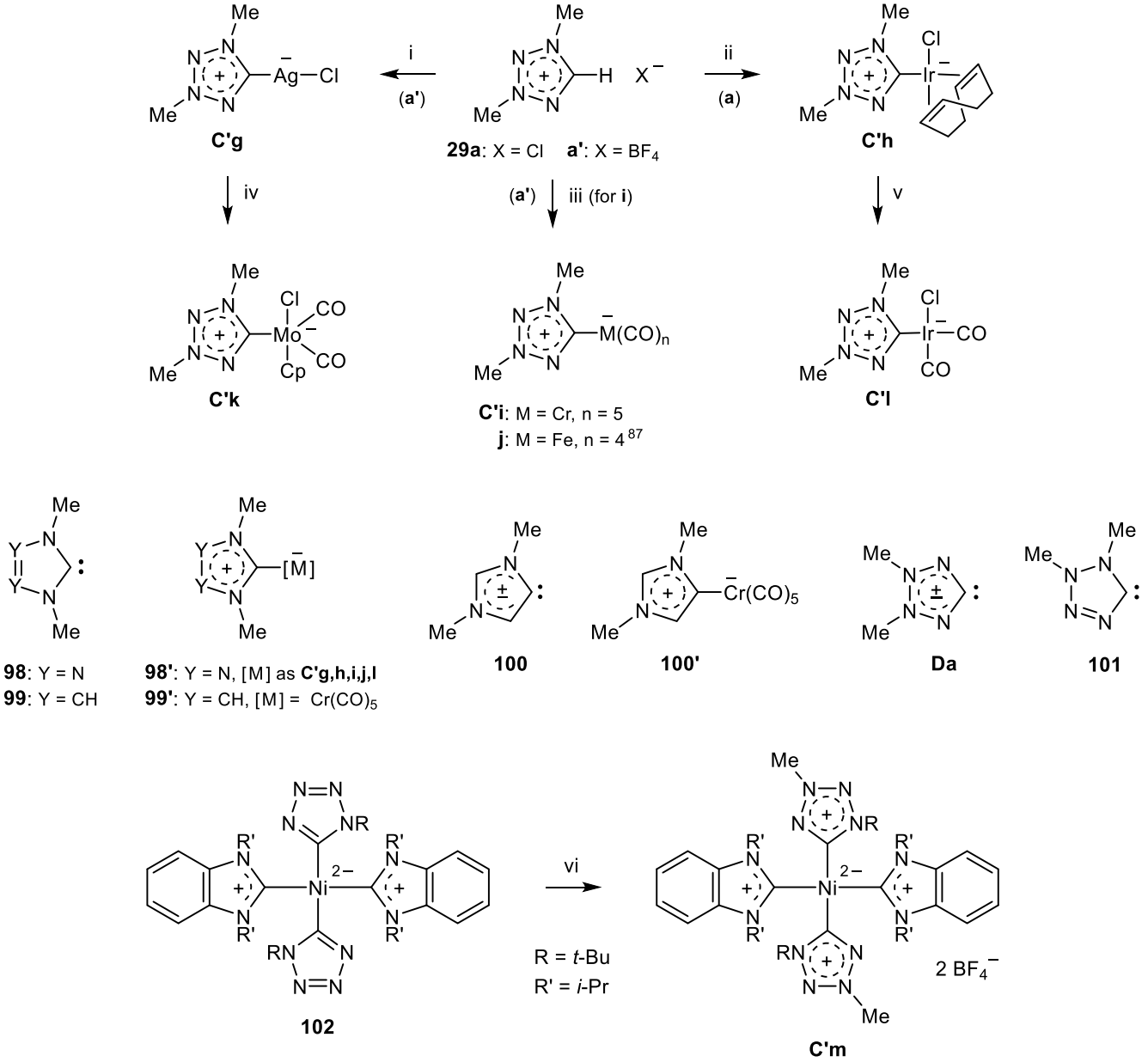
i: $Hg(OAc)_2$, DMSO, Δ ii: DBU (no details) iii: Cl_2, Br_2 or I_2, CH_2Cl_2, rt iv: $Pd(PPh_3)_4$, $CHCl_3$, Δ v: **97**, DBU, DMF, −60 °C

