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4,5-DIHYDRO-1*H*-TETRAZOLES — 5-ALKYL/ARYL AND 5-ALKYLIDENE DERIVATIVES

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Abstract – Nine types of 5-alkyl/aryl- and 5-alkylidene-4,5-dihydro-1*H*-tetrazoles (**A**–**H**) are reviewed in this article. Besides their synthesis and chemical behaviour, tautomerism of representatives having electron-withdrawing substituents (**E, F**) as well as polarization of the semicyclic double bond of the types (**C**–**H**) are of interest.

INTRODUCTION

The framework of 4,5-dihydro-1*H*-tetrazole occurs in two different structures having either a tetrahedral (**I**) or a trigonal ring carbon (**II**) (Chart 1). Of the former system, we know only the types (**A**) and (**B**), whereas

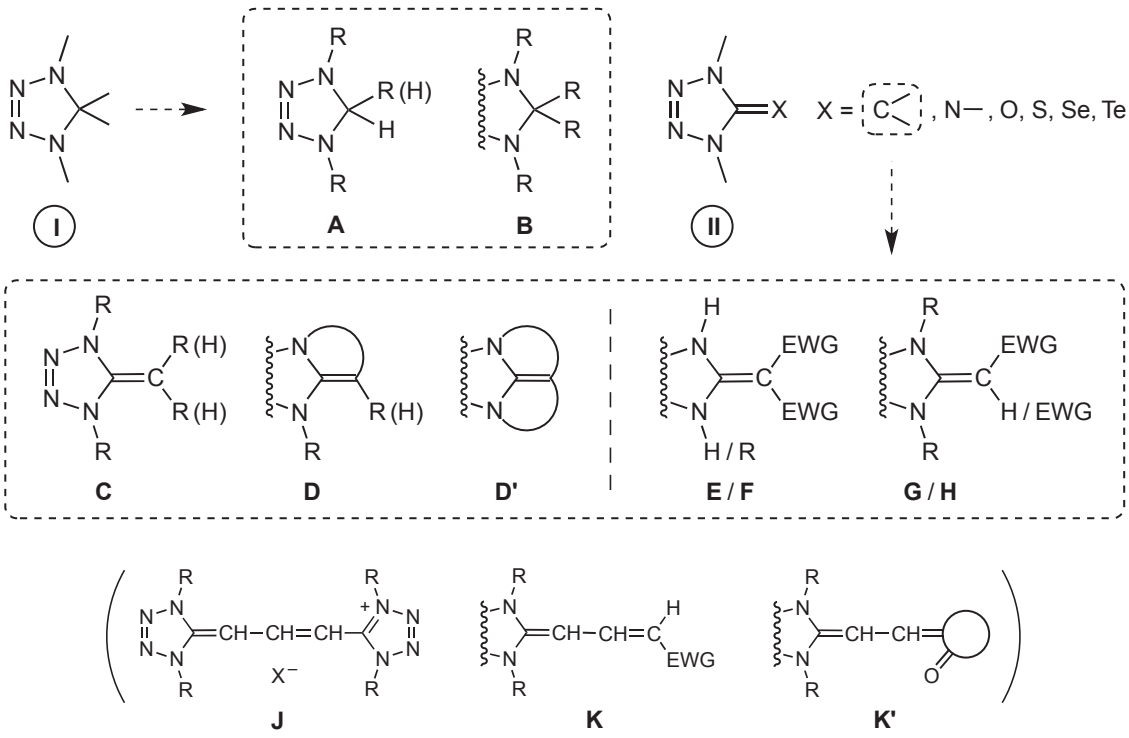


Chart 1. Title compounds (**A** − **H**) (species in brackets not dealt with)

of the latter (**II**), a plethora of representatives exist. Here the lion's share are the wide-spread compounds having a heteroatom for X, but even the alkylidene variant – proper aim of this article – abounds in a variety of types like **C**–**H**. Major contributions to that domain came from the Quast and Saalfrank groups, whereas knowledge of the classes (**A**) and (**B**) is owed to the Isida and Carboni/Carrié groups. Yet, in spite of the multifaceted chemistry of the entire field (**A**–**H**), no specific review has been produced till now.[1,2]
Structure (**II**: X = C<) is also present in tetrazole-based cyanine dyes (**J**) and merocyanines (**K**, **K'**). These derivatives, however, represent compounds of an own profile; hence, an adequate description would require a specialized report.

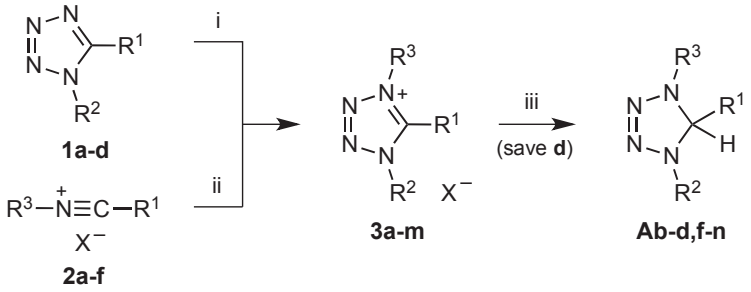
The material of this review is arranged according to Sections (1)–(6) (below). All target compounds (**A**–**H**) are available by standard procedures; routes start either from open-chain substrates or suitably preformed tetrazoles. Besides preparative aspects two phenomena will receive attention: Tautomerism of the types (**E**) and (**F**) (→ 4.c) and the ylide character of the types (**E**–**H**) (→ 6).

(1) Dihydrotetrazoles of Types (**A**) and (**B**)
  a) Synthesis b) Photolysis and Thermolysis c) Experimental Structural Methods
(2) Dihydrotetrazoles of Type (**C**)
  a) Synthesis and Addition Reactions b) Photolysis and Thermolysis c) Reactions of Cycloadducts
(3) Dihydrotetrazoles of Types (**D**) and (**D'**)
  a) Synthesis b) Photolysis
(4) Dihydrotetrazoles of Types (**E**) and (**F**)
  a) Synthesis b) Metal Complexes of Compounds (**F**) c) Tautomerism of Types (**E**) and (**F**)
(5) Dihydrotetrazoles of Types (**G**) and (**H**)
  Synthesis and Reactions
(6) Dihydrotetrazoles of Types (**C**–**H**): Experimental Structural Methods; Ylide Character

1) DIHYDROTETRAZOLES OF TYPES (A) AND (B)

a) Synthesis

Representatives of type (**A**) were first prepared in 1973 during studies on the reduction of diverse classes of azolium salts. Thus, action of sodium boranate on the tetrazolium salts (**3c,g,h,k**) (obtained from **1a-c**[3]) gave the dihydro derivatives (**Ad,h,i,l**) in reasonable to excellent yield (Scheme 1).[4] Not much later, the congener (**Ak**) was made accordingly using the precursors (**1d**) and (**3j**).[5] The reductive behaviour of **3** was found to correspond to that of 1,2,3- and 1,2,4-triazolium salts, whereas pyrazolium and imidazolium salts were reduced to the azolidine stage; on the other hand, tetrazolium salts having a 1,3,5-substitution pattern



i: R^3I (neat), 70 °C (100 °C for **3c**) ii: R^2N_3, $ClCH_2CH_2Cl$ (MeCN for **3a-c**), rt (70 / 60 / 40 °C for **3c** / **e** / **m**)
iii: $NaBH_4$, EtOH, rt ($LiAlH_4$, Et_2O for **Aa**)

1	**2**	R^1	R^2	R^3	X	**3**	from	yield (%)	ref.	**A**	yield (%)	mp or bp (°C) / Torr	ref.
		H	Ph	Me						**a** [a]	–	–	–
	a	Me	Me	Me	FSO_3	**a**	**2a**	80	6	**b**	45	25 / 10^{-3}	6
		Me	CH_2Ph	Me	FSO_3	**b**	**2a**	71	6	**c**	70	130 / 0.2	6
a		Me	Ph	Me	I // FSO_3	**c**	**1a** // **2a**	[g] // 10 [h]	3 // 6	**d**	100 // 80	oil // 110 / 10^{-3}	4 // 6
	b	Me	Et	Et	FSO_3	**d** [b]	**2b**	58	6				
		t-Bu	Me	Me						**e** [c]	–	–	–
	c	*t*-Bu	CH_2Ph	Me	FSO_3	**e**	**2c**	60	6	**f**	65	140 / 10^{-2}	6
	d	*c*-C_6H_{11}	CH_2Ph	Me	FSO_3	**f**	**2d**	60	6	**g**	53	39	6
b	**e**	Ph	Me	Me	I // FSO_3	**g**	**1b** // **2e** [d]	35 // 75	3 // 6	**h**	90 // 80	53–53.5 // 52	4 // 6
c		Ph	Et	Me	I	**h**	**1c**	76	3	**i**	67	oil	4
		Ph	CH_2Ph	Me	FSO_3	**i**	**2e** [d]	70	6	**j**	85	75	6
d		Ph	Ph	Me	I // $SbCl_6$	**j**	[e] // **2e** [f]	[g] // 78	5 // 6	**k**	[g] // 75	112 // 111	5 // 6
		Ph	Et	Et	I	**k**	**1c**	8	3	**l**	61	oil	4
	f	Ph	CH_2Ph	Ph	$SbCl_6$	**l**	**2f**	65	6	**m**	90	95	6
		Ph	Ph	Ph	$SbCl_6$	**m**	**2f**	52	6	**n**	40	188	6

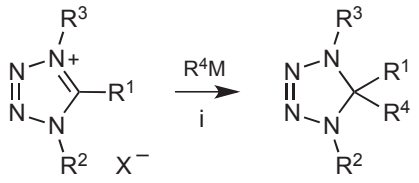
[a] Synthesis missing in ref.[6] (contrasting with authors' statement[8]). [b] Compound used for **Bb** (see Scheme 3). [c] Synthesis missing in refs.[6,8] (contrasting with authors' statement[9]). [d] X = FSO_3. [e] Obviously **1d** (unmentioned in ref.[5]). [f] X = $SbCl_6$ (compound unmentioned in ref.[6]). [g] Unreported. [h] Besides *N*-[4-(fluorosulfonyloxy)phenyl]-*N*'-methylacetamidine.

Scheme 1

were not affected at all.[4] Based on that work, a wider range of compounds (**A**) – tabulated in the Scheme – were synthesized in the mid 1980s,[6] but preparative data of the 5-unsubstituted parent (**Aa**) are missing. The necessary substrates (**3**) resulted from [3 + 2] cycloaddition of azides (R^2N_3) to the nitrilium salts (**2**). This method, which allows a specific entry to that kind of tetrazoliums, had been found some years before;[7] now it proved its general applicability, showing an azide reactivity according to $MeN_3 > PhCH_2N_3 > PhN_3$.[6] The surprisingly low yield of the salt (**3c**; X = FSO_3) is the consequence of a multi-step side reaction that eventually gave *N*-[4-(fluorosulfonyloxy)phenyl]-*N*'-methylacetamidine.

Dihydrotetrazoles of the type (**B**) – though formally related to **A** – do not arise from the latter; rather, they were prepared from the above tetrazolium salts (**3**) by treatment with organometallic reagents; in this way derivatives like **Bb-l,n,o** were obtained very readily (Scheme 2).[6,8] The modest yield of **Bb** was associated with the acidity of the methyl group of the substrate (**3d**):[6] the reagent, which was used in excess, obviously caused deprotonation to a 5-methylene species of type (**C**). This class had earlier been shown to arise on

action of alkali hydride [*cf.* Section (2.a)]. Hence, satisfactory yields of **B** require precursors (**3**) that have an aryl substituent at C(5).



3d,f,h-j **Bb-g,i,j,o**

i: Et_2O, 5 °C, then rt

3	R^1	R^2	R^3	R^4	X	**B**	from	R^4M	yield (%)	mp (°C)	ref.
	Me	Me	Me	Me		**a** [a]	–	–	–	–	–
d	Me	Et	Et	Me	FSO_3	**b**	**3d**	MeLi	25	oil	6
f	Ph	Me	Me	Me	FSO_3	**c**	**3f**	MeLi	80	40	6
	Ph	Me	Me	Ph		**d**	**3f**	PhLi	75	89	6
	Ph	Me	Me	$CH{=}CH_2$		**e**	**3f**	$H_2C{=}CHMgBr$	65	41	6
	Ph	Me	Me	$C{\equiv}CPh$		**f**	**3f**	$PhC{\equiv}CLi$	60	99	6
h	Ph	CH_2Ph	Me	Me	FSO_3	**g**	**3h**	MeLi	70	53	6
	Ph	CH_2Ph	Me	Ph		**h**	[b]	[b]	50	94	10
j	Ph	Ph	Me	Me	$SbCl_6$	**i**	**3j**	MeLi	80	52	6
	Ph	Ph	Me	Ph		**j**	**3j**	PhLi	71	106	6
	Ph	Et	Et	Me		**k**	[b]	[b]	75	34	10
	Ph	Et	Et	Ph		**l**	[b]	[b]	73	87	10
	Ph	CH_2Ph	Ph	Me		**m** [c]	–	–	–	–	–
	Ph	CH_2Ph	Ph	Ph		**n**	[b]	[b]	52	107	10
m	Ph	Ph	Ph	Me	$SbCl_6$	**o**	**3m**	MeLi	48	106	6

[a] Synthesis missing in refs.[6,8] (contrasting with authors' statement[9]). [b] Procedure (**3** ➔ **B**) not detailed. [c] Synthesis missing in ref.[6] (contrasting with authors' statement[8]).

Scheme 2

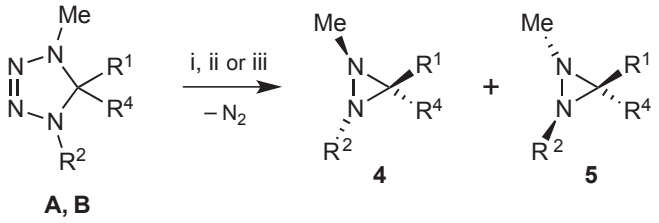
Finally, a spiro structure of type (**B**), *viz.* 1,4-diphenyl-5,5-trimethylene-4,5-dihydro-1*H*-tetrazole (featured in SciFinder), was tentatively assigned to the material obtained from phenyl azide and cyclopentanone anil; however, after the experiment had been repeated using modified reactants, that constitution was abandoned in favour of a cyclopentatriazole derivative.[11] A reinvestigation of this work appears desirable.

b) Photolysis and Thermolysis

Typical reactions of the dihydrotetrazoles (**A**) and (**B**) include: (i) elimination of molecular nitrogen to give diaziridines (Scheme 3), and (ii) cycloreversion to yield azides and imines (Scheme 4).

(i) The first examples of this process were reported in 1974 when the substrates (**Ad,h,k**) were photolyzed at room temperature. The derivative (**Ah**) gave the diaziridine (**4e**) [or (**5e**)] as a single substance, whereas **Ad** and **Ak** produced mixtures of **4d** + **5d** and **4g** + **5g**, respectively. The method was felt preparatively useful, in

particular for 1-aryldiaziridines.[5] A later study, carried out at below –100 °C, not only confirmed the earlier findings, but was extended to include substrates such as **Aa-c,j** and **Bc-f,i**.[8]



i: hν, CH_2Cl_2, rt ii: hν, benzene, – 155 °C (matrix) iii: 100 °C, toluene-d_8, 8 / 22 / 22 / 3 h for **Aa** / **b** / **c** / **d**

A	**B**	R^1	R^2	R^4	**4, 5**	method	yield (%)	ref.	ratio {**4** : **5**}	ref.
a		H	Ph	H	**a**	ii / iii [a]	85 / 70	8 / 8		
b		Me	Me	H	**b**	ii / iii	85 / 30	8 / 8		
c		Me	CH_2Ph	H	**c**	ii / iii	78 / 48	8 / 8	50 : 50 / 40 : 60	8 / 8
d		Me	Ph	H	**d**	i / ii / iii	71 / 70 / 40	5 / 8 / 8	[b] / 45 : 55 / 20 : 80	5 / 8 / 8
h		Ph	Me	H	**e**	i / ii	16 / 40–45	5 / 8		
j		Ph	CH_2Ph	H	**f**	ii	40	8	65 : 35	8
k		Ph	Ph	H	**g**	i / ii	62 / 89	5 / 8	60 : 40 / 55 : 45	5 / 8
	c	Ph	Me	Me	**h**	ii	40	8		
	d	Ph	Me	Ph	**i**	ii	0	8		
	e	Ph	Me	$CH{=}CH_2$	**j**	ii	0	8		
	f	Ph	Me	$C{\equiv}CPh$	**k**	ii	0	8		
	i	Ph	Ph	Me	**l**	ii	80	8	40 : 60	8

[a] 80 °C. [b] According to NMR two species formed (ratio unreported).

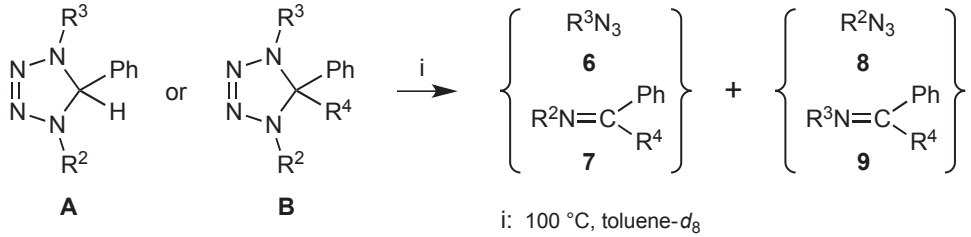
Scheme 3

The above experiments showed that diaziridines were obtained only when the ring carbon of the precursors (**A, B**) bears at least one aliphatic ligand (or a hydrogen), whereas with unsaturated substituents as the sole groups (see **Bd-f**) the method failed. In certain cases also thermolysis led to diaziridines, as exemplified by the conversion of **Aa-d** to the corresponding products (**4**) and/or (**5**).[8]

(ii) The said cycloreversion was first observed with the substrate (**Ah**) which, on being heated at > 120 °C, decomposed to methyl azide (**6**: R^3 = Me) and *N*-benzylidenemethylamine (**7**: R^2 = Me, R^4 = H) (Scheme 4).[5] This preliminary experiment was followed by a systematic study directed to the influence of substituents.[8] It turned out that the thermal stability decreases appreciably when a methyl group in **A** and **B** is replaced with a phenyl group or another unsaturated ligand, as evidenced on passing from **Af,h** to **Ak,m** and from **Bc,g** to **Bd-f,h-j,m,n**. As for the direction of that cycloreversion, both pathways giving {**6** + **7**} and {**8** + **9**} occurred to an equal extent with the derivatives (**Aj,k,m**) irrespective of the substituents, whereas with series (**B**) the second way predominated; moreover, the latter became the sole mode when a phenyl group was introduced at N(1/4) (*cf.* **Bg,h** *vs.* **Bi,j,m,n**). But despite the distinct proclivity to

disintegrate, the cyclic 2-tetrazene system as in **A** and **B** appears rather stable compared to 6- and 7-membered analogues.

Cycloreversion products like **6** / **7** and **8** / **9** were also observed in the CAD/MIKE spectra; with substrates (**A**) and (**B**) that are devoid of a phenyl substituent at C(5), these species represent the main fragments.[10]



A **B**

i: 100 °C, toluene-d_8

					A / **B**			
A	**B**	R^2	R^3	R^4	period (h)	conversion (%)	{**6** + **7**} (%)	{**8** + **9**} (%)
h	**c**	Me	Me	Me	18 [a] / 14.5	75 [a] / 65		
	d	Me	Me	Ph	− / 2	− / 60		
	e	Me	Me	CH=CH_2	− / 2	− / 45		
	f	Me	Me	C≡CPh	− / 2	− / 50		
j	**g**	CH_2Ph	Me	Me	18 / 18	80 / 80	50 / 30	50 / 70
	h	CH_2Ph	Me	Ph	− / 2	− / 80	− / 35	− / 65
m	**m**	CH_2Ph	Ph	Me	1 / 1	55 / 60	50 / 0	50 / 100
	n	CH_2Ph	Ph	Ph	− / 1	− / 100	− / 0	− / 100
k	**i**	Ph	Me	Me	2 / 1	70 / 50	50 / 0	50 / 100
	j	Ph	Me	Ph	− / 1	− / 100	− / 0	− / 100

[a] Also 14.5 h and 60% (misprint?).

Scheme 4

Finally, a few compounds (**A**) and (**B**), such as **Ab,d,e,h** and **Ba**, have been thermolyzed in the gas phase at 370–400 °C and the conversions analyzed by photoelectron spectroscopy (PE): While the derivative (**Ad**) released nitrogen to give the diaziridine (**4**/**5d**) (*cf.* Scheme 3), the compounds (**Ab,e,h**) and (**Ba**) underwent cycloreversion to afford methyl azide and the respective imine (*cf.* Scheme 4). The identity of the products resulted easily from the PE spectra, their assignment was partly supported by MNDO calculations.[9]

c) Experimental Structural Methods

Crystallographic data are available for compound (**Be**) (Table 1, top line).[12] To explain the photochemical behaviour of **B** (*cf.* Scheme 3), X-ray data have also been collected at 110 K, but the structure was quite similar. The envelope geometry of the five-membered ring appears quasi symmetrical, the methyl groups adopting an equatorial position; the dihedral angle between the N(1)–N(2)–N(3)–N(4) and N(1)–C(5)–N(4) planes shows 29.3°. In an additional DFT study (B3LYP/6-31G**; gas phase) the structures of the relevant

conformers (*i.e.*, axial vinyl–equatorial phenyl and axial phenyl–equatorial vinyl) have been calculated; the former (shown left) has been found to be slightly lower in energy, the dihedral angle being about 24.2°.[13]

Table 1. Selected bond distances (Å) and angles (deg) for compound (**Be**) from X-ray diffraction at 293 K[12] and DFT calculation [a][13]

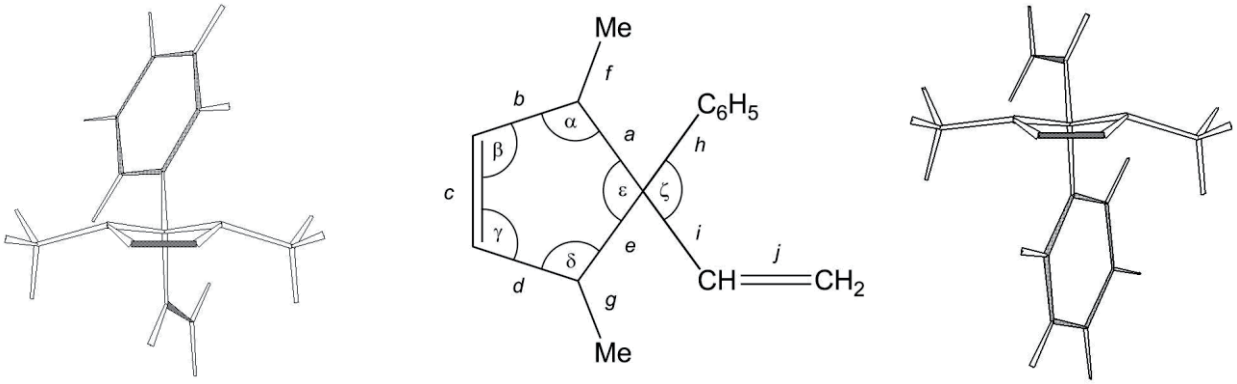
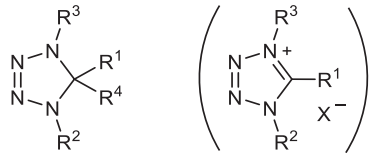


fig.	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	α	β	γ	δ	ε	ζ	ref.
mid	1.478	1.389	1.256	1.384	1.479	1.454	1.453	1.524	1.518	1.306							12
left	1.484	1.396	1.252	1.387	1.483	1.452	1.448	1.533	1.532	1.333	109.2	110.0	109.8	108.8	95.5	115.3	13
right	1.475	1.379	1.253	1.397	1.489	1.445	1.451	1.546	1.521	1.333	110.5	109.7	109.6	109.1	95.1	115.6	13

[a] B3LYP/6-31G** (gas phase): left: E = -646.51658 a.u.; right: E = -646.51544 a.u. (ΔE = 2.99 kJ/mol).

Typical ^{1}H NMR data of derivatives (**A**) and (**B**) are gathered in Table 2. The resonances of the proton at C(5) are appreciably influenced by an adjacent phenyl group and are gradually shifted downfield as this group enters the following positions: N(1/4); C(5); both C(5) and N(1/4); throughout C(5), N(1), N(4).[4–6]

Table 2. ^{1}H NMR data of selected compounds (**A**) and (**B**) compared to precursors (**3**) [a]

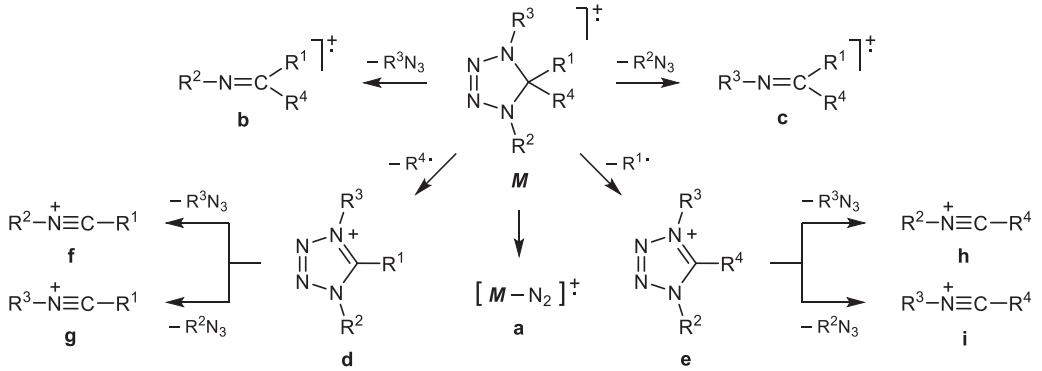


A	**B**	**(3)**	R^1	R^2	R^3	R^4	$\delta_{5\text{-H}}$	$\delta_{5\text{-Me}}$	$\delta_{1(4)\text{-Me}}$	solvent [b]	ref.
b		**(a)**	Me	Me	Me	H	3.12	1.02 (2.80)	2.55 (4.16)	*A* ([c])	6
d		**(c)**	Me	Ph	Me	H	4.15 / 4.12	1.52 (3.00) / 1.05 (2.81)	1.52 (3.00) / 1.05 (2.81)	*B* (*C*) / *A* ([c])	4 / 6
h		**(g)**	Ph	Me	Me	H	4.48 / 4.45		2.86 (4.30) / 2.85 (4.18)	*B* (*B*) / *A* ([c])	4 / 6
k		**(j)**	Ph	Ph	Me	H	5.28 / 5.06		2.97 / 2.56 (4.36)	[c] / *A* ([c])	5 / 6
n			Ph	Ph	Ph	H	6.32			*B*	6
	b	**(d)**	Me	Et	Et	Me		0.75 (2.78)		*A* ([c])	6
	i	**(j)**	Ph	Ph	Me	Me		1.46	2.59 (4.36)	*A* ([c])	6
	o		Ph	Ph	Ph	Me		1.75		*B*	6

[a] Shift values in ppm; all parenthesized figures refer to precursors (**3**). [b] A = C_6D_6, B = $CDCl_3$, C = D_2O. [c] Unreported.

The shift values of the methyl groups at C(5) of (**B**) show a similar (but conceivably less pronounced) dependence.[6] Expectedly, in all cases the methyl groups at both C(5) and N(1/4) resonate at higher field compared to those of the precursors (**3**).

Table 3. MS data of selected compounds (**A**) and (**B**) [a][10]



M	R^1	R^2	R^3	R^4	***M***	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
Bb	Me	Et	Et	Me	156 (16)	128 (0.1)	85 (8) [b]		141 (65) [c]			70 (100) [d]		
Bl	Ph	Et	Et	Ph	280 (6.7)	252 (0.1)	209 (35) [b]		203 (25) [c]			132 (67) [d]		
Ah	Ph	Me	Me	H	176 (14.5)	148 (2.7)	119 (42) [b]		175 (12)	99 (95)	118 (100) [e]		42 (68) [f]	
An	Ph	Ph	Ph	H	300 (3.5)	272 (2)	181 (100) [b]		299 [k]	223 (0.7)	180 (91) [e]		104 (18) [f]	
Bf	Ph	Me	Me	[i]	276 (3.6)	224 (0.1)	195 (18.5) [b]		175 (3.5)	199 (100)	118 (14) [e]		142 (98) [f]	
Aa	H	Ph	Me	H	162 (22.5)	134 (47.5)	43 (6)	105 (100)	161 (0.7) [e]		104 (63) [g]		42 (20) [h]	
Bh	Ph	[j]	Me	Ph	328 (2.2)	300 (0.5)	271 (16)	195 (23)	251 (36) [e]		194 (41) [g]		118 (74) [h]	
Ad	Me	Ph	Me	H	176 (22)	148 (17)	119 (77)	57 (11)	175 (1.2)	161 (48)	118 (36)	56 (27)	104 (90)	42 (42)
Am	Ph	[j]	Ph	H	314 (4.4)	286 (1.4)	195 (18)	181 (81)	313 (0.3)	237 (2.7)	194 (13)	180 (56)	118 (2.9)	104 (25)
Bg	Ph	[j]	Me	Me	266 (3)	238 (0.4)	209 (5)	133 (10)	251 (26)	189 (11)	194 (1.3)	118 (36)	132 (7)	56 (14)

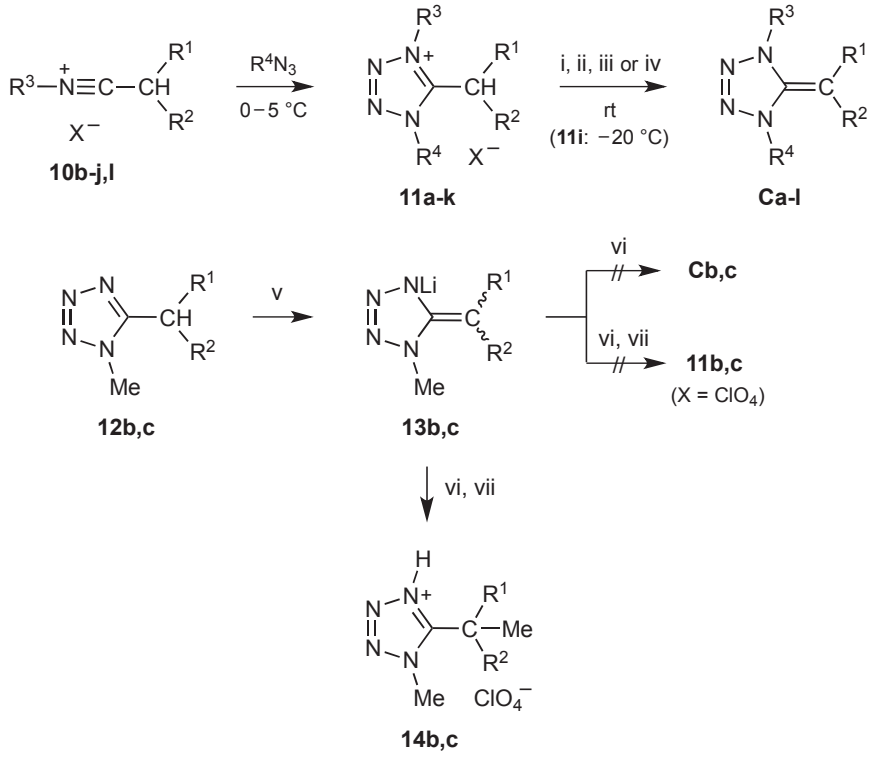
[a] 70 eV, *m/z* (%); base peaks of **Bl**, **Bh**, **Ad**, **Am**, and **Bg** (not shown in Table) = 104, 91, 77, 91, and 91, respectively. [b] **b** = **c**. [c] **d** = **e**. [d] **f** = **g** = **h** = **i**. [e] **f** = **g**. [f] **h** = **i**. [g] **f** = **h**. [h] **g** = **i**. [i] Phenylethynyl. [j] Benzyl. [k] Unreported.

The mass spectrometric behaviour of compounds (**A**) and (**B**) shows three competing reactions (Table 3): (i) extrusion of molecular nitrogen (→ **a**), (ii) cycloreversion as in Scheme 4 (→ **b**; **c**), and (iii) loss of a C(5)-ligand (→ **d**; **e**), followed by another cycloreversion (→ **f**, **g**; **h**, **i**);[10] the listed examples are arranged in the order of increasing diversity of the substituents. The abundance of species (**a**) is generally small except for derivatives having R^1 = H or Me and R^4 = H (see **Aa** and **Ad**). Also loss of hydrogen from C(5) is scarcely observed, compound (**Ah**) being an exception. A major finding concerns the unusual separation of $R^{1/4}$ = Ph, this process competes with the (expected) loss of a methyl radical (as shown by **Bg**).

2) DIHYDROTETRAZOLES OF TYPE (C)

a) Synthesis and Addition Reactions

Compounds of the type (**C**) belong to the category of heterocyclic methylene bases. Hence, the general approach implies deprotonation of their conjugate acids, *i.e.*, the tetrazolium salts (**11**) (Scheme 5). By this



i: NaH, THF ii: KH, 18-crown-6, THF or Et_2O iii: NaH, Et_2O iv: KH, THF v: BuLi, THF, –65 °C vi: FSO_2OMe vii: $HClO_4$

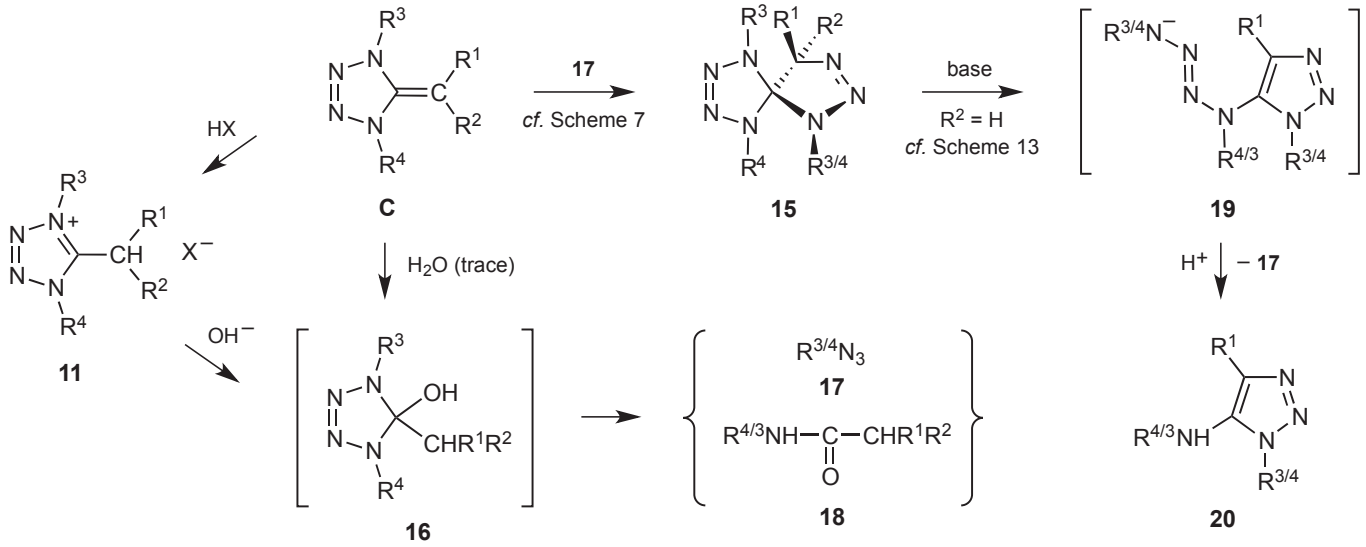
10– 14, **C**	R^1	R^2	R^3	R^4	**11**: yield (%)	X	method	**C**: yield (%)	bp (°C) [l] / Torr	ref. (**11** / **C**)
a	H	H	Me	Me	62 [a]	BF_4	i / ii	73 / 57 [g]	30–40 / 10^{-2}	17 / 17
b	Me	Me	Me	Me	88	CF_3SO_3 [d]	i	62–76	30–40 / 10^{-3}	16 / 16 [m]
c	*t*-Bu	H	Me	Me	76	CF_3SO_3 [d]	i	62–71	30–40 / 10^{-3}	16 / 16 [m]
d	CH=CH_2	H	Me	Me	51	PF_6 [e]	iii	[h,i]	20–30 / 10^{-5}	17 / 17
e	(*E*)CH=CHMe	H	Me	Me	48	PF_6 [e]	iii	[h,i]	20–30 / 10^{-5}	17 / 17
f	(*E*)CH=CHBu-*t*	H	Me	Me	57	PF_6 [e]	iii	[h,i]	20–30 / 10^{-5}	17 / 17
g	Ph	H	Me	Me	87	BPh_4 [e]	ii	85 [j]	100 / 10^{-2}	15 / 17
h	Ph	Me	Me	Me	50	CF_3SO_3 [d]	iii	73	30–40 / 10^{-5}	17 / 17
i	–$[CH_2]_2$–		Me	Me	97 [b]	PF_6 [e]	iv	[h]	0–20 / 10^{-5}	17 / 17
j	Me	Me	Me	CH_2Bu-*t*	77	BF_4 [f]	i	69	30–40 / 10^{-3}	15 / 16
k	Me	Me	Me	Ph	38 [c]	PF_6	iii	90 [k]	30–50 / 10^{-5}	15 / 17
l	Me	Me	Et	Et	85	CF_3SO_3 [d]	iii	59	40–50 / 10^{-3}	18 / 18

[a] From methylation of 1,5-dimethyltetrazole with dimethyl sulfate and treatment with HBF_4. [b] Based on **11i** (X = CF_3SO_3) obtained from **10i** (X = CF_3SO_3). [c] From methylation of 5-isopropyl-1-phenyltetrazole with dimethyl sulfate and treatment with NH_4PF_6. [d] From **10b,c,h,l** (X = CF_3SO_3). [e] From **11d-g,i** (X = CF_3SO_3) by treatment with NH_4PF_6 or $NaBPh_4$. [f] From **10j** (X = BF_4). [g] Each containing *ca.* 5% THF. [h] Not determined. [i] Low melting solid. [j] Mp 32–35 °C. [k] Crude product. [l] Bath temperature for distillation or sublimation. [m] Preparation of **Cb,c** by method (i) first mentioned in ref.[14] (no data).

Scheme 5

method a wide variety of examples of **C**, such as **Ca-l**, have been made.[14–18] These compounds are intensely yellow oils (in part low melting solids) that exhibit an extreme sensitivity towards oxygen and moisture; therefore, no microanalyses could be obtained. On addition of Brønsted acids they revert to the starting salts (**11**) (*cf.* Scheme 6); accordingly, treatment of **Cb** with D_2SO_4 gave the α-deuterated salt (**11b**).[16]

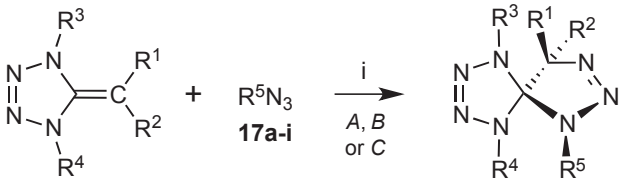
Most salts (**11**) – just as the precursors (**3**) of class (**A**) (Scheme 1) – were advantageously provided by [3+2] cycloaddition of organoazides to the nitrilium salts (**10**).[15–18] An alternative entry to **C**, which consists in sequential metallation of the tetrazole (**12**) and alkylation of the species (**13**), failed: Attempts with **12b,c** did not give the desired derivatives (**Cb,c**) or – after addition of perchloric acid – the quaternary salts (**11b,c**; X = ClO_4); instead, side chain methylation occurred to afford the protonated tetrazoles (**14b,c**).[16]



Scheme 6

During the synthesis of **C** certain byproducts arose, the most prominent being the spiro compound (**15**). Its formation is understood as proceeding *via* **16**. This intermediate results either from addition of water to **C** or from nucleophilic attack of hydroxide ion on **11** (both agents are present unless rigorous exclusion of moisture). As long known, species like **16** rapidly disintegrate into azide (**17**) and amide (**18**), whereupon the former adds on **C** which – as a ketene aminal – has an especially reactive double bond. When R^2 = H, further transformation may occur, *i.e.*, into the aminotriazole (**20**): This material is formed *via* base-assisted ring opening of the dihydrotetrazole region of **15** to generate the tetrazenide ion (**19**) which extrudes the azide (**17**) to be followed by protonation.[16] A conspicuous example for the occurrence of the entire process (**C** → **15** → **20**) is given by the parent (**Ca**; $R^1 = R^2 = H$, $R^3 = R^4 = Me$): Obviously due to traces of moisture, neat **Ca** is converted to **20a** (R^2 = H, $R^{3/4} = R^{4/3}$ = Me) at room temperature within 1–2 days.[17]

The unexpected formation of the spirocycles (**15**) during the preparation of **C** led to many direct syntheses (Scheme 7).[16,18–20] The process proved to have a wide scope (often giving excellent yields) and, owing to the highly electron-rich partner (**C**), proceeded with particular ease (LUMO/dipole–HOMO/dipolarophile controlled[16]) – not only with methyl azide (**17a**), but also with bulky congeners such as **17d,f**; aromatic azides reacted faster.



Ca-c,g-i,k,l **15[a],b-n,[o],p-w**

i: benzene, toluene, Et_2O or THF / pentane (1 : 1)

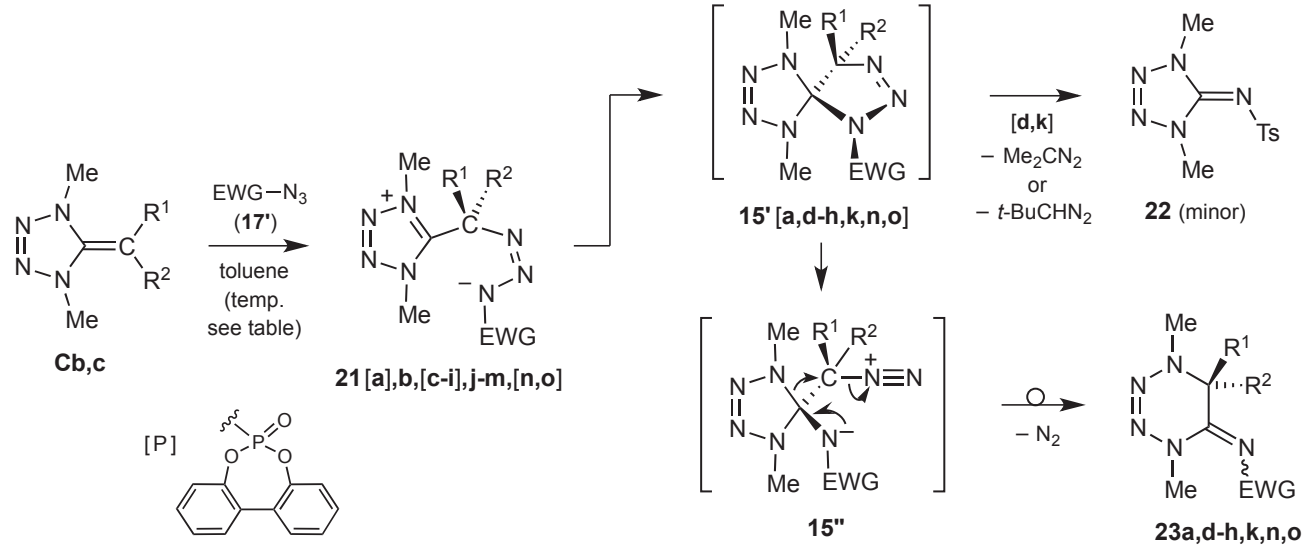
C	15	17	R^1	R^2	R^3	R^4	R^5	method [a]	temp. (°C)	period	yield (%)	ref.
a	**a**	**a**	H	H	Me	Me	Me	[b]	−40 ➛ 10	15 h	[c]	20
b	**b**		Me	Me	Me	Me	Me	*A*	0 ➛ 25	0.7 d	89	16
	c	**b**	Me	Me	Me	Me	CD_3	*A*	0	2 d	89	19
	d	**c**	Me	Me	Me	Me	CH_2Bu-*t*	*A*	20−25	0.7 d	90	18
	e	**d**	Me	Me	Me	Me	*t*-Bu	*A*	20−25	1.5 d	80	18
	f	**e**	Me	Me	Me	Me	Ph	*A*	0−5	0.2 h	86	18
	g	**f**	Me	Me	Me	Me	2,6-$Me_2C_6H_3$	*A*	−30 ➛ 0	1 h	78	18
	h	**g**	Me	Me	Me	Me	4-$NO_2C_6H_4$	*A*	0−5	1 h	89	18
	i	**h**	Me	Me	Me	Me	2-$NO_2C_6H_4$	*A*	0 ➛ 20	2 h	90	18
	j	**i**	Me	Me	Me	Me	2,6-Me_2-4-$NO_2C_6H_4$	[d]	[d]	[d]	[e]	18
c	**k**		*t*-Bu	H	Me	Me	Me	*A*	0−5	1 d	54 [f]	16
	l		*t*-Bu	H	Me	Me	CH_2Bu-*t*	*A*	20−25	1.6 d	78	18
	m		*t*-Bu	H	Me	Me	Ph	*A*	0−5	0.2 h	65	18
	n		*t*-Bu	H	Me	Me	4-$NO_2C_6H_4$	*A*	0−5	1 h	71	18
g	**o**		Ph	H	Me	Me	Me	[b]	0−5	3 d	[g]	20
h	**p**		Ph	Me	Me	Me	Me	*B* (3 h)	5	5 d	60	18
	q		Ph	Me	Me	Me	Ph	*B* (3 h)	20−25	15 h	82	18
i	**r**		−[CH_2]$_2$−		Me	Me	Me	*C*	−70 ➛ 5	0.5 d	30	18
k	**s**		Me	Me	Me	Ph	Me	*B* (18 h)	5	4 d	63	18
	t		Me	Me	Me	Ph	Ph	*C*	5	[b]	80	18
l	**u**		Me	Me	Et	Et	Ph	*A*	0	1 h	67	18
	v		Me	Me	Et	Et	4-$NO_2C_6H_4$	*C*	20	3 h	62	18
	w		Me	Me	Et	Et	2-$NO_2C_6H_4$	*C*	20	3 h	44	18

[a] *A*: From isolated substrate (**C**); *B*: from solution of **C** made after Scheme 6 (time indicates duration of deprotonation step); *C*: as with method (*B*), but deprotonation carried out in the presence of **17a,e,g**, and **h**, respectively. [b] Unspecified (probably *B*; THF). [c] Not isolated (underwent ring opening to give **20a**; *cf.* Scheme 14). [d] Unreported. [e] Decomposed above *ca.* −30 °C. [f] Besides 34% **20b** (*cf.* Scheme 14); a further experiment gave **15k** quantitatively. [g] Not isolated (underwent ring opening to give **20e**; *cf.* Scheme 14).