9	29	C'	Ar	Ar'	Hal		yield (%)	mp (°C)	ref.		yield (%)	mp (°C)	ref.
a	**b**	**a**	Ph	Ph	Cl	**C'a**	82	*ca.* 290 [a]	5	**9a**	59	185−188 [a]	5
d			Ph	Ph	Br	**b**	76	211−212 [a]	5	**d**	54	207−209 [a]	5
e			Ph	Ph	**I**	**c**	56	*ca.* 175 [a]	5	**e**	78	212−215	5
f	**c**	**b**	Ph	4-MeC_6H_4	**I**	**d**	88	184 [a]	5	**f**	71	216−218	5
g	**d**	**c**	4-$MeOC_6H_4$	Ph	**I**	**e**	31 [b]	165	83	**g**	62	188−190	5
						f	26 [b]	152−154	83	**91**	79	(see Scheme 35)	5

[a] Decomp. [b] From equimolar amounts of **29b** and **97**.

Scheme 37

(**9a,d-g**), the chloro derivative of which was converted into the palladium complex (**C'd**).[5] For synthesizing the rhodium congeners (**C'e,f**), again a 5-unsubstituted tetrazolium salt was used.[83] The same applies to the silver (**C'g**), iridium (**C'h**), and chromium complexes (**C'i**), whereas the derivatives (**C'k**) and (**C'l**) were made through carbene transfer reaction and ligand exchange.[86] As a congener of **C'i**, also the iron complex



C'	yield (%)	ref.	C'	yield (%)	ref.	C'	yield (%)	ref.
g	60	86	**i**	41	86	**l**	57	86
h	78	86	**k**	46	86	**m**	63	89

Scheme 38

(**C'j**) has been provided (details not disclosed).[87] But the true incentive to prepare these materials was to compare them with the corresponding complexes (**98'**) of the 'normal' carbene (**98**). Indeed, conspicuous differences emerged: The compounds (**C'**) were more stable than their isomers (**98'**) and were obtained in higher yields, because the latter – like the free carbene (**98**) – tend to release dinitrogen. Moreover, detailed spectroscopic, crystallographic, and computational studies led the authors to conclude that the carbene (**Ca**) has a stronger donor strength than **98**. While considering also the carbene complexes (**99'**) and (**100'**), they found through DFT calculations a decreasing donor strength in the order **100** > **Ca** > **99** > **98**.[86] Another DFT study directed to all possible 'normal' and 'abnormal' azolic carbenes (a total of 14) showed that the donor strength of **Da** surpasses that of **Ca**.[88] Thermodynamically, **Da** proved to be the least stable species: it is higher in energy than **Ca** by *ca.* 30 kcal/mol and lies even 47 kcal/mol above the 'normal' carbene (**98**), whereas the carbene (**101**) – chemically irrelevant because of the 1,2-substitution pattern (*cf.* ref.[26c]) – is intermediate between **Ca** and **Da**.[88] Recently, this relationship was also found with the dimethyl-substituted olates (**A**) and (**B**) and the two covalent tetrazol-5-ones.[1c]

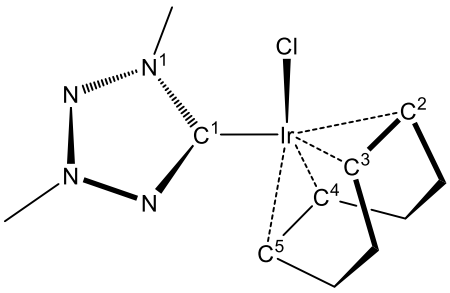
Finally, to synthesize the nickel complex (**C'm**), a divergent route was followed: the entry took advantage from the regioselective quaternization of the tetrazole ring in the derivative (**102**); but to accomplish the process, a strong electrophile was needed, ethyl iodide – even used in excess – did not affect the substrate.[89] Notably, **C'm** combines the features of a 'normal' and an 'abnormal' carbene (benzimidazole and tetrazole, respectively).

Experimental structural methods

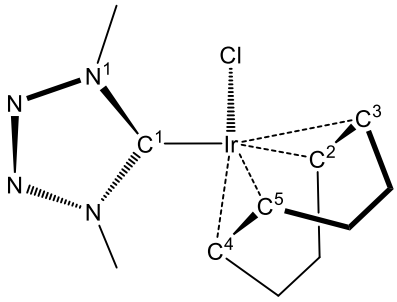
Crystallographic data are available for the complexes (**C'e,f**),[83] (**C'g-i,k,l**) and (**98'h,i**)[86] as well as (**C'm**);[89] for a direct comparison of structural parameters of the isomers (**C'h**) and (**98'h**), see Table 3. The elongated bonds C(2)–C(3) and C(4)–C(5) of the former derivative point to a more pronounced donor strength of the 'abnormal' ligand (**Ca**).[86]

Spectral data were determined throughout; for a selection, see Table 4. The majority of the complexes (**C'**) are coloured materials, but UV/Vis data have been reported for two derivatives only (**C'e,f**).[83] A detailed comparative EIMS study has been performed with the isomers (**C'i,j**) and (**98'i,j**).[87] In the ^{13}C NMR spectra, the tetrazole carbon appears at relatively low field, depending on the metal. Data that testify to an increased donor strength of the carbene (**Ca**) include, *inter alia*, the upfield shift of the low-field olefinic signal of the cyclooctadiene (COD) ligand in **C'h** and, in the case of carbonyl complexes like **C'i**, the appearance of the CO stretching bands at lower wavenumbers.[86]

Table 3. Selected bond distances (Å) and angles (deg) from X-ray diffraction [a] [86]



C'h



98'h

Ir–C^1	202.7	Cl–Ir–C^1	90.3	Ir–C^1	201.2	Cl–Ir–C^1	89.9
Ir–Cl	236.8			Ir–Cl	235.8		
C^2–C^3	139.2			C^2–C^3	138.1		
C^4–C^5	142.9	Cl–Ir–C^1–N^1	74.2	C^4–C^5	141.1	Cl–Ir–C^1–N^1	–79.8

[a] Perspective drawing only approximate.

Table 4. Selected spectral data of compounds (**C'**), (**98'**), and (**D'**)

Compd (Scheme), ref.	[A]	[B]	Compd (Scheme), ref.	[A]	[B]
C'a (37), 5	183.3 [a, b]		**C'g** (38), 86	182.4 [a]	51 [h, i]
C'd (37), 5	172.6 [c, d]		**C'k** (38), 86	196.7 [j]	5 [k]
C'e (37), 83	187.7 [c, e]	384 [f]	**C'm** (38), 89	172.0 [j]	
C'f (37), 83	185.3 [c, g]	409.5 [f]	**D'a** (39), 43	191.2 [a, l]	

Compd (Scheme), ref.	[A]	[B]	[C]
C'h / 98'h (38), 86	186.8 / 179.0 [m]	20 / 36 [h]	85.1 / 87.7 [m]
C'i / 98'i (38), 86	190.3 / 200.9 [c]	100 / 100 [n]	1910 / 1925 [o]
C'j / 98'j (38), 87		45 / 47 [p]	
C'l / 98'l (38), 86	182.1 / 173.1 [j]	66 / 100 [h]	