Scheme 7

Strongly electrophilic azides (**17'**), however, gave divergent products (Scheme 8): Instead of the anticipated cycloadducts (**15'**) the betaines (**21**) or the tetrazinimines (**23**) were found [the latter partly accompanied by some tetrazolimine (**22**)].[18,21,22] The species (**21**) were established – also by MNDO-PM3 calculations [23] – as intermediates of the cycloaddition (**C** + **17'** → **15'**); their structure was confirmed by X-ray diffraction of isolable **21l**.[21] Due to steric hindrance derivatives obtained from the *t*-butyl substituted substrate (**Cc**) are more stable, as evidenced by a comparison of the reactions (**21k** → **23k**) and (**21d** → **23d**): The former required heat and proceeded more slowly. While the conversion (**15'** → **22**) matches common diazoalkane

chemistry, the ring expansion (**15'** → **23**) appears remarkable: After opening of the dihydrotriazole ring the resultant species (**15''**) extrudes molecular nitrogen to be followed by a nitrogen 1,2-shift (a rare process) and cyclization. The configurations of (*Z*)-**23a**, (*Z*)-**23e**, (*E*)-**23f**, and (*E*)-**23o** (*cf.* Scheme 8) were elucidated by X-ray diffraction.[22]



C	15', 17' 21, 23	R^1	R^2	EWG	temp. (°C) 21	temp. (°C) 23	yield (%) 21	yield (%) 23	ref. 21	ref. 23
b	**a**	Me	Me	2,4-$(NO_2)_2C_6H_3$	−30	0 ➛ 20	[a]	29 [c]	18	22
	b	Me	Me	2,4,6-$(NO_2)_3C_6H_2$	0 ➛ 20		90		21	
	c	Me	Me	2-NO_2-4,6-$Me_2C_6H_2$	−75		[a]		18	
	d	Me	Me	4-$MeC_6H_4SO_2$	−30 / −20	0 ➛ 20	[a]	73 [e]	18 / 21	21, 22
	e	Me	Me	$MeSO_2$		0 ➛ 20	[b]	86 [c]		21, 22
	f	Me	Me	Me_2NSO_2		0 ➛ 20	[d]	71 [f]		22
	g	Me	Me	$(PhO)_2PO$		0 ➛ 20	[d]	92		22
	h	Me	Me	[P]		0 ➛ 20	[d]	86		22
c	**i**	*t*-Bu	H	2-$NO_2C_6H_4$	− 30		[a]		18	
	j	*t*-Bu	H	2,4,6-$(NO_2)_3C_6H_2$	0 ➛ 20		37		18, 21	
	k	*t*-Bu	H	4-$MeC_6H_4SO_2$	0 ➛ 20	80	quant.	68 [e]	18, 21	21, 22
	l	*t*-Bu	H	$MeSO_2$	− 20		77 / 52		18 / 21	
	m	*t*-Bu	H	Me_2NSO_2	20		86		21	
	n	*t*-Bu	H	$(PhO)_2PO$		0 ➛ 20	[d]	86		22
	o	*t*-Bu	H	[P]		0 ➛ 20	[d]	83 [f]		22

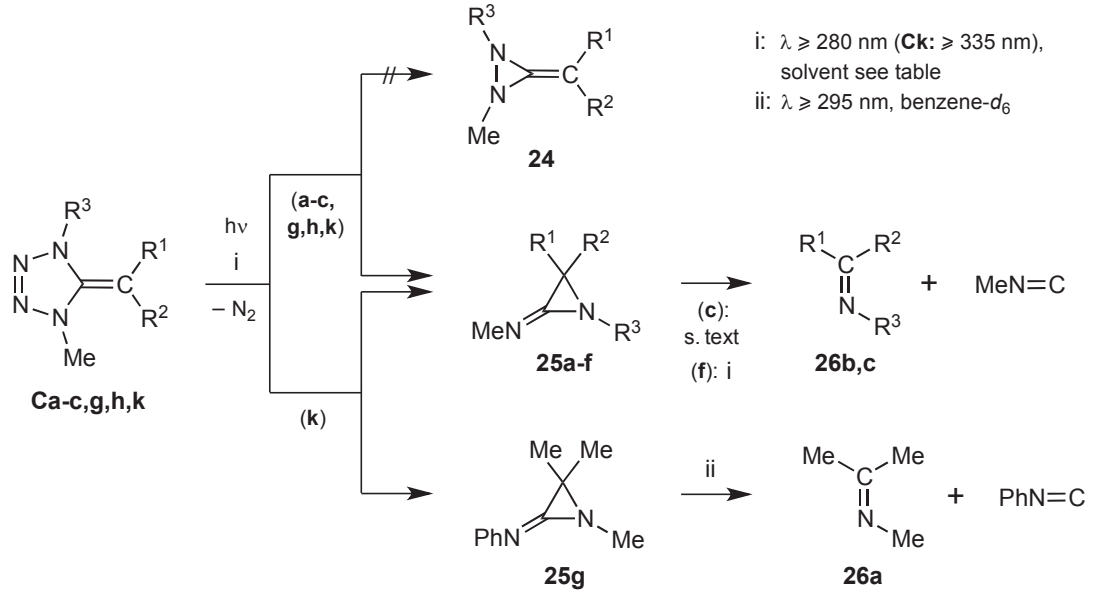
[a] Short-lived intermediate generated at low temp.; recorded at temp. indicated. [b] Intermediate not mentioned in refs.[21,22] [c] *Z* isomer. [d] Intermediate not mentioned in ref.[22] [e] Besides some **22**.[21] [f] *E* isomer.

Scheme 8

b) Photolysis and Thermolysis

Upon irradiation representatives (**C**) undergo ring contraction, but – divergent from the classes (**A**) and (**B**) and the oxo and imino analogues of **C** – no diaziridines arise (Scheme 9).[14,24,25] Thus, instead of giving **24**, substrates like **Ca-c,g,h** led to the aziridinimines (**25a-e**), while from **Ck**, which has different substituents at N(1/4), two products (**25f,g**) were formed (even with light of longer wavelengths and especially fast). The

reaction proceeds diastereoselectively, affording *E* isomers which slowly equilibrate with the *Z* isomers. To rationalize the stereoselectivity, singlet diazatrimethylenemethane diradicals (expectedly configurationally stable) were assumed as intermediates.[24,26] While sustaining the photolytic conditions of its formation from **C**c, the aziridinimine (**25c**) slowly decomposed to the imine (**26b**) and methyl isocyanide when using light of shorter wavelengths.[24] The same applies to the derivatives (**25f,g**) which fragmented to **26c** and **26a** and the respective isocyanides.[25] – For a detailed *ab initio* study of the aziridinimine ring opening, see ref.[27]



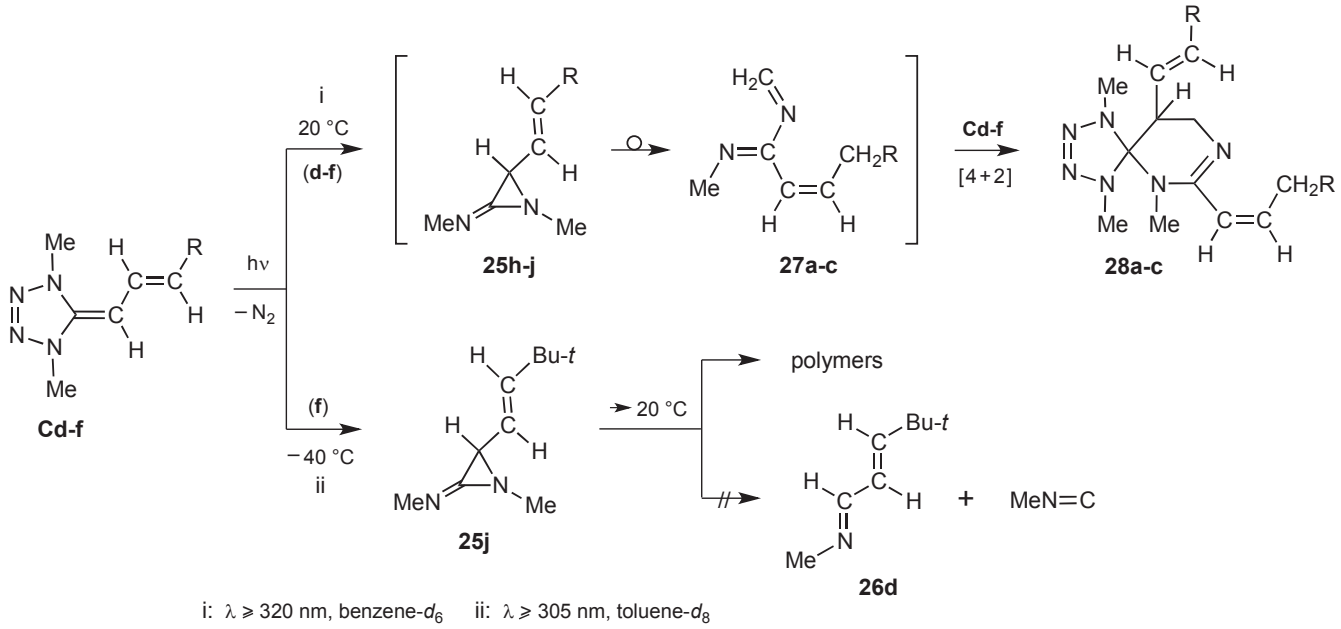
C	25	26	R^1	R^2	R^3	solvent	temp. (°C)	period (h)	conversion (%)	(*E*)-**25** : (*Z*)-**25**	ref.
a	**a**		H	H	Me	cyclohexane-d_{12}	20	1.5	50	> 99 : < 1	25
b	**b**	**a**	Me	Me	Me	benzene-d_6	20	11	quant.	71 : 29	24
						THF-d_8	– 60	60	quant.	90 : 10	14, 24, 25
c	**c**	**b**	*t*-Bu	H	Me	benzene-d_6	20	40	quant.	75 : 25	24
						THF-d_8	– 60	60	quant.	95 : 5	14, 24
g	**d**		Ph	H	Me	benzene-d_6	20	4	70	83 : 17	25
						THF-d_8	– 40	2.5	89	97 : 3	25
h	**e**		Ph	Me	Me	benzene-d_6	20	5	quant.	68 : 32	25
						THF-d_8	– 40	2.5	90	95 : 5	25
k	**f**	**c**	Me	Me	Ph	cyclohexane-d_{12}	20	0.5	quant.	87 : 13 [a]	25
	g									81 : 19 [a]	25

[a] {(*E*)-**25f** + (*Z*)-**25f**} : {(*E*)-**25g** + (*Z*)-**25g**} = 1 : 1.

Scheme 9

A most interesting behaviour was encountered with substrates (**C**) having 5-alkenylidene groups like **Cd-f** (Scheme 10).[25] Irradiation with λ ≥ 320 nm at 20 °C generated the anticipated aziridinimines (**25h-j**), but the latter rearranged to the species (**27a-c**) which, as 1,3-diazabutadienes, cycloadded to unconsumed **Cd-f** to eventually afford the spirocycles (**28a-c**). However, working with shorter wavelengths and at –40 °C, an

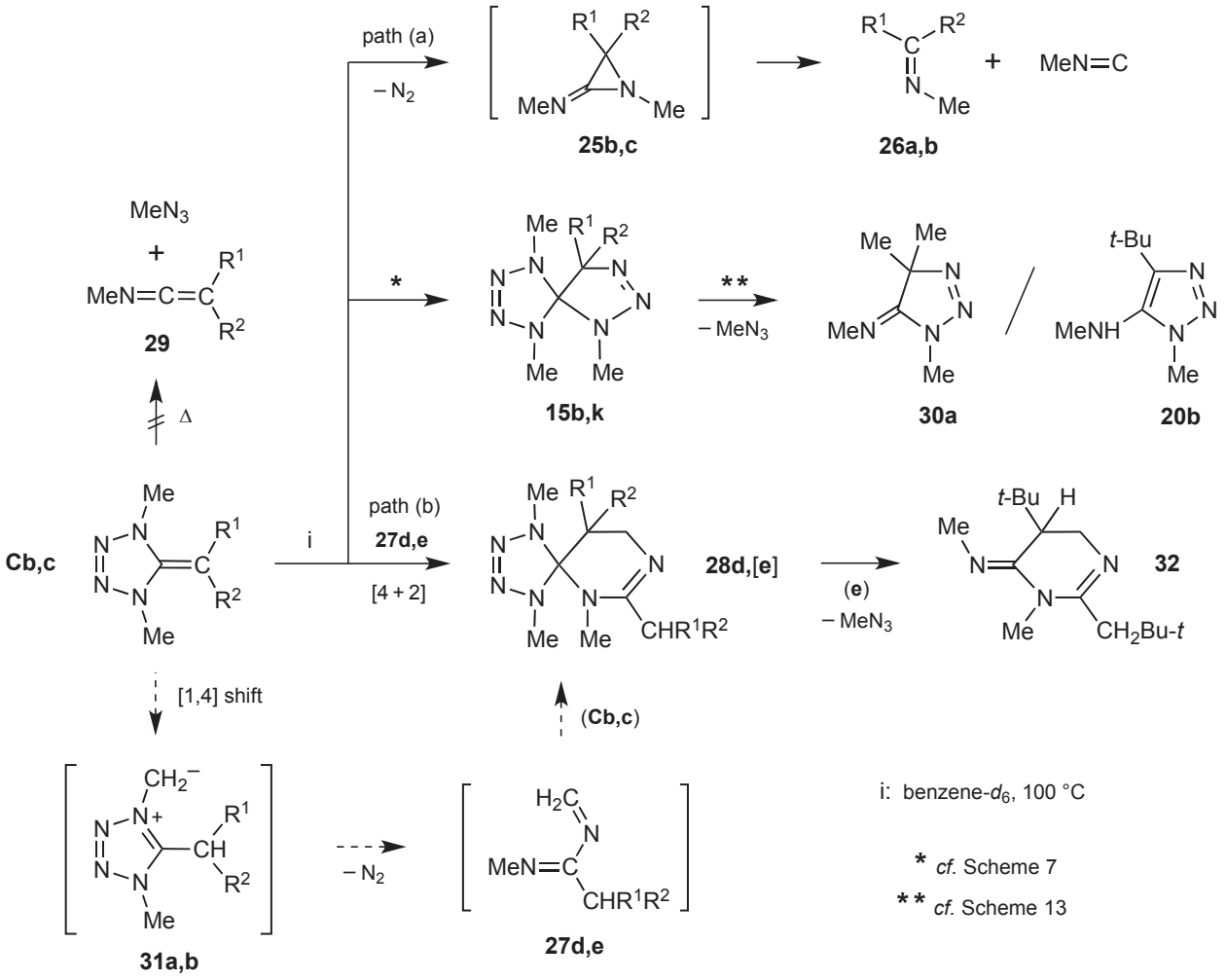
aziridinime such as **25j** could be obtained indeed, but on raising the temperature the material polymerized instead of giving the imine (**26d**) and methyl isocyanide.



C	25	27, 28	R	method	period (h)	conversion (%)	(*E*)-**25j** : (*Z*)-**25j**	ref.
d	**h**	**a**	H	i	5	quant.		25
e	**i**	**b**	Me	i	5	quant.		25
f	**j**	**c**	*t*-Bu	i	6	quant.		25
	j			ii	3	95	> 99 : < 1	25

Scheme 10

Thermolysis: Contrasting with the classes (**A**) and (**B**), which undergo [3 + 2] cycloreversion to azides and imines [*cf.* Section (1.b)], the derivatives (**C**) do not react accordingly, *i.e.*, azides and ketenimines, such as **29**, are not formed (Scheme 11).[27] A careful ^{1}H NMR study of the behaviour of **Cb** showed that elimination of molecular nitrogen predominates [path (a)]; the resultant aziridinimine (**25b**), although observable for a certain period of time, eventually decomposed to the imine (**26a**) and methyl isocyanide (*cf.* Scheme 9). Beside these components the spirocycle (**28d**) was found – a ring type known from the photolysis dealt with in Scheme 10. About the origin of the crucial building block, *i.e.*, the 1,3-diazadiene species (**27d**), there were speculations: Out of the possible sources, the *N*-ylide (**31**) and the diazatrimethylenemethane diradical were proposed;[28] but, formally, rearrangement of **25b** could afford **27d**, too. Finally, small quantities of the spirocycle (**15b**) were present, giving rise to the triazole (**30a**); the extruded methyl azide regenerated **15b**. The second substrate (**Cc**) behaved differently in that the main reaction followed path (b); compound (**28e**), however, was unstable and converted to **32**. As this cleavage produced further azide, the amount of the spirocycle (**15k**) [including its decomposition product (**20b**)] increased appreciably.



C, 25	15	26, 31	27, 28	R^1	R^2	substrate	approx. proportions (%) of products after 66 h (**Cb**) and 27 h (**Cc**)	ref.
b	**b**	**a**	**d**	Me	Me	**Cb**	**15b** (3), **30a** (≤4), **26a** (78), **28d** (7)	28
c	**k**	**b**	**e**	*t*-Bu	H	**Cc**	**15k** (30), **20b** (8), **26b** (16), **32** (30) [a]	28

[a] Preparative run: yield 42%.

Scheme 11

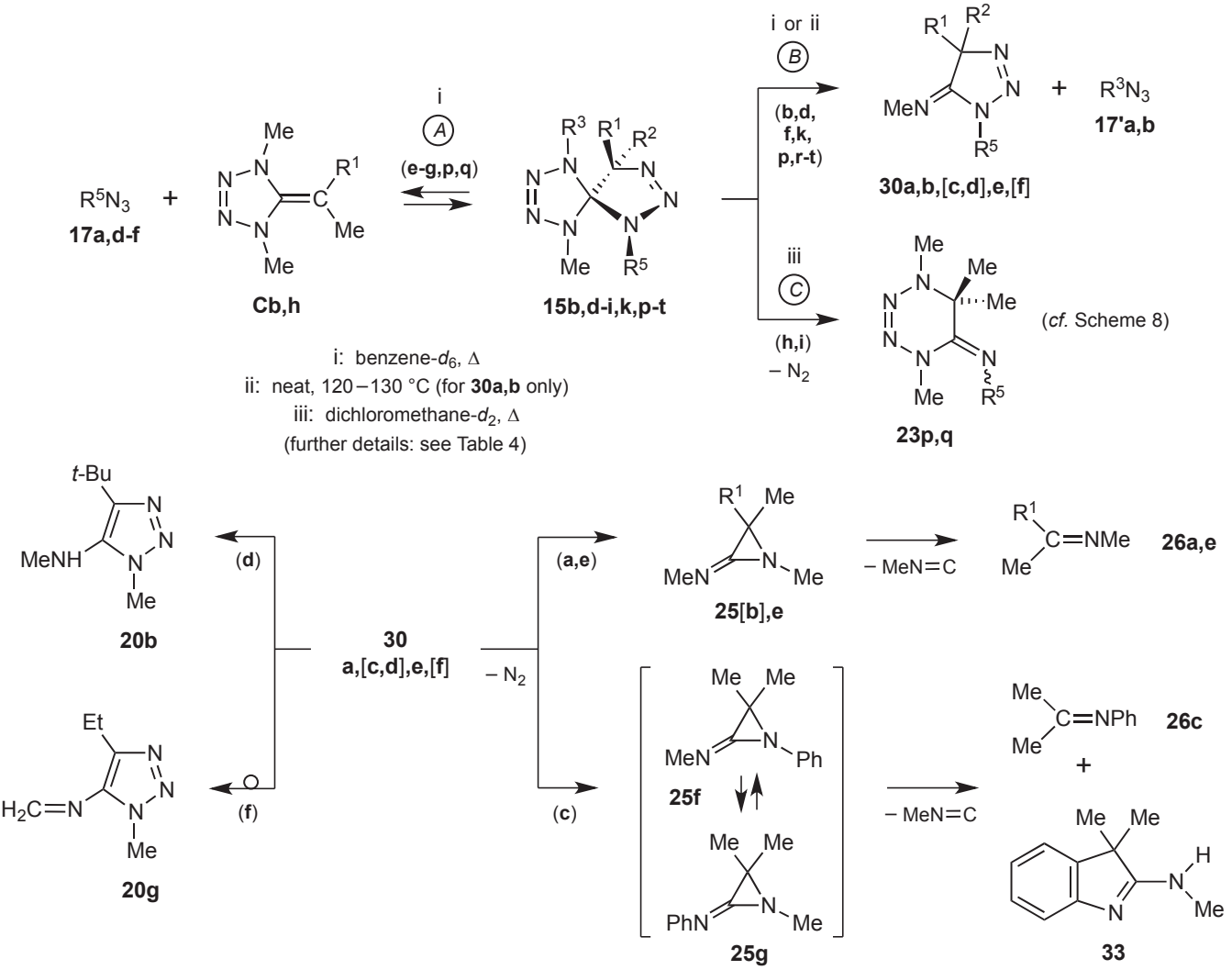
c) Reactions of the Spirocycles (15)

The paramount rôle of **15** in the field of synthesis and transformations of class (**C**) prompted the authors to undertake separate studies on these compounds, concerning: (i) thermolysis,[29] (ii) reactions with bases,[20] and (iii) behaviour towards Brønsted acids.[31]

(i) Three reaction modes (*A*), (*B*), and (*C*) were found typical (Scheme 12). A fourth mode, *i.e.*, extrusion of an diazoalkane from the triazole half-ring is of minor moment (*cf.* Scheme 8). Substrates were chosen such as to show the influence of substituents (*cf.* Table 4).

Reaction (*A*), which implies extrusion of an azide from the dihydrotriazole ring, constitutes the reversion of the synthesis from **C**. The process, whose extent increases on raising the temperature, proceeded more

easily with **15g** (which has for R^5 the bulky *o*-xylyl ligand) than with **15q** (which has a phenyl substituent); substrates (**15**) with aliphatic ligands are on the whole more stable. In reaction (*B*) an azide is expelled from



C	15	17	17'	23	25	26	30	R^1	R^2	R^3	R^5
b	**b**	**a**	**a**		**b**	**a**	**a**	Me	Me	Me	Me
	d						**b**	Me	Me	Me	CH_2Bu-*t*
	e	**d**						Me	Me	Me	*t*-Bu
	f	**e**					**c**	Me	Me	Me	Ph
	g	**f**						Me	Me	Me	2,6-$Me_2C_6H_3$
	h			**p**				Me	Me	Me	4-$NO_2C_6H_4$
	i			**q**				Me	Me	Me	2-$NO_2C_6H_4$
	k						**d**	*t*-Bu	H	Me	Me
h	**p**				**e**	**e**	**e**	Ph	Me	Me	Me
	q							Ph	Me	Me	Ph
	r						**f**	– $[CH_2]_2$–		Me	Me
	s		**b**					Me	Me	Ph	Me
	t							Me	Me	Ph	Ph

Scheme 12 (for proportions of products, see Table 4)

Table 4. Proportions of products from processes (*A*), (*B*), and (*C*) of Scheme 12 [a][29]

(*A*)			(*B*) (top) (*C*) (bottom)					(*A*) and (*B*)				
start	*a*	**C** : **15**	start	*a*	*b*	*c*	products	start	*a*	*b*	*c*	products
15e	70	25 : 75	**15b**	130	7	87	**17a**, **30a**	**15f**	140	1	70	**15b** : **30a** : **26a** : **26c** = 19 : 22 : 36 : 23
15g	22	14 : 86	**15k**	130	5	97	**20b**	**15p**	130	10	60	{**Ch** + **17a**} : {**17a** + **30e**} : **25e** : [b] = 2 : 68 : 6 : 24
15g	27	19 : 81	**15r**	150	4	56	**17a**, **20g**					
15g	32	25 : 75	**15s**	80	1	93	**17e**, **30a**					
15g	37	32 : 68	**15t**	100	6	> 98	[a]					
15g	42	40 : 60										
15q	25	2 : 98	**15b**	80	20	100	**23p**					
15q	120	30 : 70	**15b**	60	8	100	**23q**					

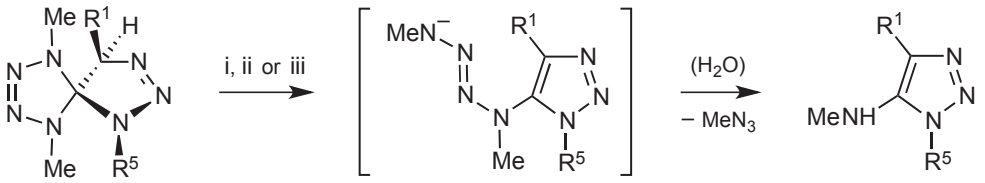
a: temperature (°C)
b: period (h)
c: conversion (%)

[a] Determined by ^{1}H NMR spectroscopy. [b] {**26c** + methyl isocyanide} : **33** = 53 : 47. [c] {**26e** + methyl isocyanide}.

the tetrazole half-ring to afford dihydrotriazolimines (**30**) which may stabilize to **20** or, under the conditions of thermolysis, partly release molecular nitrogen to give (*E*)- and (*Z*)-aziridinimines (**25**) and/or products derived therefrom. In the case of thermally stable derivatives (**30**), reaction (*B*) is of preparative value, since representatives like **30a,b** could be isolated in high yield.[19] Reaction (*C*), which affords tetrazinimines (**23**), was encountered with **15** that has for R^5 electron-withrawing substituents (*cf.* Scheme 8). Finally, the concomitant occurrence of two modes, *viz.* (*A*) and (*B*), was observed when the dihydrotriazole ring has a phenyl ligand either for R^1 or for R^5. However, the overall picture is complex and can be treated here only selectively; for a detailed discussion, see ref.[29]

(ii) As realized during the synthesis of compounds (**C**) from tetrazolium salts (**11**), aminotriazoles (**20**) can occur as side products (or may be formed on storage of neat **C** [17]); they arise from **15** that have hydrogen for R^2 (*cf.* Scheme 6).[16] Indeed, treatment of substrates like **15m,n** with sodium hydride gave the derivatives (**20c,d**) very readily and, remarkably, in quantitative yield (Scheme 13).[20] In the case of **15a,o**, the products (**20a,e**) arose even before said substrates could be isolated from the reaction mixtures of **Ca,g** and methyl azide (**17a**) (*cf.* Scheme 7). Mechanistically, the base-mediated conversion (**15** → **19** → **20**) has a formal parallel in the behaviour of the bicycle (**33**): On treatment with butyllithium, this compound suffers opening of the dihydrotetrazole half-ring (→ **34**) to eventually give the imidazole (**35**).[30]

(iii) When compounds (**15**) are exposed to Brønsted acids, it is the dihydrotriazole ring that opens, in contrast to the region affected by bases. Thus, from **15b,e,f,k** high yields of the triazenes (**36a-d**) were obtained (Scheme 14). These materials were shown to exist as the tautomers depicted, although proton attack, which takes place at N(3) of the dihydrotriazole unit, would imply an –NH–N=NR^5 structure. Such arrangement, however, occurred in the methylation product (**37**) representing a 'fixed' tautomer. In alkaline solution both triazenes (**36**) and (**37**) reverted to the starting compounds (**15**).[31]

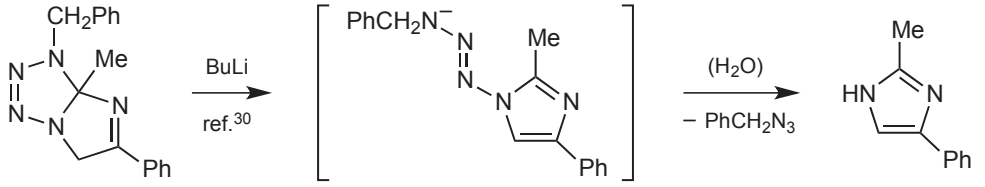


15[**a**],**k**,**m**,**n**,[**o**] **19** **20a-e**

i: THF, –40 ➔10 °C ii: NaH, Et_2O, rt iii: Et_2O, 0 –5 °C

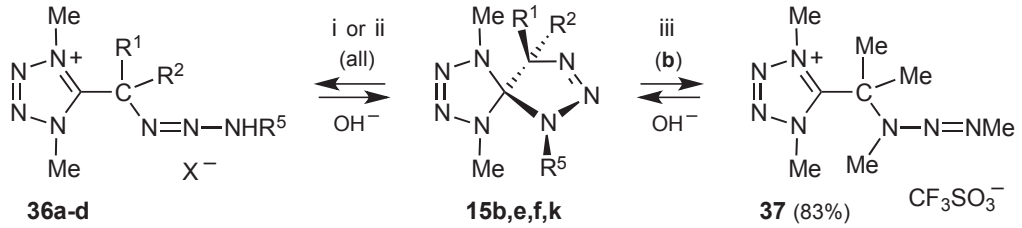
15	**20**	R^1	R^5	conditions	yield (%)	ref.
a	**a**	H	Me	i [a]	88	20
k	**b**	*t*-Bu	Me		[b]	16
m	**c**	*t*-Bu	Ph	ii	quant.	20
n	**d**	*t*-Bu	4-$NO_2C_6H_4$	ii	quant.	20
o	**e**	Ph	Me	iii [a]	89	20

[a] Substrates (**15a**) and (**15o**) reacted *in situ* (*cf.* Scheme 7); no extra base, traces of base obviously present from process (**11a** ➔ **Ca**) and (**11g** ➔ **Cg**), respectively (see Scheme 5). [b] Observed as side product (34%) during the synthesis of **15k** from **Cc** (*cf.* Scheme 7).



33 **34** **35**

Scheme 13



36a-d **15b,e,f,k** **37** (83%)

i: HBF_4, Et_2O, – 10 °C, then – 20 ➔ – 40 °C ii: AcOH, NH_4PF_6, aq. EtOH, 0 °C
iii: CF_3SO_3Me, $CDCl_3$, then Et_2O, – 20 °C

15	**36**	R^1	R^2	R^5	X	yield (%)
b	**a**	Me	Me	Me	BF_4 / PF_6	91 / 70
e	**b** [a]	Me	Me	*t*-Bu	PF_6	76
f	**c**	Me	Me	Ph	BF_4	95
k	**d**	*t*-Bu	H	Me	BF_4 / PF_6	quant. / 91

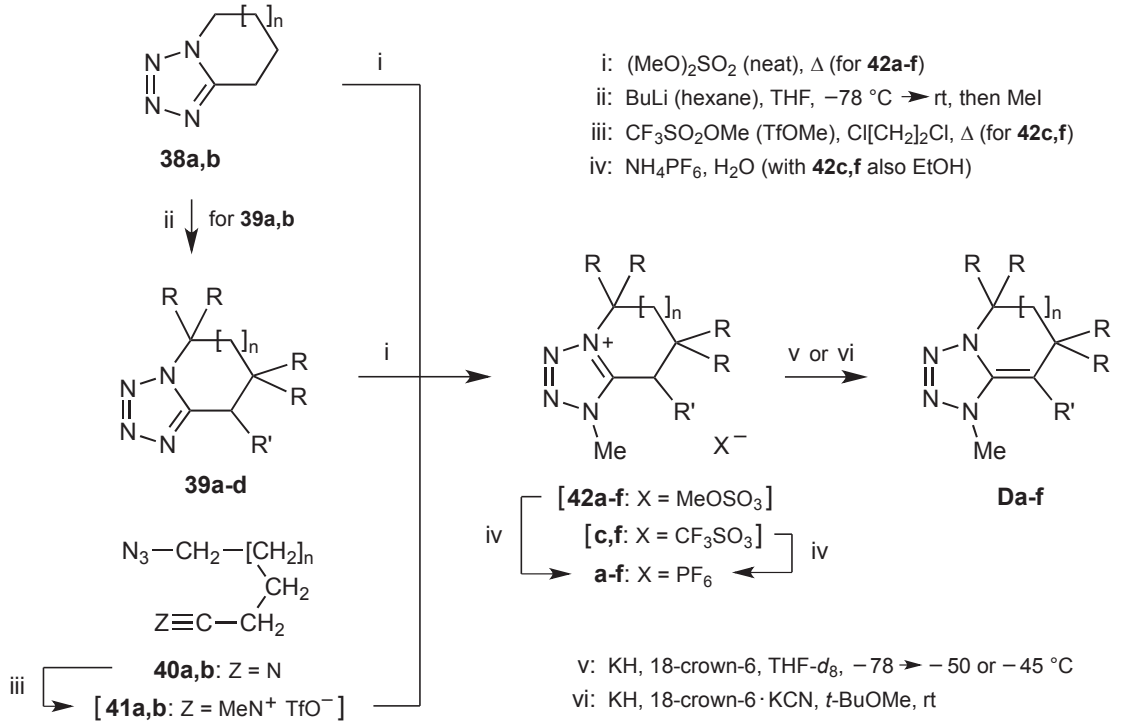
[a] Equilibrates with the —NH—N=NBu-*t* tautomer.

Scheme 14

3) DIHYDROTETRAZOLES OF TYPES (D) AND (D')

a) Synthesis

Access to these classes was effected by following the concept applied to class (**C**) (*cf.* Scheme 5), *i.e.*, by deprotonation of the tetrazolium salts (**42**) (Scheme 15) and (**44** / **46**) (Scheme 16), respectively.[32,33] The substrates (**42**) resulted from quaternization of the bicycles (**38**) and (**39**) or from intramolecular [3 + 2] cycloaddition of the nitrilium salts (**41**); the latter reacted *in situ* upon methylation of the nitriles (**40**). The precursors (**39a,b**) – required for **42b,d** – had to be provided through α-methylation of **38a,b**, since they are

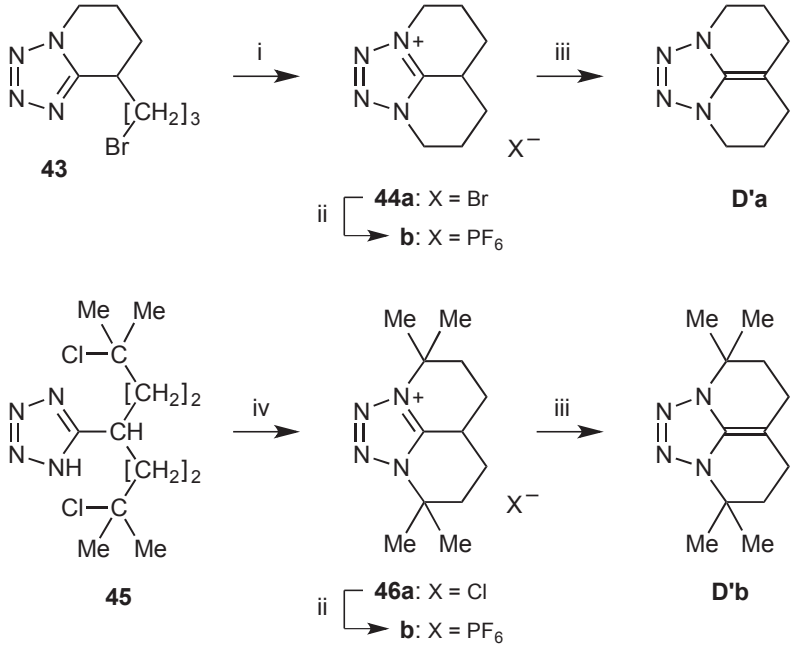


38	39	40, 41	n	R	R'	42	from	yield (%) [a]	ref.	D [b]	method	ref.
a			0	H	H	**a**	**38a**	60	32	**a**	v	33
	a		0	H	Me	**b**	**39a**	56	32	**b**	v	33
b		**a**	1	H	H	**c**	**38b** / **40a**	61 / 61	32	**c**	vi	33
	b		1	H	Me	**d**	**39b**	61	32	**d**	vi	33
	c		1	Me	H	**e**	**39c**	51	32	**e**	vi	33
	d	**b**	2	H	H	**f**	**39d** / **40b**	55 / 22	32	**f**	vi	33

[a] X = PF_6. [b] **Da,b** not isolable (directly studied by ^{1}H NMR); **Dc-f**: viscous oils, distilled at 20 − 40 °C (bath) / 10^{-5} Torr.

Scheme 15

inaccessible *via* Schmidt reaction of the respective α-methylcycloalkanones. Save the derivatives (**Da,b**) that have a dihydropyrrole half-ring, the products (**D**) are isolable materials.



i: MeCN, Δ ii: NH_4PF_6, EtOH / H_2O, rt iii: KH, 18-crown-6, *t*-BuOMe, 0 °C or rt (**46b**)
iv: $CHCl_3$, Δ (sealed tube)

	yield (%)	ref.		yield (%)	ref.
44a	78	32	**46a**	80	32
44b	77	32	**46b**	62	32
D'a	[a]	33	**D'b**	[a]	33

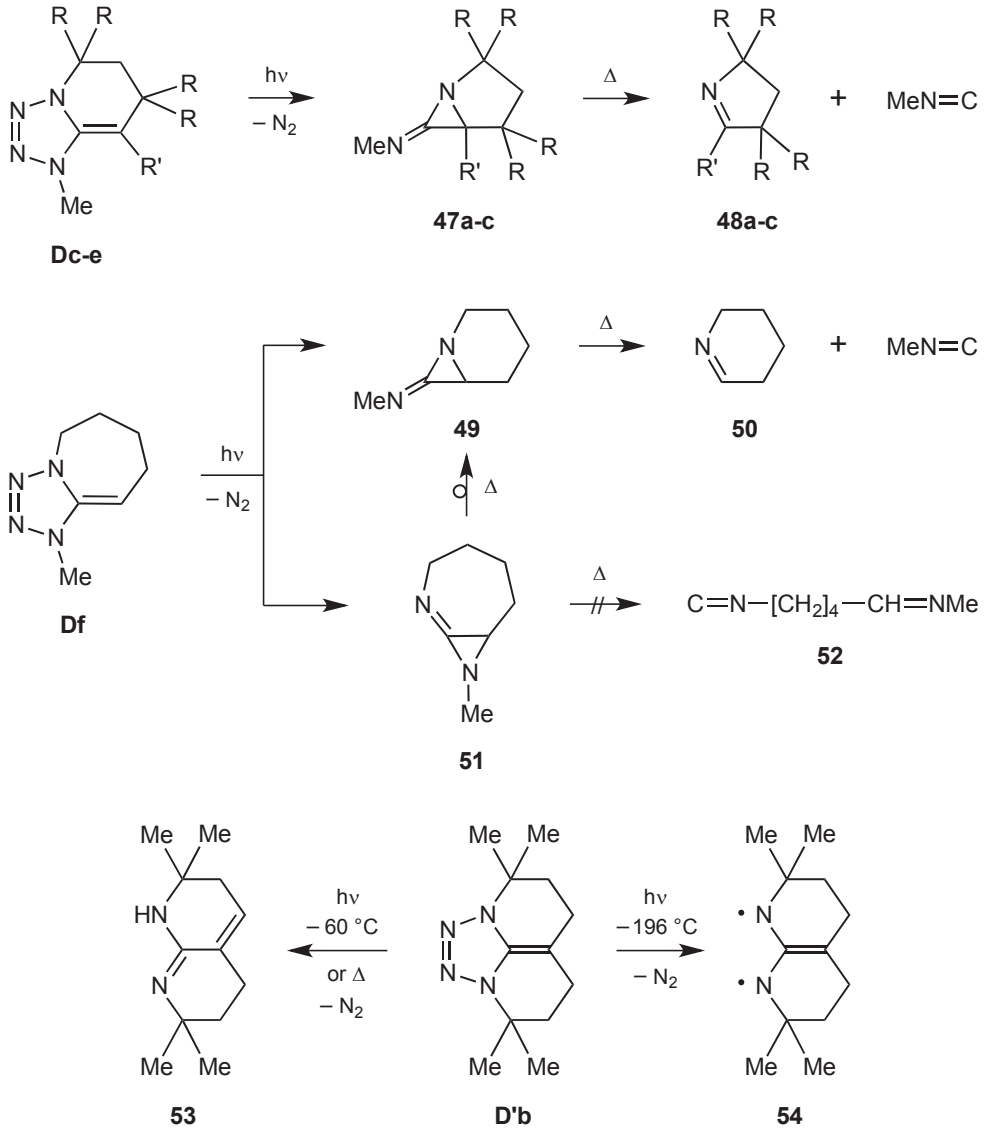
[a] **D'a**: see **Dc-f** (Scheme 16); **D'b**: solid (mp *ca.* 30 °C), sublimed at 30−40 °C (bath) / 10^{-5} Torr.

Scheme 16

Regarding the bisanellated precursors of **D'**, the salt (**44a**) was obtained very readily through heating of the tetrazole (**43**). However, in the case of double cyclization (**45** → **46a**), the quaternization step required that the experiment was carried out in a sealed system; otherwise hydrogen chloride was eliminated to form an unsaturated side chain. Attempts to prepare a congener of **44a** that has a dihydropyrrole ring adjacent to the six-membered cycle failed because of ring strain.[32]

b) Photolysis

In line with the behaviour of class (**C**) towards UV light (*cf.* Schemes 9, 10), anellated congeners like **Dc-f** extrude molecular nitrogen to form the aziridinimines (**47a-c**) and (**49**), respectively (Scheme 17). The process has been investigated under varied conditions, showing in most cases the expected dependence on temperature and wavelength. The substrate (**Df**) gave as second product the azirinoazepine derivative (**51**); but this type of isomer, *i.e.*, the bicyclo[4.1.0]system having a cyclic double bond, could not be detected on



	products [a]	R	R'	λ (nm)	solvent	temp. (°C)	period (h)	(*E*)-**47** / -**49** : (*Z*)-**47** / -**49** [d]
Dc	**47a** [b]	H	H	⩾ 320	toluene-d_8	– 60	3.5	> 99 : < 1 (46 : 54; 32 d)
				⩾ 305	benzene-d_6	20	0.75	66 : 34 (52 : 48; 37 d) [e]
Dd	**47b**	H	Me	⩾ 320	toluene-d_8	– 60	4	57 : 43 (36 : 64; 7 d) [f]
De	**47c**	Me	H	⩾ 320	toluene-d_8	– 60	3	41 : 59 (76 : 24; 7 d)
				⩾ 320	THF-d_8	20	0.67	38 : 62 (77 : 23; 7 d)
				⩾ 320	benzene-d_6	20	0.33	39 : 61 (78 : 22; 10 d)
Df	**49**, **51** [c]			⩾ 320	benzene-d_6	– 60	3.5	98 : 2
				⩾ 305	benzene-d_6	20	3	85 : 15 (66 : 34; 14 d)
D'b	**53**			⩾ 320	toluene-d_8	– 60	1.25	

[a] Conversions and yields > 95%. [b] Yield only 30 and 50%, respectively. [c] Ratio **49** : **51** = 47 : 53 and 49 : 51, respectively. [d] In parentheses: Equilibrium after specified time at 20 °C. [e] 48 : 52 after 1 h at 60 °C. [f] 38 : 62 after 1 h at 80 °C.