[A] ^{13}C NMR, tetrazole carbon, shift values (δ, ppm) relative to $SiMe_4$. — [B] **C'e,f** : UV/Vis, longest wavelength maxima (nm); **C'g-l**, **98'h-j,l**: MS, relative intensities of parent ions (%). — [C] **C'h**, **98'h**: ^{13}C NMR, olefinic carbon atoms of COD ligand (shift values as above); **C'i**, **98'i**: IR, wavenumbers of CO ligands (cm^{-1}).
[a] DMSO-d_6. [b] ^{15}N NMR, $\delta_{N(1)/N(2)/N(3)/N(4)}$ = –118.4 / –26.9 / –87.2 / –59.7 ppm, relative to $MeNO_2$ [δ_{199Hg} = –1176.3 ppm (half-width 90 Hz)].[6,73] [c] $CDCl_3$. [d] $^2J_{(C–Pd–P)}$ = 9.0 Hz. [e] $^1J_{(Rh–C)}$ = 51.6 Hz. [f] MeCN. [g] $^1J_{(Rh–C)}$ = 54.8 Hz. [h] FAB. [i] M–Cl. [j] CD_2Cl_2. [k] ESI. [l] $^1J_{(Hg–C)}$ not observed. [m] CD_3CN. [n] CI. [o] Solid. [p] EI.

4) MESOIONIC TETRAZOLYLIDENES OF TYPE (D)

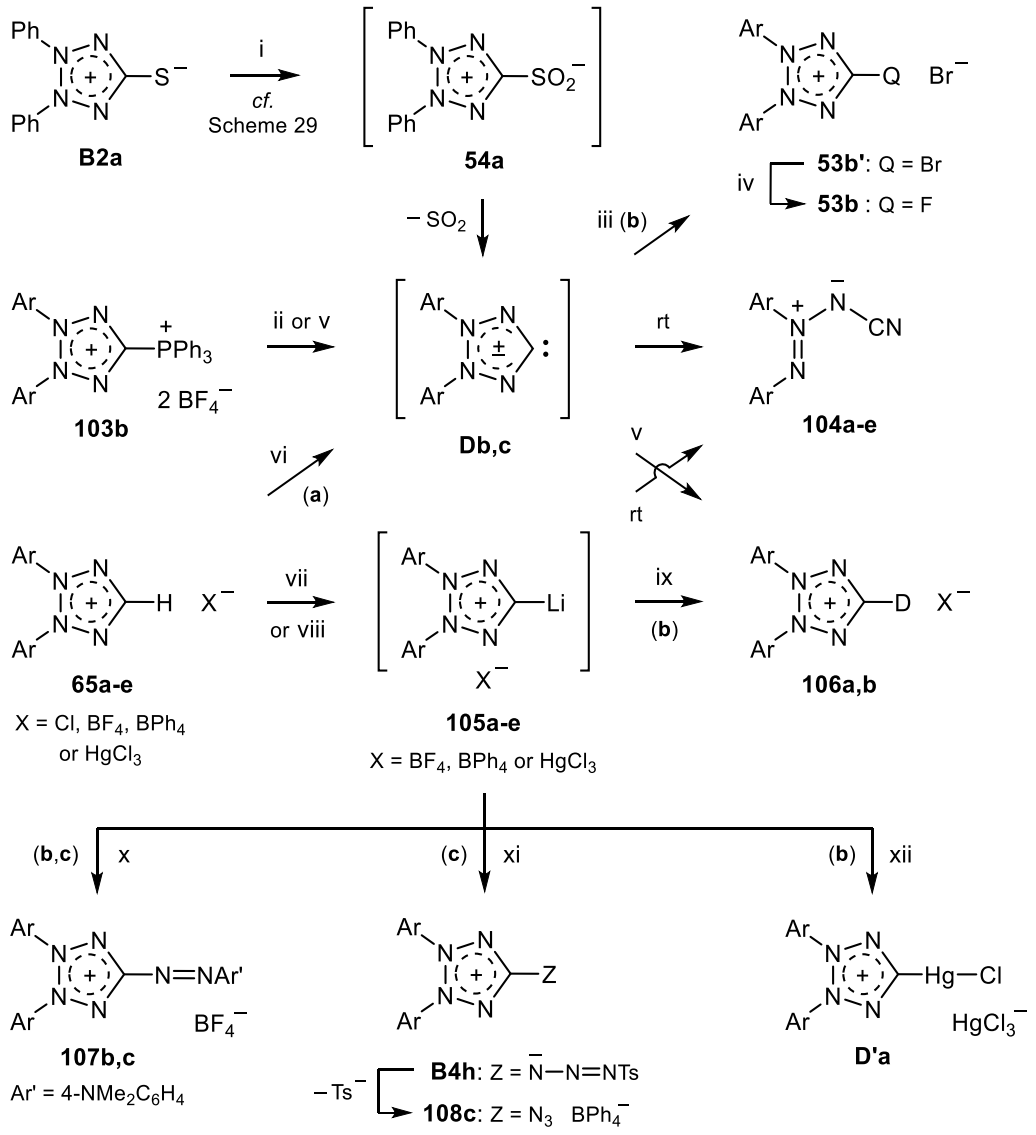
Similarly to the congeners (**C**), the class (**D**) has first been envisaged fifty years ago as an intermediate of base-catalyzed H/D exchange, *viz.* **Db** in the course of the process [**65a** (X = Cl) → **106a**] (Scheme 39).[90] But the 'preparative chemistry' of these carbenes did not begin until the early 1990s. Three procedures of generation have been described [*cf.* routes (s) and (r) of Scheme 1]: (i) desulfurization of the thiolate (**B2a**), (ii) dephosphonionation of the substrate (**103b**), and (iii) deprotonation of the salts (**65a-e**).[43,45,63] The latter reaction is known to proceed more slowly than the analogous entry to the carbenes (**C**) (*cf.* also ref.[43]). – For another review of these methods, see reference.[2c]

(i) Recurring to Section (2b), treatment of **B2a** with sodium periodate led, *inter alia*, to the sulfinate (**54a**) which by loss of sulfur dioxide gave the carbene (**Db**); the latter ring-opened to the cyanoazimine (**104a**),[91] but since also some olate (**B1a**) was found, it was speculated that part of **Db** took up atmospheric oxygen.[45]

(ii) On exposure to water or mineral acid, the tetrazolium salt (**103b**) was hydrolyzed to triphenylphosphine oxide and the 5-defunctionalized derivative (**65b**; X = BF_4), the latter arose through protonation of transient **Dc**; accordingly, treatment of **103b** with deuterium oxide gave the derivative (**106b**).[43] However, on action of cesium fluoride, the functional group of **103b** was split off as triphenylphospine difluoride to leave **Dc** which ring-opened to **104b**. Yet, using an electrophilic trapping agent such as bromine, **Dc** was intercepted to give compound (**53b'**) which, through excess cesium fluoride, was converted to the 5-fluoro derivative (**53b**); this sequence demonstrated that compound (**53b**) does not simply arise by nucleophilic attack of fluoride ion on the 5-position of **103b**.[45]

(iii) Treatment of **65a-e** with strong bases like butyllithium or lithium hexamethyldisilazide generated the carbenoids (**105a-e**).[45,63] These species, which could be studied spectroscopically at –100 °C, showed the behaviour of **D**: On warming to room temperature, they ring-opened to the azimines (**104a-e**), and action of deuterated sulfuric acid on **65b** gave the above salt (**106b**).[45] Trapping of **105b,c** with a benzenediazonium ion led to azo compounds like **107b,c**, whereas interception of **105c** with tosyl azide gave the 5-azido salt (**108c**) [the primarily formed aminide (**B4h**) was elusive]; however, treatment with chlorine or bromine restored the starting salts (**65**; X = Cl or Br) instead of yielding 5-halotetrazolium salts like **53b'**; also trapping with dinitrogen oxide failed [*cf.* Section (2c)].[63]

Metal complexes of **D** seem to have been made only once: Treatment of **65b** (X = $HgCl_3$) with mercury(II) chloride in the presence of lithium hydroxide gave a material of the composition (**D'a**), auxiliary bases like hydrogencarbonate or acetate ion turned out to be too weak.[43] Also no reaction occurred between the metal salt and the carbenoid (**105c**; X = BPh_4) when generated with butyllithium.[63] On pyrolysis, compound (**D'a**) released the carbene (**Dc**), as evidenced by detection of the azimine (**104b**); attemps of bromination to give the salt (**53b'**) failed.[43]