Scheme 17

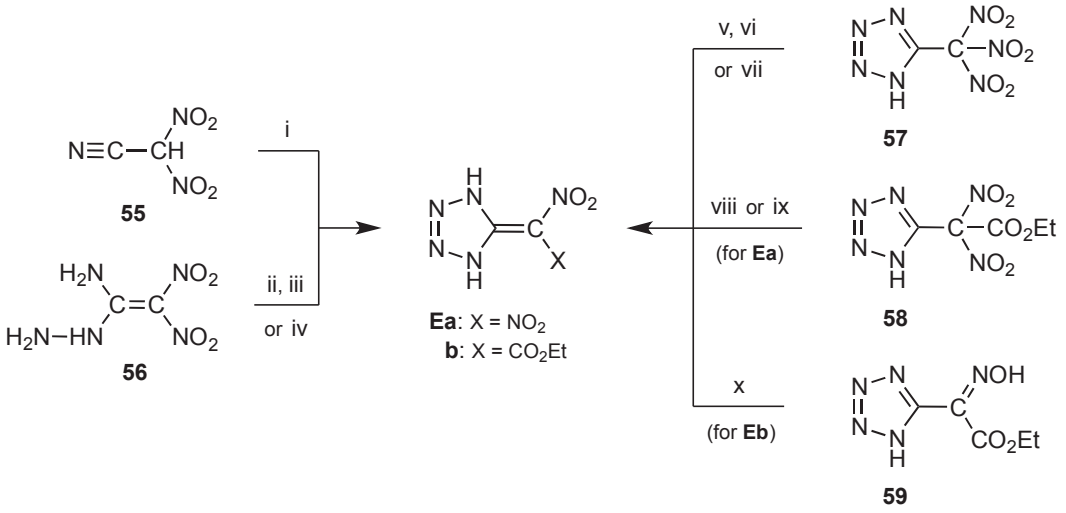
irradiation of **Dc-e**, even at –60 °C. Thermolysis of **47a-c** and **49** caused [2 + 1] cycloreversion to methyl isocyanide and the imines **48a-c** and **50**, respectively, whereas heating of **51** led to **49** rather than to **52**.[33]

Regarding the behaviour of compounds (**D'**), irradiation of **D'a** gave unidentified products, whereas its homologue (**D'b**) afforded either the 1,8-naphthyridine derivative (**53**) (obtained also on thermolysis) or, at lower temperature in a matrix, the diradical (**54**) – the first observed triplet diazatrimethylenemethane.[33]

4) DIHYDROTETRAZOLES OF TYPES (E) AND (F)

a) Synthesis

Representatives of class (**E**) comprise derivatives having as electron-withdrawing groups: (α) nitro (**Ea**), (β) nitro + ester (**Eb**), and (γ) cyano + ester (**Ec**) (Schemes 18, 19). As energetic material of importance, compound (**Ea**) [including the two series of salts (**E^{s}a**) and (**E$^{s'}$a**) listed in Chart 2)] is receiving continuous interest.[34] Therefore, a wide variety of preparations have been reported, following the two major principles:



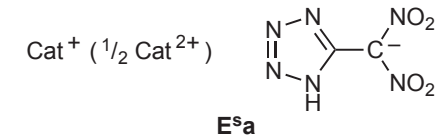
i: (starting from sodium salt): NaN_3 / NH_4Cl, H_2O, Δ, then conc. HCl ii: $NaNO_2$, AcOH, H_2O, rt
iii: (starting from hydrazinium salt): $NaNO_2$, AcOH, H_2O, rt, then conc. H_2SO_4 iv: KNO_2, AcOH, H_2O, rt, then conc. HCl ➛ pH 1
v: (starting from ammonium salt): KOH, $[NH_3OH]Cl$, aq. EtOH, 0−5 °C to give dipotassium salt of **Ea**, then H_2SO_4
vi: aq. NH_2OH or N_2H_4, H_2O, rt to give hydroxylammonium or dihydrazinium salt of **Ea**, then H_2SO_4 vii: 10 M KOH, rt
viii: H_2O, Δ ix: NaOH, H_2O, 0 °C, then conc. HCl x: HNO_3 (60%) / conc. H_2SO_4, rt

	method	yield (%)	mp (°C)	ref.	method	yield (%)	mp (°C)	ref.
Ea	i	9 [a]		35	vi	86 [f]	103.1 [h]	40
	ii	91 [b]	155 [b, c]	36	vii	77 [g]	291 [d]	41
	iii	87	104 –106 [d]	37	viii	82	122 –123 [d]	42
	iv	57		38a	ix	96		34
	v	86 [e]	110 –112 [d]	39a				
Eb	x	45	88– 89	39a				

[a] Besides 21% 5,5'-bitetrazole (Bitet); starting from ammonium salt gave lower yield of both **Ea** and Bitet.
[b] Sodium salt of **Ea**. [c] Violent explosion. [d] Decomp. [e] Based on dipotassium salt of **Ea** (yield 74%).
[f] Based on hydroxylammonium or dihydrazinium salt of **Ea** (yield 92% each). [g] Dipotassium salt of **Ea**.
[h] Dihydrate; DTA (5 °C / min), explosion.

Scheme 18

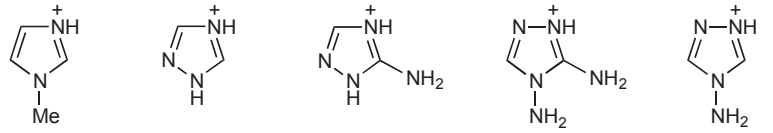
(i) Cyclization of open-chain precursors, *i.e.*, treatment of the nitrile (**55**) with ammonium azide[35] or action of nitrous acid on the tautomer (**56**) of dinitroacetamidrazone;[36–38a] and (ii) side chain modification of preformed 1*H*-tetrazoles, *i.e.*, by removal of one nitro group in **57** with hydroxylamine[39a,40] or concentrated aqueous alkali[41] or, alternatively, by hydrolysis of the ester function in **58** followed by decarboxylation.[34,42] Access to the mixed functionalized compound (**Eb**) was accomplished through oxidation of the oximino group in **59**.[39a]



E^{s}a **E$^{s'}$a**

Cat	yield (%)	ref.	X-ray (ref.)	yield (%)	ref.	X-ray (ref.)
Na	83 [a] / [b] / 91	34 / 35a,b / 36	34	89 [g] / [b]	34 / 35a,b	34
K	92 / [c]	40 / 42	40	74 / 77 / [c] / 36	39a / 41 / 42 / 43	
NH_4	99 / [b] / [c] / [b]	34 / 35a,b / 42 / 43		75 / 68	34 / 46	34 / 46
(Sr)	90	34		91	34	
(Pb), (Cu), (Mn)				[b]	38b	
(Fe), (Co), (Ni), (Zn)				[b]	38b	
$HONH_3$	92	40	40			
H_2NNH_3				[b,h] / 92 [e] / [b,e]	34 / 40 / 47	40 / 47
$C(NH_2)_3$	78 / [b]	34 / 35a,b		63	34	
$C(NHNH_2)_3$	92	34	34			
$H_2NNHC(NH_2)_2$	68 / 82	34 / 44		75	44	
$Me_2C{=}NNHC(NH_2)_2$	[d]	34	34			
$O_2NNHC(NH_2)_2$	71	34				
$H_2NNHCONHNH_3$	87	44		85	44	
$H_2NC(NHNH_2)_2$	57	34				
$HOC(NH_2)_2$	98	34	34			
{HetH}^{1}	85	44		80	44	
{HetH}^{2}	83	44				
{HetH}^{3}	86	44				
{HetH}^{4}	79 [e]	45		85	45	
{HetH}^{5}	81	44	44 [f]			

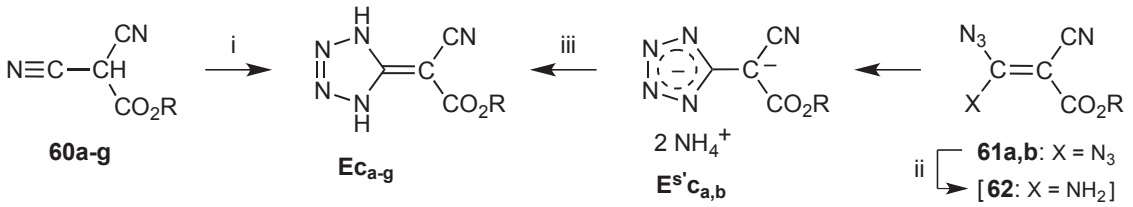
[a] Trihydrate. [b] Unreported. [c] High yield, unspecified. [d] Unreported; made from aminoguanidinium salt. [e] Monohydrate. [f] Co-crystallized with 2 mol 4*H*-1,2,4-triazol-4-amine and 1 mol water. [g] Dihydrate. [h] Material apparently impure.



{HetH}^{1} {HetH}^{2} {HetH}^{3} {HetH}^{4} {HetH}^{5}

Chart 2. List of salts (**E^{s}a**) and (**E$^{s'}$a**) prepared[48]
(for pK_a values of **Ea** and **E^{s}a**, *cf.* refs.[35b,39b])

Derivatives of the type (**Ec**) were obtained from both the nitriles (**60**)[50] and the geminal vinyl diazides (**61**)[51] (Scheme 19). The second mode takes advantage of a synthetic method mainly developed for class (**F**) (see later, Schemes 21, 23, 24): On exposure to ammonia, **61a,b** underwent partial ammonolysis to give the respective intermediates (**62**); rapid ring closure of the latter afforded the diammonium salts (**E$^{s'}$c$_{a,b}$**) which were transformed into **Ec$_{a,b}$** using mineral acid. Quite expectedly, two equivalents of potassium hydroxide converted isolated **Ec$_a$** to the corresponding dipotassium salt (quantitative yield).[51]



i: Me_3SiN_3, $CHCl_3$, rt ii: $\{NH_3\}_g$, CH_2Cl_2, − 40 °C iii: MeOH / DMSO, conc. HCl, rt

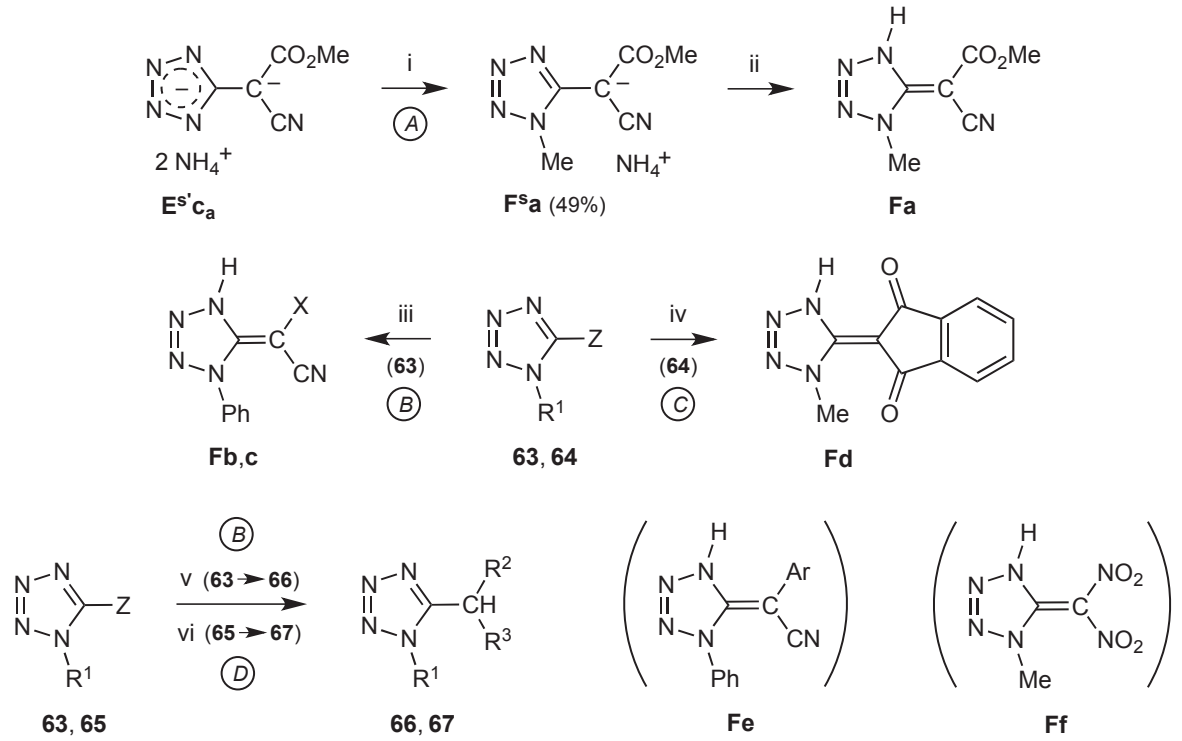
Ec, **60**, **61**	R	method	yield (%)	mp (°C)	ref.
a	Me	i / ii, iii	52 / 61 [a]	> 330 [c] / 177 [d]	50 / 51
b	Et	i / ii, iii	44 / 99 [b]	> 330 [c] / 241 [d]	50 / 51
c	Bu	i	41	> 330 [c]	50
d	*i*-Bu	i	43	242 [c]	50
e	CH_2CCl_3	i	12	> 330	50
f	CH_2Ph	i	48	233 [c]	50
g	$CH_2CH{=}CH_2$	i	15	231 [c]	50

[a] Based on **E$^{s'}$c$_a$** (yield 84%). [b] Based on **E$^{s'}$c$_b$** (yield 72%). [c] Sublimation begins at *ca.* 200 °C. [d] Decomp.

Scheme 19

Similar to the above class (**E**), access to compounds (**F**) consists in (i) modification of preformed tetrazoles and (ii) cyclization of open-chain precursors.

(i) Four variants of this approach have been reported (Scheme 20): (*A*) Methylation of the salt (**E$^{s'}$c$_a$**) gave the ammonium salt (**F^{s}a**) which on treatment with mineral acid yielded the final product (**Fa**) as *E* isomer.[51] (*B*) Nucleophilic replacement of the sulfonyl group of compound (**63**) with cyanoacetate and malononitrile gave the derivatives (**Fb**) and (**Fc**), respectively; the reagent (4-nitrophenyl)acetonitrile worked equally well,[52] but DFT calculations showed that the product exists as 1*H*-tetrazole (**66**) rather than as tautomer (**Fe**) [*cf.* Section (4.c)].[13] (*C*) Conversely, base-assisted condensation of 1,5-dimethyltetrazole (**64**) with diethyl phthalate produced the dioxoindanylidene derivative (**Fd**).[53a] (*D*) In close analogy to the conversion of **57** to the derivative (**Ea**) (*cf.* Scheme 18), one nitro group of the substrate (**65**) was reductively removed using hydroxylamine;[39a] yet, in contrast to the parent (**Ea**), the product was computed to be compound (**67**), not the anticipated tautomer (**Ff**) [*cf.* Section (4.c)].[13]



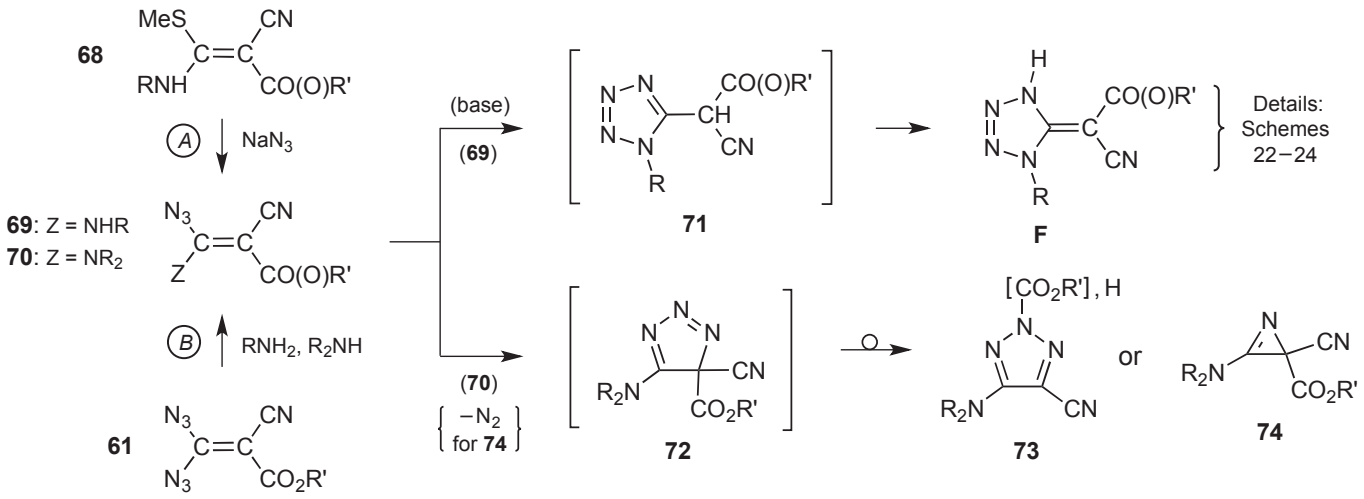
i: $(MeO)_2SO_2$, Δ ii: MeOH / DMSO, conc. HCl, rt iii: XCH_2CN, NaOH, MeCN, rt, then conc. HCl until pH 1
iv: 1,2-$(CO_2Et)_2C_6H_4$, NaH, DME, rt v: 4-$NO_2C_6H_4CH_2CN$ according to method (iii)
vi: KOH, $[NH_3OH]Cl$, aq. EtOH, 0−5 °C to give potassium salt of **67**, then H_2SO_4

	X	yield (%)	mp (°C)	ref.		Z	R^1	R^2	R^3	yield (%)	mp (°C)	ref.
Fa		85	189 [a]	51	**63**	SO_2Me	Ph					
b [b]	CO_2Et	84	187	52	**64**	Me	Me					
c	CN	84	195	52	**65**	$C(NO_2)_3$	Me					
d		70	234	53a	**66**		Ph	Ar [c]	CN	95	152−153	52
					67		Me	NO_2	NO_2	75 [d]	oil [e]	39a

[a] Decomp. [b] Presumedly *E* isomer formed. [c] Ar = 4-$NO_2C_6H_4$. [d] Based on potassium salt of **67** (yield 76%). [e] Unstable, decomposed at room temperature.

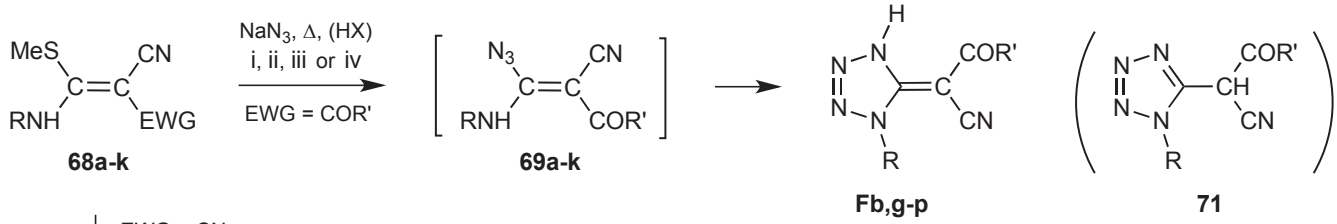
Scheme 20

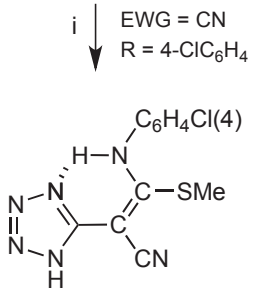
(ii) Of this mode, two variants exist (Scheme 21): The first (*A*) starts from ketene *S*,*N*-acetals (**68**),[54–59] the second (*B*) from vinyl diazides (**61**).[60–64] Both routes proceed through a joint intermediate (**69**) (assumedly *E* configured), whose cyclization to the product (**F**) (throughout *E*) comprises three consecutive steps: **69**–imidoyl azide tautomerism // imidoyl azide–alkyltetrazole (**71**) isomerism // **71**–alkylidenedihydrotetrazole (**F**) tautomerism. The process (**61** → **69**) requires primary amines (for details and analogous conversions, see Schemes 23, 24). Aminolysis with secondary amines affords the congener (**70**), which is also capable of undergoing cyclization: Depending on the conditions, either 1,2,3-triazoles (**72** / **73**) or 2*H*-azirines (**74**) are formed;[65] this interesting behaviour, however, falls outside the scope of the present review.



Scheme 21

(*A*) This variant was initially used for derivatives such as **Fb,l** (Scheme 22);[54,55] an attempt with **68** (EWG = CN), however, failed as the azide ion did not replace the MeS group but attacked one of the cyano groups to form the vinyltetrazole (**75**).[55] Later, additional ester- (**68b-g**) and also keto-functionalized substrates (**68h-k**) could be converted, thereby illustrating the scope of the method.[56–59] As for the products obtained from **68d,e**, these materials were reported to be (exclusively or partly) the respective tetrazoles (**71**),[56,58] whereas the product resulting from **68k** should be **Fp** (not **71** as shown by the authors[59]) [*cf.* Section (4.c)].



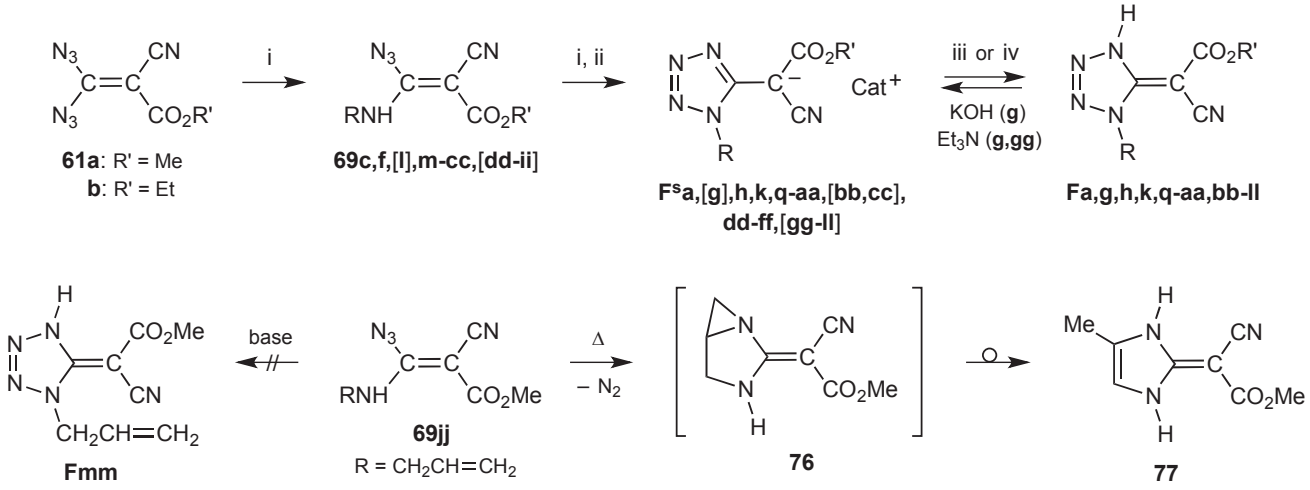


i: DMF
ii: DMSO
iii: DMSO / Me_2CO
iv: DMSO / MeCN

68, **69**	**F**	R	R'	solvent	yield (%)	mp (°C)	ref.
a	**b**	Ph	OEt	i / ii	74 / 77	[c] / 190−191	54 / 55
b	**g**	Ph	OMe	iii	68	177 [d]	56
c	**h**	*i*-Bu	OMe	iii	45	131	57
d	**i** [a]	*t*-Bu	OMe	iii	73	124	56
e	**j**	*t*-Bu	OBu-*t*	iv	83 [b]	139 [b]	58
f	**k**	CH_2Bu-*t*	OMe	iii	50	173	57
g	**l**	CH_2Ph	OEt	ii	73	151−152	55
h	**m**	*t*-Bu	*t*-Bu	iii	37	101	56
i	**n**	Ph	Me	iii	40	172	56
j	**o**	4-MeC_6H_4	*t*-Bu	iii	60	166	57
k	**p** [e]	Me	Ar [f]	iv	74	[g]	59

[a] Tautomer (**71**) instead of **Fi**. [b] Mixture of **Fj** and **71** (18 + 82). [c] 182 –183 (decomp.). [d] Decomp. [e] In ref.[59] shown as **71**. [f] Ar = 2-$MeSO_2$-4-$CF_3C_6H_3$. [g] Unreported.

Scheme 22

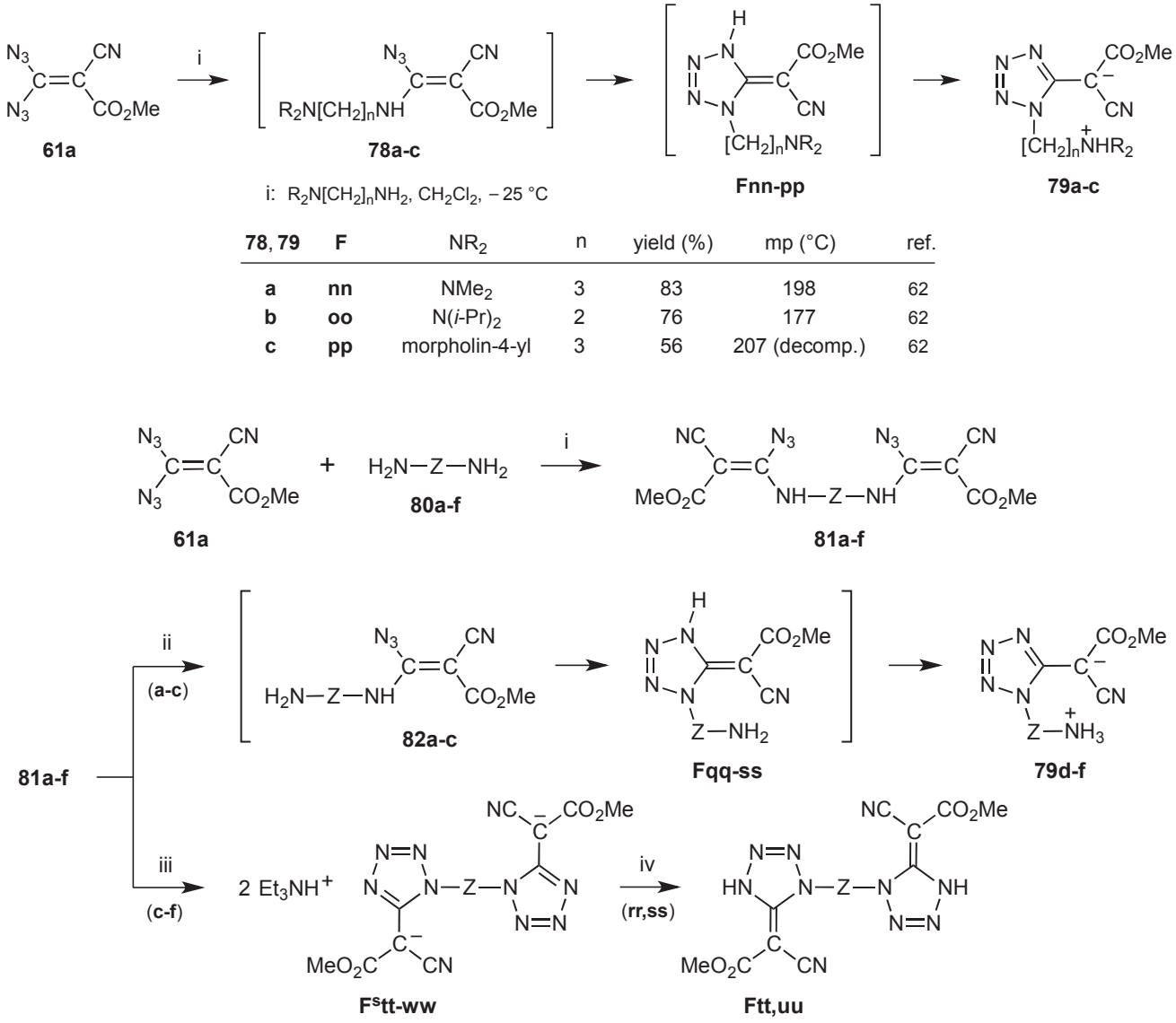


i: RNH_2, CH_2Cl_2, −30 °C (−20 °C for **69m,n**; − 25 °C for **69x-z**) ii: Et_3N, CH_2Cl_2, rt iii: MeOH / DMSO, conc. HCl, rt
iv: CH_2Cl_2, dil. HCl, rt

					69 / **F**^{s} / **F**		**F**	
69	**F**^{s}, **F**	R	R'	Cat	method	yield (%)	mp (°C)	ref.
l	**a**	Me	Me	$MeNH_3$	i / i / iii	[c] / 86 / [d]	189	51
c	**h**	*i*-Bu	Me	Et_3NH	i / ii / iv	92 / 90 / 64	138	61
f	**k**	CH_2Bu-*t*	Me	Et_3NH	i / ii / iv	92 / 95 / 97	150	61
m	**q**	$[CH_2]_7$Me	Me	Et_3NH	i / ii / iv	66 / 76 / 52	113	62
n	**r**	$[CH_2]_3Si(OEt)_3$	Me	Et_3NH	i / ii / iv	97 / 94 / 71	129	62
o	**s**	CH_2X [a]	Me	Et_3NH	i / ii / iv	95 / 93 / 52	152	61
p	**t**	$[CH_2]_3Ph$	Me	Et_3NH	i / ii / iv	94 / 97 / 59	141	61
q	**u**	$CH(CO_2Me)CHMe_2$	Me	Et_3NH	i / ii / iv	92 / 95 / 79	113	61
r	**v**	$CH(CO_2Me)CH(Me)Et$	Me	Et_3NH	i / ii / iv	90 / 96 / 82	74	61
s	**w**	$CH(CO_2Et)CH_2Ph$	Me	Et_3NH	i / ii / iv	86 / 99 / 77	123	61
t	**x**	$CH(CO_2Et)[CH_2]_2SMe$	Me	Et_3NH	i / ii / iv	90 / 100 / 76	92	61
u	**y** [b]	$CH(CO_2Me)CH_2OH$	Me	Et_3NH	i / ii / iv	49 / 82 / 55	122	61
v	**z**	*c*-$C_{12}H_{23}$	Me	Et_3NH	i / ii / iv	64 / 96 / 80	144 [e]	61
w	**aa**	indan-1-yl	Me	Et_3NH	i / ii / iv	56 / 86 / 79	190 [e]	61
x	**g**	Ph	Me	K, Et_3NH [f]	i / [g]	78 / [c] / 84	176	60
y	**bb**	4-MeC_6H_4	Me		i / [g]	75 / [c] / 82	193 [e]	60
z	**cc**	4-$MeOC_6H_4$	Me		i / [g]	60 / [c] / 75	182 [e]	60
aa	**dd**	4-EtC_6H_4	Me	Et_3NH	i / ii / iv	100 / 97 / 78	155	61
bb	**ee**	2-$MeOC_6H_4$	Me	Et_3NH	i / ii / iv	80 / 80 / 76	174 [e]	61
cc	**ff**	3,4-$Me_2C_6H_3$	Me	Et_3NH	i / ii / iv	100 / 98 / 82	171 [e]	61
dd	**gg**	NHPh	Me	Et_3NH [f]	i [h]	[c] / [c] / 81	164 [e]	63
ee	**hh**	NHPh	Et		i [h]	[c] / [c] / 70	148 [e]	63
ff	**ii**	NHCOMe	Me		i [h,i]	[c] / [c] / 82	174 [e]	63
gg	**jj**	NHCOPh	Me		i [h,i]	[c] / [c] / 77	182 [e]	63
hh	**kk**	NHCOPh	Et		i [h]	[c] / [c] / 74	176 [e]	63
ii	**ll**	OCH_2Ph	Me		i [h]	[c] / [c] / 67	162 [e]	63

[a] X = perhydro-2-furyl. [b] Both **F**^{s}**y** and **Fy** unstable (deviating NMR spectra). [c] Not isolated. [d] Unreported. [e] Decomp. [f] Salts (**F**^{s}**g**) (74%)[60,64] and (**F**^{s}**gg**) (67%)[63] prepared from isolated **Fg** and **Fgg**. [g] Direct conversion of **69** to **F**, catalyzed by RNH_2; no experimental details. [h] Direct conversion of **61** to **F**. [i] Working at 20 °C, 1,2,4-triazoles arose instead of **F**.[63]

Scheme 23



78, 79	F	NR_2	n	yield (%)	mp (°C)	ref.
a	**nn**	NMe_2	3	83	198	62
b	**oo**	$N(i\text{-}Pr)_2$	2	76	177	62
c	**pp**	morpholin-4-yl	3	56	207 (decomp.)	62

				yield (%)						mp (°C) [a]			
79	**80– 82**	**F^s, F**	Z	**79**	ref.	**81**	ref.	**F^s**	ref.	**F**	ref.	**79**	ref.	**F**	ref.
d	**a**	**qq**	$[CH_2]_4$	81	64	91	64					203	64		
e	**b**	**rr**	$[CH_2]_6$	76	64	87	64					203	64		
f	**c**	**ss**	$CH_2C_6H_4CH_2(4)$	74	64	85	64					202	64		
	d	**tt**	$CH(CO_2Me)[CH_2]_4$			84	61	100	61	64	61			105	61
	e	**uu**	[b]			78	61	100	61	85	61			110	61
	f	**vv**	$[CH_2]_3$			73	64	86	62						
		ww	$[CH_2]_4$					82	62						

[a] Decomp. [b] Z = $CH(CO_2Me)CH_2SSCH_2CH(CO_2Me)$.

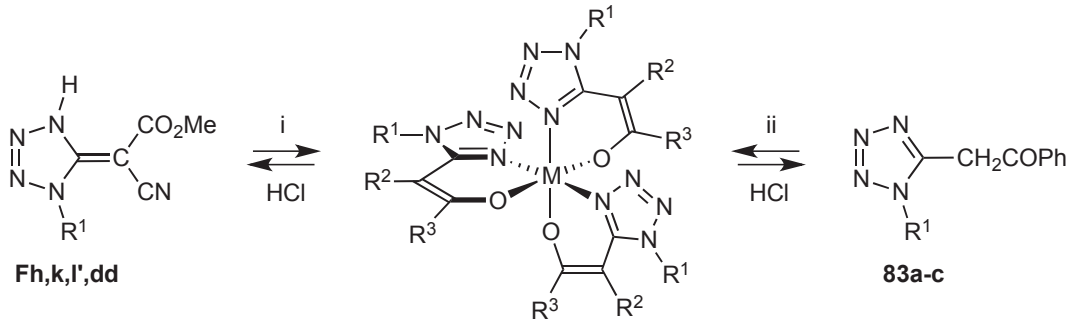
Scheme 24

(*B*) This procedure proved to be especially prolific – judged by the conspicuous diversity of primary amines used (Schemes 23, 24). Particular attention is drawn to the following: Cyclization of the vinyl azides (**69**)

including their analogues (**78, 81, 82**) proceeds under milder conditions than the process (**68** → **69**). As the reaction is base-catalyzed, most conversions of **69** and **81** were carried out in the presence of triethylamine, giving the salts (**F**^{s}) which, in a separate step, were converted to **F** using mineral acid. However, in the case of the vinyl azides (**78**) and (**82**) [the latter arose through cleavage of **81** by **80**], no external base was needed, since here the ring closing influence was exerted by the internal NR_2 and NH_2 functions – with the consequence that these groups deprotonated the products (**F**) to afford the betaines (**79a-c**) and (**79d-f**).[62,64] As a surprising exception, the allylamino substituted vinyl azide (**69jj**) (Scheme 23) could not be caused to undergo cyclization (→ **Fmm**); on being heated, it was converted to the 2-alkylidenedihydroimidazole (**77**), obviously *via* the bicyclic species (**76**) which resulted from a nitrene reaction.[60] In pursuing this experiment, further vinyl azides (**69**), *inter alia* the derivatives (**69o,x**), were thermolyzed. Here, extrusion of molecular nitrogen led to 2*H*-azirines (**74**; NHR instead of NR_2) (*cf.* Scheme 21) which, under the forcing conditions (boiling toluene), isomerized to 2-(R-amino)-5-methoxyoxazole-4-carbonitriles.[66]

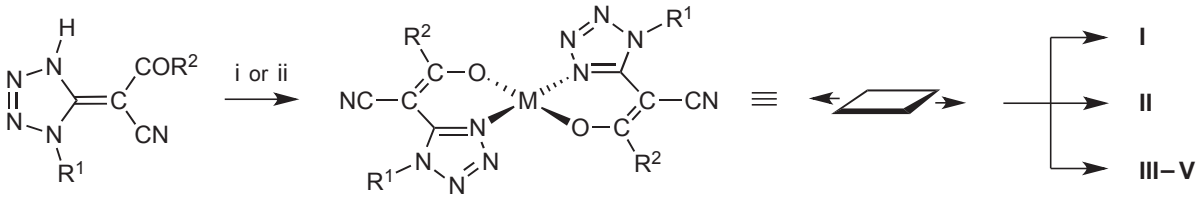
b) Metal Complexes of Compounds (F)

Towards M^{3+} ions (Fe^{3+}, Al^{3+}) compounds (**F**) function as bidentate ligands to form ML_3-type complexes, such as **84a-e** (Scheme 25); the same type, *i.e.*, **84f-h**, resulted from the 5-phenacyl-1*H*-tetrazoles (**83a-c**); the iron-containing complexes of this series represent a novel kind of siderophores.[67,68] – A quite different behaviour was observed with M^{2+} ions (Scheme 26): Towards Fe^{2+} ions the compounds (**Fk,l',dd**) acted as



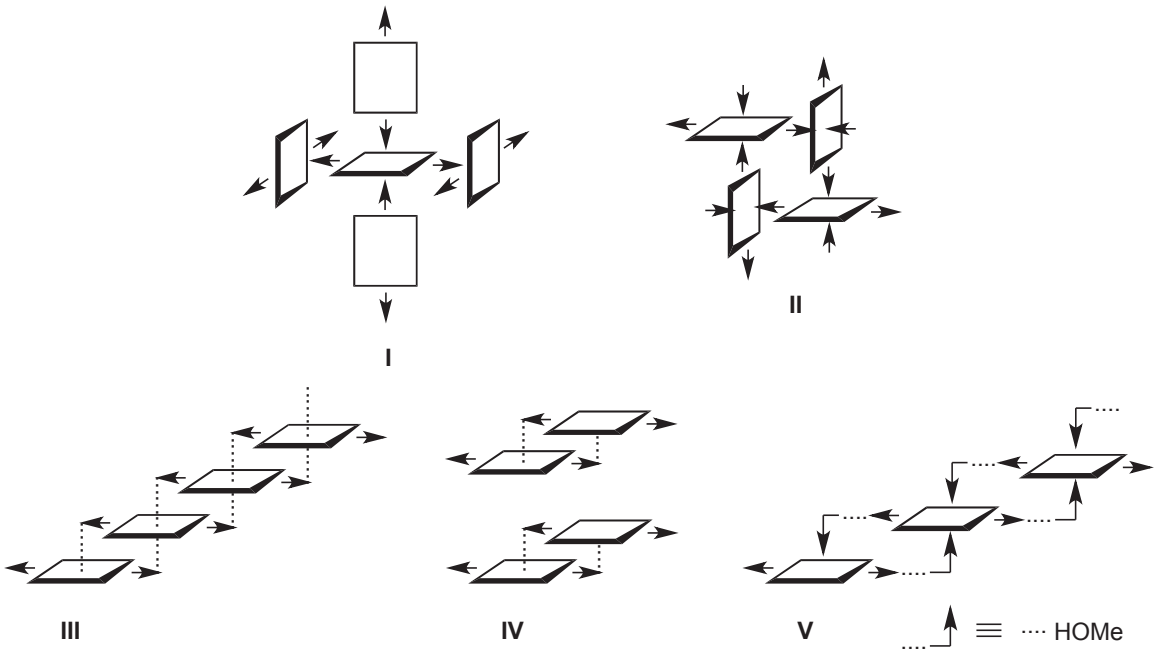
F	83	R^1	R^2	R^3	M	84	from	ref.
h		CH_2Bu-*i*	CN	OMe	Fe	**a**	**Fh**	68
k		CH_2Bu-*t*	CN	OMe	Fe	**b**	**k**	67
		CH_2Bu-*t*	CN	OMe	Al	**c**	**k**	67
l'		CH_2Ph	CN	OMe	Fe	**d**	**l'**	67
dd		4-EtC_6H_4	CN	OMe	Fe	**e**	**dd**	67
	a	Et	H	Ph	Fe	**f**	**83a**	67
	b	Pr	H	Ph	Fe	**g**	**b**	67
	c	*t*-Bu	H	Ph	Fe	**h**	**c**	67

Scheme 25



Fg-o,dd,xx **85[a],b,[c-k],l,[m-o]**

i: $FeSO_4$, Et_2O, rt ii: $Cu(OAc)_2 \cdot H_2O$ or $Zn(OAc)_2 \cdot 2\ H_2O$, MeOH, rt

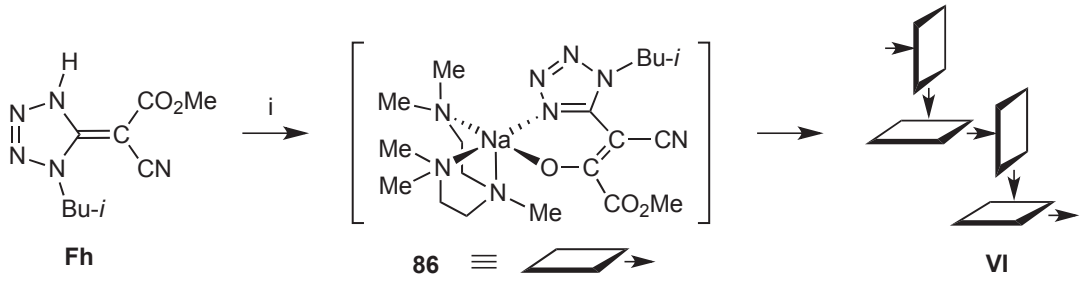


F	R^1	R^2	M	**85**	type	ref.	X-ray (ref.)
g	Ph	OMe	Fe	**a**	[a]	69	
	Ph	OMe	Cu	**b**		57, 70	70
h	*i*-Bu	OMe	Cu	**c**	**III**	58	58
(**i**)	*t*-Bu	OMe	Fe	**d**	[a]	69	
j	*t*-Bu	OBu-*t*	Cu	**e**	**I**	59	59, 71
	t-Bu	OBu-*t*	Fe	**f**	[a]	69	
k	CH_2Bu-*t*	OMe	Fe	**g**	**I**	67, 69	
	CH_2Bu-*t*	OMe	Cu	**h**	**IV**	58	58
l'	CH_2Ph	OMe	Fe	**i**	**I**	67	
m	*t*-Bu	*t*-Bu	Cu	**j**	**II**	57	57
n	Ph	Me	Cu	**k**	**II**	57	57
	Ph	Me	Zn	**l** [b]		57	57
o	4-MeC_6H_4	*t*-Bu	Cu	**m**	**V**	58	58
dd	4-EtC_6H_4	OMe	Fe	**n**	**I**	67	
xx	Et	OMe	Fe	**o**	[a]	69	

[a] Type of coordination polymer not specified. [b] Containing 2 mol MeOH [no hydrogen bridges as occurring in type (**V**)].

Scheme 26

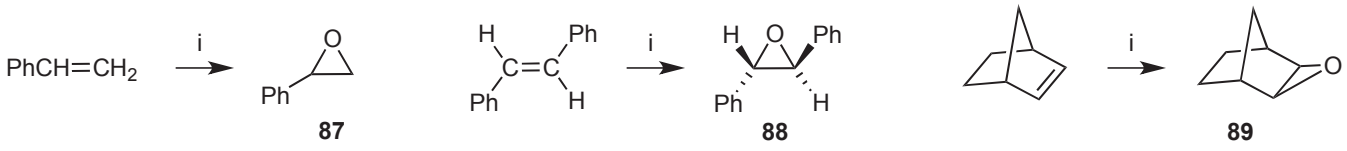
terdentate ligands to afford 3D-coordination polymers (**I**), *viz.* by spontaneous self-organization of the initially formed (coordinatively unsaturated) complexes (**85g,i,n**) which functioned as bidentate ligands *via* their cyano groups; hence, no reaction occurred on treating the above substrates (**83**) with iron(II) reagent.[67] Depending on the metal ion and the substituents of the substrate (**F**), other types of coordination polymers were obtained, such as the 2D type (**II**) and several 1D types (**III**–**V**), as detailed in the Scheme. As a conspicuous exception, the mononuclear complex (**85b**) did not polymerize, contrasting with the behaviour of its close congener (**85k**); the authors rationalized this with the reduced Lewis acidity of the Cu(II) centre of **85b** (methoxy *vs.* methyl group).[56] In the case of the isolable zinc complex (**85l**), coordination with two molecules of the solvent stabilized the mononuclear structure.