53, **65**, **103**–**108**	Ar	
a	Ph	**Db**
b	4-MeC_6H_4	**D'a, Dc**
c	4-$MeOC_6H_4$	**B4h**
d	4-$NMe_2C_6H_4$	
e	[4-$NMe_3C_6H_4$]BPh_4	

i: $NaIO_4$, MeCN, rt ii: CsF, CH_2Cl_2, rt iii: Br_2, CH_2Cl_2
iv: CsF, $SOCl_2$ v: D_2O (THF), rt vi: borate buffer (D_2O, pD 8.85), rt
vii: $LiN(SiMe_3)_2$ or LiBu, THF, –78 °C or – 90 °C viii: LiOH, H_2O–THF, rt
ix: D_2SO_4, ➔ rt (for **106b**) x: [4-$NMe_2C_6H_4N_2$]BPh_4, ➔ rt, then $LiBF_4$
xi: 4-$MeC_6H_4SO_2N_3$, ➔ rt xii: $HgCl_2$

product	yield (%)	method	mp (°C)	ref.	product	yield (%)	method	mp (°C)	ref.
53b [a]	73	ii, iii, iv	110	45	**106a**	[d]	vi, v		90
104a	9.2 [b] / 68	i / vii	92	45	**b** [e]	63 / 58	ii, v / vii, ix	181–183	43 / 45 [f]
b	64 / 70	ii / vii	177	45	**107b**	25	vii, x	172–180 [g]	63 [h]
c	66	vii	136	45	**c**	56	vii, x	148–149 [g]	63
d	63	vii	195–198	45	**108c** [i]	43	vii, xi	158–168 [g]	63
e [c]	85	vii	>280	45	**D'a** [j]	80	viii / xii	240–243 [g]	43

[a] Containing 1 mol $SOCl_2$. [b] For further products, see Scheme 29. [c] Containing 1.5 mol DMSO. [d] H/D exchange experiment with **65a** (X = Cl). [e] Containing 1 mol MeCN; X = BPh_4. [f] Yield (recalculated) and mp from ref.[43] [g] Decomp. [h] Yield and mp from ref.[43] [i] **B4h** elusive, small amounts detected in crude **108c** by MS. [j] From **65b** (X = $HgCl_3$).

Scheme 39

CONCLUSION

Comparing the preparative achievements made with the classes (**A**) and (**B**), some areas of the **B** series wait for further studies: (i) A conspicuous gap concerns the aminides (**B4**); there are only derivatives having electronegatively substituted functions, while representatives with the parent NH functionality and simple NR groups are unknown. Considering the instability of the derivatives (**B4**) having Z = NCH_2R, a general study of the ring opening of **B4**, *i.e.* the valence isomerism {tetrazolium ⇄ tetraazapentadiene}, is needed. (ii) Turning to the series (**B5**), it is still open whether the cyclopentadienide (**B5e**) detected in the EIMS spectra of the phenolates (**B1'**) can also be synthesized. (iii) In view of the theoretical conclusion that the carbene (**D**) exhibits a more pronounced donor strength than its isomer (**C**), the preparation of appropriate metal complexes (**D'**) seems desirable.

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Dietrich Moderhack, born 1940 in Berlin, graduated from Technical University of Braunschweig, Germany, where he took his PhD in 1968 (mentor: Prof. G. Zinner). From October 1974 to September 1975 he held a DFG scholarship for joining Prof. Katritzky's group at the University of East Anglia in Norwich, UK. After his Habilitation in Braunschweig (1978), he became a full Professor (1982); since October 2005, he has been retired. His major interests include triazole and tetrazole chemistry, but azapentalenes, four-membered rings with two adjacent heteroatoms, and isocyanides are being looked at as well.