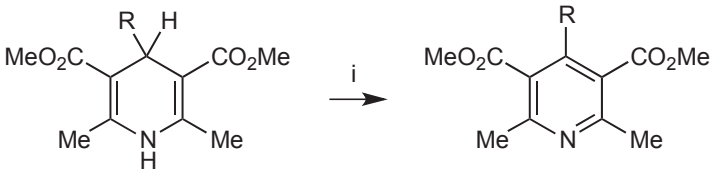
i: $(Me_2NCH_2CH_2)_2NMe$, NaH, toluene, rt

Scheme 27

Finally, a mixed 1D-sodium coordination polymer (**VI**) was obtained from the reaction of sodium hydride with the substrate (**Fh**) and bis[2-(dimethylamino)ethyl]methylamine (Scheme 27); the species (**86**) acted as monodentate ligand *via* its cyano group. The structure of **VI** was established by X-ray analysis.[72]



i: O_2, catalyst (**84h**) (see Scheme 25), *i*-PrCHO, $Cl[CH_2]_2Cl$, rt



	yield (%)	cat. (mol%)	period (h)	**90**	R	**91**	from	yield (%)	cat. (mol%)	period (h)
87	96	2	12	**a**	Ph	**a**	**90a**	57	4	7
88	46	2	4	**b**	CH_2Ph	**b**	**b**	80	4	72
89	85	1	5	**c**	H	**b**	**c**	100	4	72

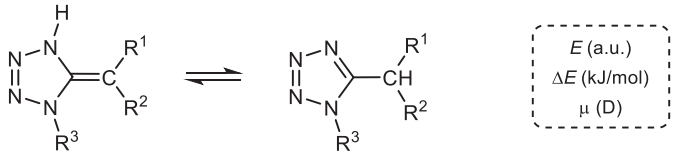
Scheme 28

An important preparative application of the complexes (**84**) concerns catalysis of aerobic oxygenation of alkenes as well as dehydrogenation of 1,4-dihydropyridines (Scheme 28).[68] Epoxides, *inter alia* **87**–**89**, arose on treatment of the respective alkenes with molecular oxygen and **84h** in the presence of an electron source like isobutyraldehyde. By the same procedure, dehydrogenation of the 1,4-dihydropyridines (**90a,c**) could be effected (→ **91a,b**), while in the case of **90b** dealkylation occurred (→ **91b**). These conversions have a direct bearing on cytochrome P-450 catalyzed reactions.[68,73]

c) Tautomerism ($T^1 \rightleftharpoons T^2$) of Compounds (E) and (F): Theoretical Study

Spectroscopic and X-ray diffraction data [see Section (6)] suggest that the above equilibrium is shifted to (**T**^{1}) with all derivatives (**E**) and the majority of compounds (**F**) prepared in Section (4.a). To support this, energy calculations have been performed. Indeed, in the case of **Ea**, recent computations at the HF/6-31G* and B3LYP/6-31G* levels of theory showed (**T**^{1}) to be lower in energy by 0.75 and 3.90 kcal/mol (3.14 and 16.32 kJ/mol), respectively.[42] A recalculation at the HF/6-31G** and B3LYP/6-31G** levels gave even greater differences between (**T**^{1}) and (**T**^{2}) (*cf.* Table 5).[13] In pursuit of this, derivatives like **Eb,c**$_a$, **Fa-g,n**, and the model (**Fp'**) were studied too; except for the cases (**Fe**) and (**Ff**), all equilibria lie on the side of (**T**^{1}).

Table 5. Calculated energies of tautomers (**T**^{1}) and (**T**^{2}) [a][13]



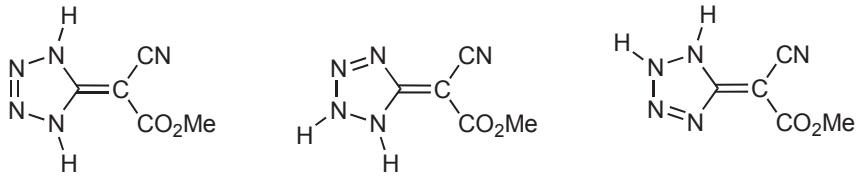
(**T**^{1}) (**T**^{2})

compd	R^1	R^2	R^3	(**T**^{1})	(**T**^{2})	compd	R^1	R^2	R^3	(**T**^{1})	(**T**^{2})
Ea [b]	NO_2	NO_2	H	-706.55344	-706.54449	**Fd**	1,3-dioxoindan-		Me	-793.42147	-793.40429
				0.00	23.50		2-ylidene or 2-yl			**0.00**	45.11
				4.24	*1.68*					*1.35*	*6.72*
Eb	CO_2Et	NO_2	H	-769.27278	-769.26201	**Fe**	CN	Ar [d]	Ph	-1056.41013	1056.41849
				0.00	28.28					21.95	**0.00**
				2.68	*6.86*					*5.78*	*2.75*
Ec$_a$	CO_2Me	CN	H	-617.69286	-617.68028	**Ff**	NO_2	NO_2	Me	-745.85795	-745.86010
				0.00	33.03					5.64	**0.00**
				2.28	*6.90*					*5.18*	*2.34*
Fa	CO_2Me	CN	Me	-657.00929	-656.99662	**Fg**	CO_2Me	CN	Ph	-848.74564	-848.73447
				0.00 [c]	33.27					**0.00**	29.33
				1.70	*5.35*					*1.31*	*6.53*
Fb	CO_2Et	CN	Ph	-888.06769	-888.05709	**Fn**	COMe	CN	Ph	-773.52094	-773.50760
				0.00	27.83					**0.00**	35.02
				1.03	*6.25*					*2.29*	*5.22*
Fc	CN	CN	Ph	-713.08996	-713.08357	**Fp'**	COPh	CN	Me	-773.52247	-773.51037
				0.00	16.78					**0.00**	31.77
				5.38	*3.30*					*0.89*	*6.34*

[a] B3LYP/6-31G** (gas phase). [b] Values at the HF/6-31G** level: (**T**^{1}): -702.70982 / **0.00** / *4.85*; (**T**^{2}): -702.70556 / 11.18 / *1.19*. [c] *Z* isomer higher in energy by 31.30 kJ/mol. [d] Ar = 4-$NO_2C_6H_4$.

Regarding the 1,3-dicarbonyl compound (**Fd**), a more preferred tautomer might be the corresponding β-hydroxyenone, *i.e.*, 3-hydroxy-2-(1-methyltetrazol-5-yl)inden-1-one; this species, however, was found higher in energy than **Fd** by 7.01 kJ/mol. In the case of **Fe**, the less favoured tautomer (**T[1]**) obviously reflects the reduced electron-withdrawing influence exerted by the 4-nitrophenyl group, whereas the finding with **Ff** is surprising in view of the result obtained for the parent (**Ea**); at the HF/6-31G** level, **Ff** was found still higher in energy, *viz.* by 23.94 kJ/mol.[13]

Beyond the study of the above equilibrium (**T[1]** ⇌ **T[2]**),[13,42] also species like **Ec$_a$'** and **Ec$_a$"** were computed (Chart 3).[51] However, in relation to the tautomer (**Ec$_a$**) they appear unfavourable *a priori* because of their irregular 2,5-dihydro-1*H*-tetrazole nucleus.



Ec$_a$ 60.78 **Ec$_a$'** 74.76 **Ec$_a$"** 77.92

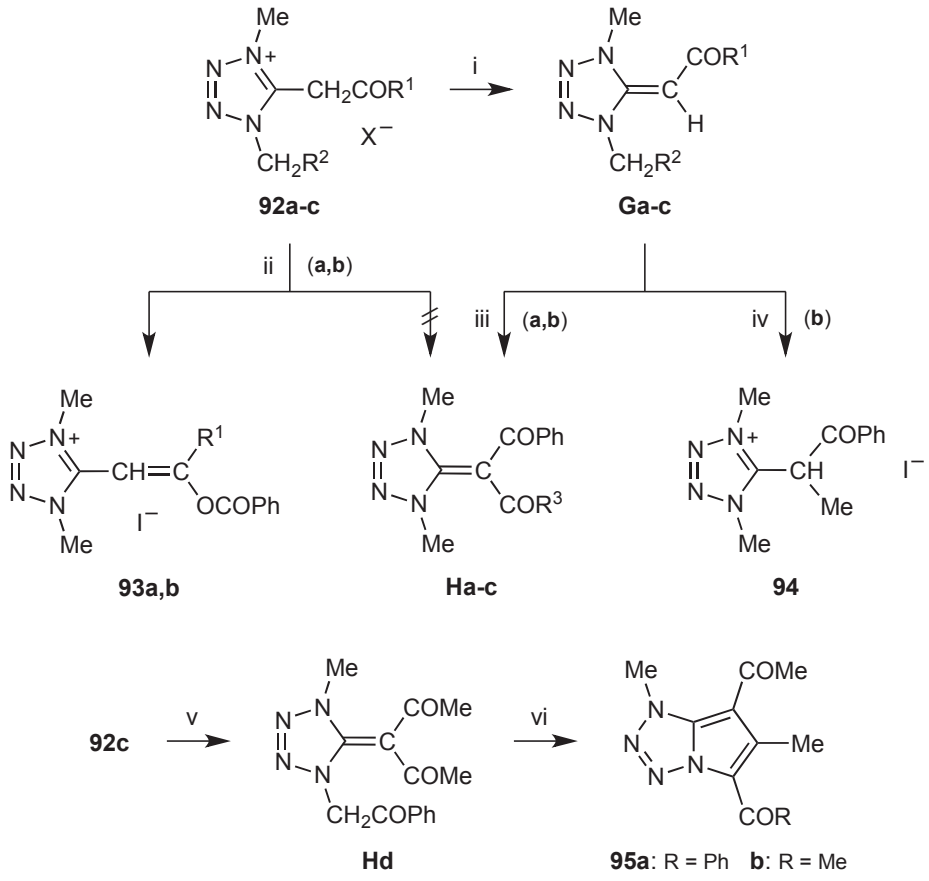
Chart 3. Heats of formation (kcal/mol) calculated by AM1[51]

5) DIHYDROTETRAZOLES OF TYPES (G) AND (H)

Synthesis and Reactions

Derivatives (**G**) having an acyl ligand as α-acceptor group, such as **Ga-c**, were accessible by deprotonation of the appropriate tetrazoliums salts (**92a-c**) (Scheme 29).[74] This kind of access corresponds to the approach to the classes (**C**) and (**D**, **D'**) [see Sections (2.a) and (3.a)]. In the case of the substrate (**92c**), the base did not affect the phenacyl group at N(1), as this function is distinctly less acidic than the acetonyl group at C(5) (*ca.* 4 pK units).[75] Insertion of a second acceptor group at **Ga-c** was attempted with the derivatives (**Ga,b**): Indeed, reactions with benzoyl chloride or phenyl isocyanate took place smoothly to afford representatives of the class (**H**), such as **Ha-c**. Attempts to prepare **Ha,b** by simply submitting the tetrazolium salts (**92a,b**) to the Schotten-Baumann procedure failed, as under these conditions *O*-acylation occurred to give the enol esters (**93a,b**). Yet, alkylation of **Gb** with methyl iodide proceeded as expected to yield the salt (**94**).[74]

A direct formation of a derivative (**H**) like **Hd** occurred on treatment of the 5-acetonyltetrazolium salt (**92c**) with acetic anhydride and a base at room temperature.[76a] Heating of the product (or even **92c**[76b]) with these reagents caused cyclization to give the 1*H*-pyrrolotetrazoles (**95a,b**)[76a,b] which, at that time, were the first azapentalenes of this kind to be synthesized.[76b] The concomitant formation of the diacetyl derivative (**95b**) was understood to originate in partial benzoyl–acetyl exchange with compound (**Hd**) to be followed by ring closure.[76a]



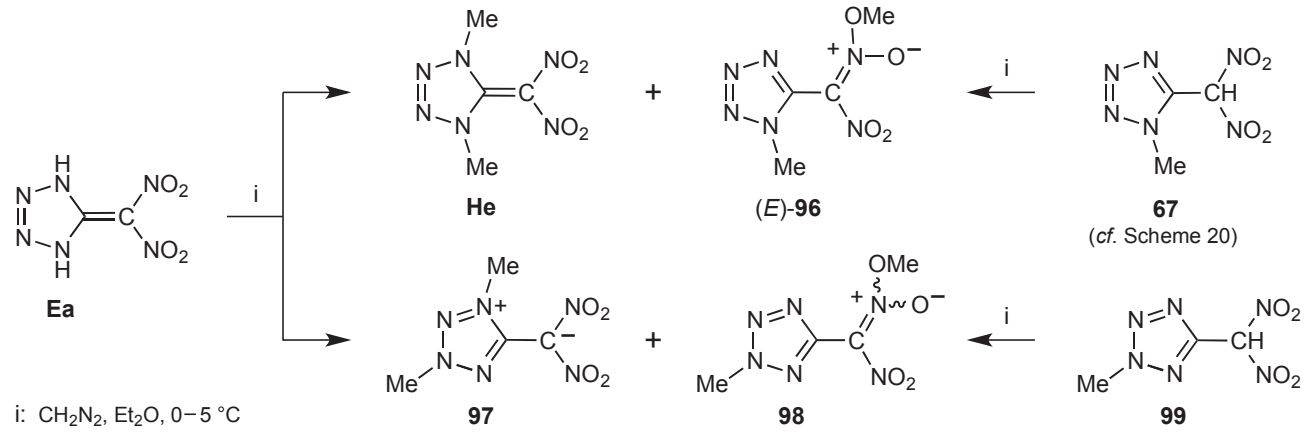
i: aq. K_2CO_3, 0 °C ii: PhCOCl, CH_2Cl_2, aq. K_2CO_3, 0 °C
iii: $(PhCO)_2O$ (neat), Δ (for **Ha,b**) or PhNCO, CH_2Cl_2, rt (for **Hc**) iv: MeI, DMF, rt
v: Ac_2O, Et_3N, rt vi: Ac_2O, Et_3N, Δ

					yield (%) / mp (°C) [a]					
92, **93**, **G**, **H**	R^1	R^2	R^3	X	**G**	**H**	ref.		**93**–**95**	ref.
a	Me	H	Me	I	88 / 69	[b] / oil	74	**93a**	64 / 154–160	74
b	Ph	H	Ph	I	79 / 85	57 / 209–210	74	**b**	76 / 158–160	74
c	Me	COPh	NHPh	BF_4	91 / 165	95 / 189–190	74	**94**	11 / 166	74
d						45 / 134–137	76a	**95a**	8 [c] / 210	76a
								b	16 [d] / 130–131	76a

[a] **G**, **93**, and **94** with decomp. [b] Unreported. [c] Yield 14% directly from **92c**, using method (vi).[76b] [d] Trace amounts directly from **92c**, using method (vi).[76b]

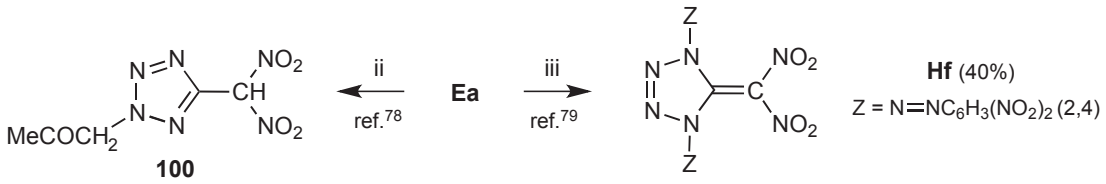
Scheme 29

Beyond *C*-functionalization of compounds (**G**), *N*-substitution of substrates (**E**) and (**F**) provides another route to class (**H**) (Schemes 30, 31): (i) Treatment of the dibasic acid (**Ea**) with diazomethane[39a] caused, firstly, double *N*-methylation to afford the target compound (**He**) along with the mesoionic tetrazole (**97**),[77] and, secondly (to a greater extent), *N*,*O*-dimethylation with formation of the nitronates (**96**) and (**98**) (of the latter isomer, both *E* and *Z* form arose). On the other hand, the tetrazole (**67**, formally **Ff**) gave a mixture of **He** and (*E*)-**96**, from which **He** could be separated on a preparative scale; a similar mixture, *i.e.*, {**97** + **98**},



products {mixtures}	from	yield (%)	ratio **He** : **97**	ratio (*E*)-**96** : (*E*)-**98** : (*Z*)-**98**	mp (°C) [b]	ref.
{**He**, **97**} + {(*E*)-**96**, (*E*)-**98**, (*Z*)-**98**}	**Ea**	{26} + {63} [a]	2.2 : 1	1 : 5.1 : 15.5		39a
He + (*E*)-**96**	**67**	56 + 6			**He**: 245–247	39a
97 + {(*E*)-**98**, (*Z*)-**98**}	**99**	14 + {81} [c]		3 : 1	**97**: 232	39a

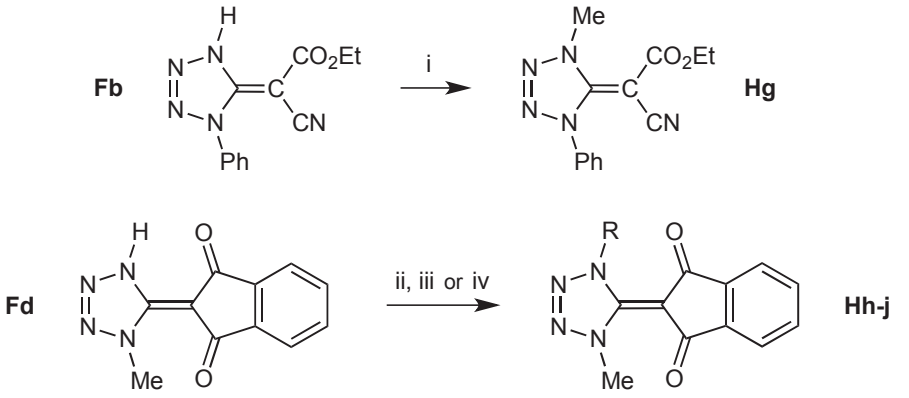
[a] Components of both mixtures not isolated. [b] Decomp. [c] Stereoisomers separated.



Scheme 30

was obtained from the tetrazole (**99**). (ii) Further substitutions of **Ea** were performed with bromoacetone[78] and a diazonium salt.[79] But while the former process took a course that is not relevant to the present context (→ **100**), the latter gave the high-nitrogen energetic compound (**Hf**) showing an interesting N_8 structure. (iii) Alkylation of **Fb** with dimethyl sulfate[54] and of **Fd** with a range of alkyl halides[53a] proceeded more or less readily to give products like **Hg** and **Hh-j**, respectively.[80] The transformation of **Fd** into **Hi** was also successful with the Mitsunobu method; however, application of this mode to the bulkier 2-piperidinoethyl reagent in order to improve the yield of compound (**Hj**) met with failure. A breakthrough was achieved only by conversion of **Fd** into its caesium salt to be followed by treatment with the said alkyl halide. In a final investigation towards the biological activities of diverse 2-(dihydrohetarylidene)indane-1,3-diones, the target compounds (**Hh-j**) proved to be anti-inflammatory materials.[53b]

An unusual entry to class (**H**) constitutes the conversion of the dichloro(ditetrazolyl)methane (**101**) through treatment with dialkyl phosphites (Scheme 32). The transient ion pairs (**102a,b**) underwent the second stage

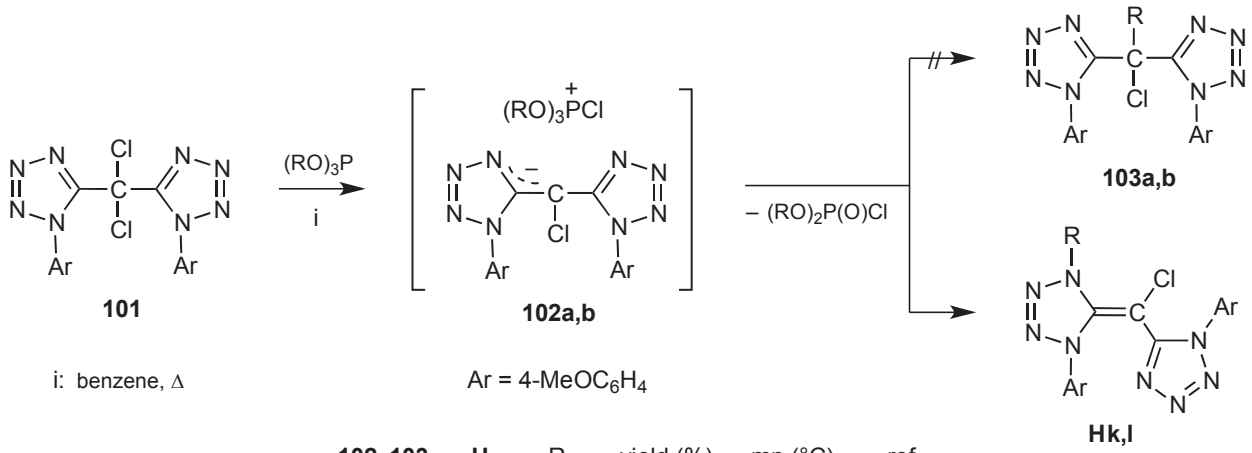


i: $(MeO)_2SO_2$, K_2CO_3, DMF, rt ii: RX, NaH, DMF, rt iii: ROH, Ph_3P, $EtO_2CN{=}NCO_2Et$, THF, rt
iv: $Cl[CH_2]_2N[CH_2]_5$, Cs_2CO_3, MeCN, Δ

H	R	method	yield (%)	mp (°C)	ref.
g		i	55	194–196	54
h	Me	ii	54 [a]	252	53a
i	Et	ii / iii	83 / 75	176	53a,b
j	$[CH_2]_2N[CH_2]_5$	ii / iv	20 / 78	162	53a,b

[a] Ref.[53b]: 34%.

Scheme 31



i: benzene, Δ Ar = 4-$MeOC_6H_4$

102, 103	H	R	yield (%)	mp (°C)	ref.
a	**k**	Et	43	123–124	81a
b	**l**	*i*-Pr	82	149–150	81a

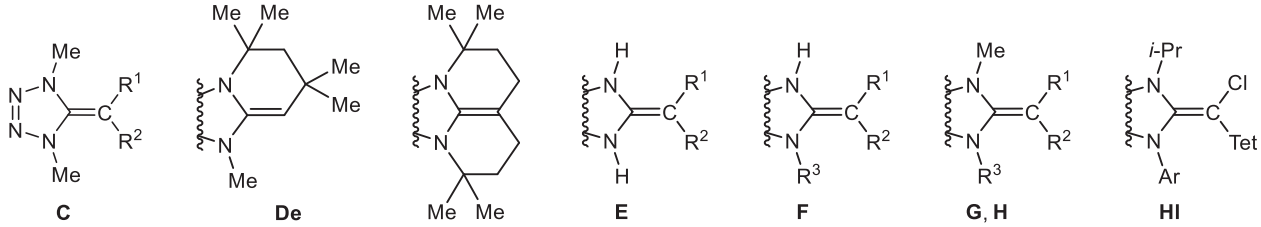
Scheme 32

of the Arbuzov reaction, *i.e.*, dealkylation of the phosphonium centre and formation of dialkoxyphosphonic chlorides. The ensuing alkylation of the anion did not occur at the side chain (→ **103a,b**) but took place at the tetrazole ring to give the derivatives (**Hk,l**).[81a] The structure of these compounds has been studied in detail, especially the nature of the olefinic bond [*cf.* Section (6)].[81b]

6) COMPOUNDS OF TYPES (C–H): Experimental Structural Methods; Ylide Character

All derivatives (**C**–**H**) prepared in Sections (2)–(5) have been characterized by spectroscopic methods; for a selection of IR, UV/Vis, and NMR data, see Tables 6–8. EI mass spectra have been taken routinely from the

Table 6. IR and UV/Vis data of selected compounds (**C**–**H**) [a]

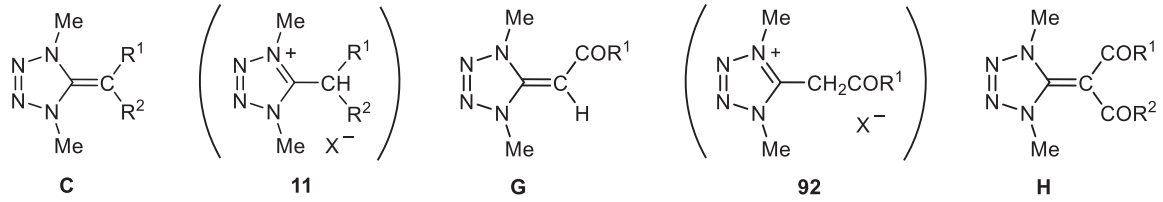


compd	R^1	R^2	$\tilde{\nu}$ (cm^{-1}) [b]	solvent	ref.
Ca	H	H	1647	*c*-C_6H_{12}	17
Cb	Me	Me	1677	CCl_4	16
Cc	*t*-Bu	H	1640	CCl_4	16
			λ_{max} (nm)		
Cb	Me	Me	348	*c*-C_6H_{12}	16
Cc	*t*-Bu	H	332	*c*-C_6H_{12}	16
De			349	MeCN	33
D'b			359 [c]	THF	33
Ea	NO_2	NO_2	360 [d]	MeOH	42 [e]

compd	R^1	R^2	R^3	$\tilde{\nu}$ (cm^{-1}) [b]	solvent	ref.
Cg	Ph	H		1638	*c*-C_6H_{12}	17
D'b				1717	THF-d_8	33
Hf	CO_2Et	CN	Ph	1545	CH_2Cl_2	54
				λ_{max} (nm) (log ε)		
Ec$_a$	CO_2Me	CN		290 (2.74) [f]	MeOH	50
Fj	CO_2Bu-*t*	CN	*t*-Bu	273 (3.23)	CH_2Cl_2	58
Fk	CO_2Me	CN	CH_2Bu-*t*	369 (2.90) [g]	MeCN	61
Gb	COPh	H	Me	337 (4.27)	$CHCl_3$	74
He	NO_2	NO_2	Me	330 (4.19) [h]	H_2O	39a,b
HI	for Tet and Ar, see Scheme 32			373 (3.77)	EtOH	81a

[a] For Raman data of **Ea** including salts (**E**^{s}**a**) and (**E**$^{s'}$**a**), *cf.* refs.[34,40] [b] C=C bond. [c] ε = 780. [d] *Cf.* salts (**E**^{s}**a**) and (**E**$^{s'}$**a**) (Cat = K each): 357 and 361 (MeOH).[42] [e] See also ref.[39b] [f] *Cf.* **E**$^{s'}$**c**$_a$ (Cat = NH_4): 291.5 (2.79) (MeOH).[42] [g] *Cf.* **F**^{s}**k** (Cat = Et_3NH): 302 (2.86) (MeCN).[61] [h] *Cf.* the mesoionic isomer (**97**) (Scheme 30): 338 (4.21) (H_2O).

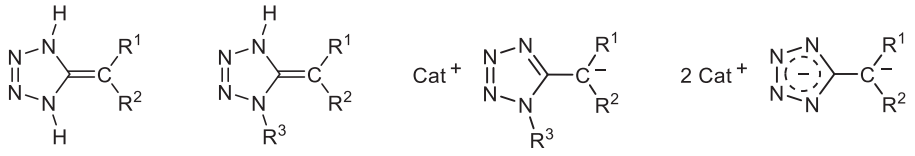
Table 7. ^1H and ^{13}C NMR data of selected compounds (**C**), (**G**), (**H**) compared to precursors (**11**), (**92**) [a]



compound	R^1	R^2	^1H NMe	^1H $C_{\alpha\text{-}H}$	^1H [b]	^{13}C NMe	^{13}C C(5)	^{13}C C_α	^{13}C [b]	ref.
Ca (**11a**)	H	H	2.79 (4.37)	2.55 (3.01)	*A* (*F*)	32.1 (36.2)	145.1 (152.7)	39.3 (8.1)	*A* (*C*)	17 [c] (15)
Cb (**11b**)	Me	Me	3.03 (4.44)	(3.90)	*B* (*F*)	37.3 (37.9)	137.3 (157.6)	63.7 (25.3)	*A* (*D*)	16 [c] (15)
Cc (**11c**)	*t*-Bu	H	2.70 / 3.24 (4.45)	3.03 (3.34)	*B* (*F*)	32.4 / 37.9 (38.3)	139.9 (154.5)	73.0 (36.8)	*A* (*D*)	16 (15)
Cd (**11d**)	[d]	H	2.71 / 3.11 (4.46)	4.12 (4.37)	*A* (*G*)	32.2 / 35.8 (37.3)	139.6 (153.0)	66.8 (26.8)	*A* (*G*)	17 (17)
Cg (**11g**)	Ph	H	2.65 / 2.86 (4.03)	4.12 (4.47)	*A* (*E*)	32.2 / 36.2 (38.1)	140.6 (153.3)	63.0 (28.8)	*A* (*E*)	17 (15)
Ga (**92a**)	Me		3.83 (4.40)	4.47 (5.10)	*H* (*I*)	36.2 (37.5)	147.9 (149.9)	68.0 (37.8)	*H* (*I*)	74 (74)
Gb (**92b**)	Ph		3.94 (4.40)	5.10 (5.60)	*H* (*I*)	36.3 (37.4)	149.3 (150.7)	66.2 (34.1)	*H* (*I*)	74 (74)
Ha	Ph	Me	3.87		*H*	37.1	155.2	92.5	*H*	74
Hc	Ph	[e]	3.80		*C*	36.8	156.1	78.4	*C*	74

[a] Shift values: δ (ppm); all parenthesized figures refer to precursors (**11**) and (**92**). [b] Solvent: *A* = C_6D_6, *B* = C_6H_6, *C* = $(CD_3)_2SO$, *D* = CD_3OD, *E* = CD_3CN, *F* = HCO_2H, *G* = $(CD_3)_2CO$, *H* = $CDCl_3$, *I* = TFA. [c] For calculated ^{13}C shifts (IGLO method), *cf.* ref.[82] [d] R^2 = CH=CH_2. [e] R^2 = NHPh.

Table 8. ^{1}H, ^{13}C, and ^{14}N NMR data of selected compounds (**E**), (**F**) and salts ($\mathbf{E}^{s}$), ($\mathbf{E}^{s'}$), ($\mathbf{F}^{s}$) [a]

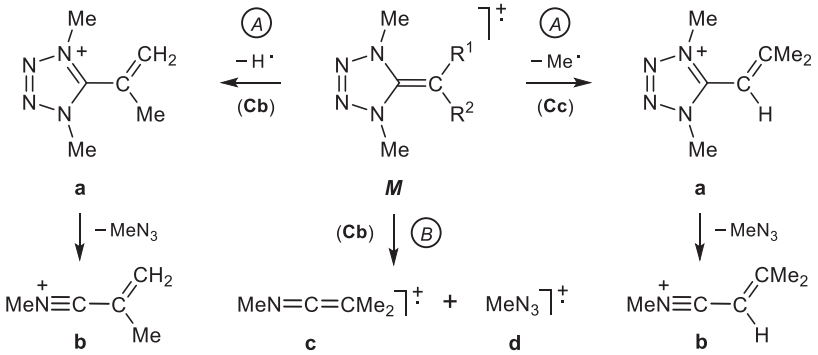


E **F** $\mathbf{E}^{s}$, $\mathbf{F}^{s}$ $\mathbf{E}^{s'}$

					^{1}H	^{13}C		^{14}N			
compd	R^1	R^2	R^3	Cat	TetNH	C(5)	C_α	Tet	NO_2	[b]	ref.
Ea	NO_2	NO_2			11.09	149.2	121.5	–39, –63	–24	*A*	34 [c]
Ec$_b$	CO_2Et	CN			13.87 br	151.1	47.0			*A*	51 [d]
E^{s}a [e]	NO_2	NO_2	H	Na	(*cf.* ref.[34])	148.8	121.3	(*cf.* ref.[34])	–24	*A*	34 [f]
E^{s}a	NO_2	NO_2	H	$HONH_3$		156.3	129.0	–68	–24.6	*B*	40
E$^{s'}$a	NO_2	NO_2		K		155.2	128.5		–23	*C*	41 [g]
E$^{s'}$a [h]	NO_2	NO_2		H_2NNH_3		156.4	129.0	–70	–24.6	*B*	40 [i]
E$^{s'}$c$_b$	CO_2Et	CN		NH_4		157.2	46.9			*D*	51
Fa	CO_2Me	CN	Me		13.07 br	148.7	47.1			*A*	51
Fg	CO_2Me	CN	Ph		15.66 br	148.8	48.5			*A*	60 [j]
Fh	CO_2Me	CN	*i*-Bu		14.20 br	148.7	49.5			*E*	61 [k]
Fn	COMe	CN	Ph		13.0 br	149.6	72.9			*E*	56
Fff	CO_2Me	CN	NHPh		15.27 br	149.1	48.7			*A*	63
Fkk	CO_2Me	CN	OCH_2Ph		9.0 br	144.6	47.6			*A*	63
F^{s}a [l]	CO_2Me	CN	Me	$MeNH_3$		154.4	47.3			*C*	51
F^{s}h	CO_2Me	CN	*i*-Bu	Et_3NH		153.6	44.6			*E*	61
F^{s}ff	CO_2Me	CN	NHPh	Et_3NH		153.7	45.2			*E*	63

[a] Shift values: δ (ppm) relative to $SiMe_4$ and $MeNO_2$, respectively; half-width of ^{14}N signals omitted. [b] Solvent: *A* = $(CD_3)_2SO$, *B* = D_2O, *C* = $(CD_3)_2CO$, *D* = $(CD_3)_2CO/CD_3OD$, *E* = $CDCl_3$. [c] For ^{1}H data *cf.* also refs.[37,39a,42]; for ^{13}C data, *cf.* also refs.[37,42]; for ^{14}N data, *cf.* also ref.[40] [d] *Cf.* also ref.[50] [e] Trihydrate. [f] For ^{1}H and ^{13}C data, *cf.* also ref.[36] [g] For ^{13}C data, *cf.* also refs.[42,43] [h] Monohydrate. [i] For ^{13}C and ^{14}N data, *cf.* also ref.[34] [j] *Cf.* also ref.[56] [k] *Cf.* also ref.[57] [l] *Cf.* also ^{13}C data of **79** (Scheme 24), *e.g.* **79b**: 155.1, 42.5 (*A*).[62]

Table 9. MS data of compounds (**Cb**) and (**Cc**) [a][83]



a ***M*** **a**

b **c** **d** **b**

M	R^1	R^2	***M***	**a**	**b**	**c**	**d**
Cb	Me	Me	140 (28)	139 (5)	82 (12)	83 (18)	57 (100)
Cc	*t*-Bu	H	168 (2)	153 (2)	96 (7)		57 (100)

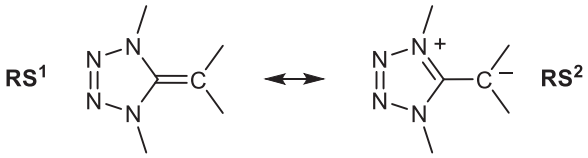
[a] 70 eV, *m/z* (%).

derivatives (**Ec$_{a-g}$**)[50,51] and the majority of compounds (**F**),[51,55–58,60–63] giving molecular ions of rather low intensity (if reported). However, a systematic investigation, as available for compounds (**A, B**) [Section

(1.b)], is lacking; there exists only a preliminary study on the derivatives (**Cb,c**) (Table 9);[83] note that the fragmentation path (*B*) was not observed on thermolysis [*cf.* Section (2.b), Scheme 11].

Ylide Character

Due to the enediamine (ketene aminal) substructure all compounds (**C**–**H**) are polarized as shown below. A comparison of the NMR data of **C** and their precursors (**11**) is instructive (Table 7): Deprotonation of **11**



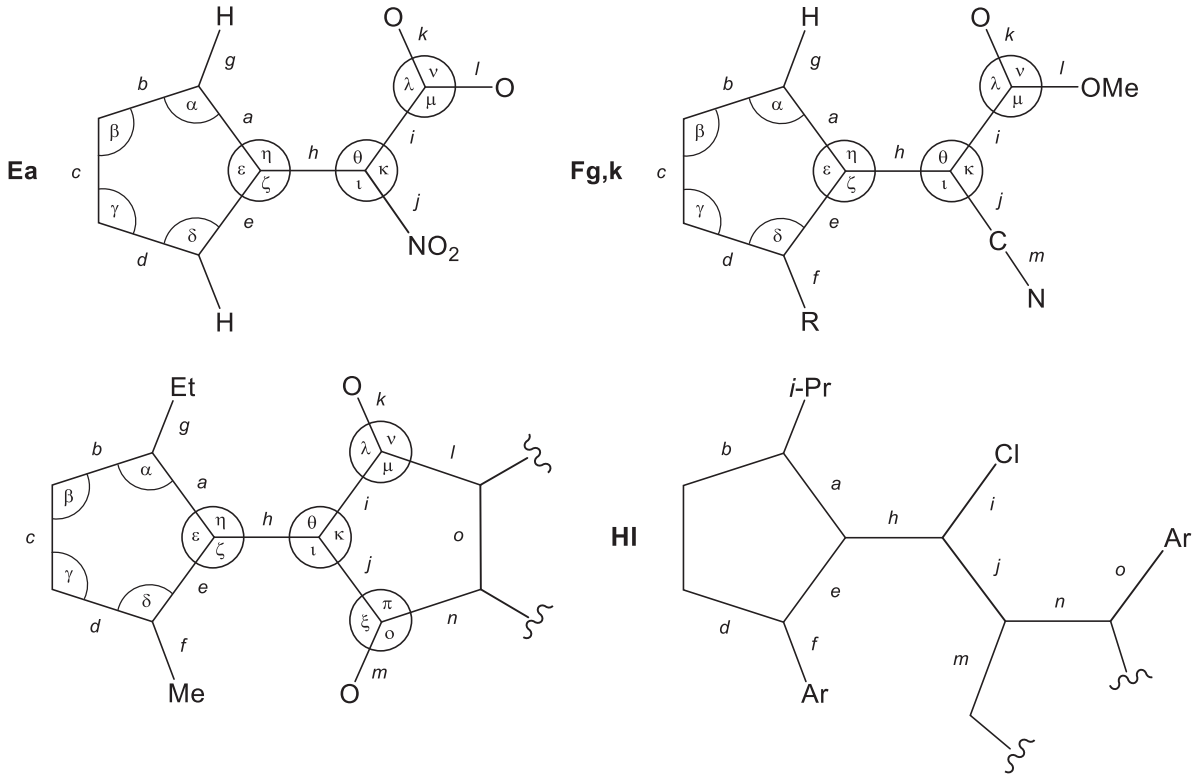
causes a downfield shift of the C_α signal, but to an extent that is too small for an $sp^3 \rightarrow sp^2$ change [even smaller than that observed on deprotonation of the 2-isopropyl-1,3-dimethyl-4,5-dihydro-1*H*-imidazolium ion[17]]. Extending this comparison to include the couple (**92** / **G**), it becomes apparent that polarization of the EWG-bearing class (**G**) is still increased (push-pull olefin): For example, the *N*-methyl groups of the precursors (**11c**) and (**92a,b**) give only one signal each, but while the product (**Cc**) shows two resonances, there are no separate signals with **Ga,b**; accordingly, C(5) of **Ga,b** resonates close to the position of C(5) of **92a,b**, whereas deprotonation of the salts (**11c-e**) causes an upfield shift of 12.7–14.6 ppm (7.6 and 20.3 ppm with **11a,b**). This points to an unhindered rotation about the 'C=C' bond, *i.e.*, to an enhanced contribution of the ylide structure (**RS²**).[74,84] The same phenomenon is deducible from the spectra of **E**, **F**, and **H** (Tables 7, 8). With compound (**Hl**) (Scheme 32) the activation barrier to interconversion of the *E* and *Z* form has been determined, both experimentally and theoretically (MNDO method): It was found to be as low as *ca.* 51 and 57 kJ/mole (average), respectively.[81b]

The ylide character follows also from X-ray diffraction data (Table 10): The compounds studied show an elongated C=C bond (*h*) together with a shortening of the adjacent bonds (*i*, *j*). Nevertheless, the solid-state structures of the compounds (**Ea**) and (**Fg,k**) are fully planar in that region. Regarding **Ea**, this finding meant a definite abandonment of the traditional formula of '5-(dinitromethyl)tetrazole', whereas the data of **Fg,k** served to establish the *E* configuration of class (**F**).

CONCLUSION

The foregoing inspection has shown that 4,5-dihydro-1*H*-tetrazoles having at C(5) either alkyl/aryl (**A, B**) or alkylidene substituents (**C–H**) attract attention for a varied pattern of behaviour, for example: (i) Ring contraction of the classes (**A**) and (**B**) affords diaziridines (a preparatively useful process), while class (**C**)

Table 10. Selected bond distances (Å) and angles (deg) for compounds (**E**), (**F**), and (**H**) from X-ray diffraction



compd (ref.)	*a* α	*b* β	*c* γ	*d* δ	*e* ε	*f* ζ	*g* η	*h* θ	*i* ι	*j* κ	*k* λ	*l* μ	*m* ν	*n* ξ	*o* ο	π
Ea	1.329	1.347	1.283				0.882	1.418	1.400		1.244	1.225				
(34)	111.2	107.3			103.1		128.5	119.9		120.2	116.3	122.6	121.2			
Ea · 2 H_2O	1.337	1.342	1.279		1.337			1.421	1.402	1.402	1.245	1.219				
(38a) [a]	110.7	107.7			103.2	128.4	128.4	119.9	119.9	120.2	116.5	122.3	121.2			
Ea · 2 H_2O	1.341	1.353	1.279	1.353	1.341			1.432	1.403	1.403						
(40)	110.1	107.9	107.9	110.1	103.9		128.0	119.9		120.2						
Fg [b]	1.349	1.350	1.265	1.377	1.357	1.439		1.391	1.436	1.413	1.223	1.330	1.146			
(86)	111.3	103.2	108.0	109.8	102.7	130.5	126.8	119.2	121.8	119.0	124.6	112.2	123.3			
Fk [c]	1.345	1.357	1.269	1.368	1.361	1.470	0.973	1.394	1.443	1.411	1.207	1.338	1.136			
(51)	111.8	107.3	108.6	109.9	102.5	130.7	126.8	118.0	122.4	119.5	125.2	112.0	122.8			
Hi [d]	1.342	1.351	1.266	1.349	1.341	1.469	1.477	1.422	1.431	1.436	1.224	1.492	1.236	1.497	1.402	
(53a)	110.1	106.9	108.9	111.4	102.8	128.3	128.9	125.1	124.8	110.1	129.9	106.3	123.7	129.3	124.1	106.6
Hl [e] (81a)	1.368	1.382		1.376	1.378	1.430		1.370	1.745	1.434			1.327	1.354	1.432	

[a] Structural parameters also calculated (HF/6-311++G** and B3LYP/6-311++G**). [b] R = Ph; dihedral angle between the two ring systems: 59.5°. [c] R = CH_2Bu-*t*. [d] Dihedral angle between the two ring systems: 41°. [e] Ar = 4-$MeOC_6H_4$; structural parameters (*E* and *Z* form) also calculated (MNDO).

forms, diastereoselectively, (*E*)-aziridinimines. (ii) Moreover, the compounds (**C**) dispose of a remarkable proclivity for undergoing cycloaddition with organoazides to afford the spirocycles (**15**) which themselves stand out for noteworthy conversions. (iii) A major aspect of the classes (**E**) and (**F**) concerns tautomerism; it was shown that, in most cases, the alkylidene structure predominates; future studies might include certain 2-(1*H*-tetrazol-5-yl)-1,3-diones,[87] as regards the preference of the β-hydroxyenone or alkylidenetetrazole structure (*cf.* **Fd**)]. (iv) With metal ions derivatives (**F**) are capable of forming novel coordination polymers

through self-organization. (v) EWG-bearing compounds such as **E**–**H** represent stable *C*-ylides; further experiments with these species seem desirable, in particular with derivatives (**F**).

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