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N-YLIDES OF 1,2,3-TRIAZOLES AND TETRAZOLES – AN OVERVIEW

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Abstract – This treatise surveys the preparative chemistry of the title ylides as it developed from the beginnings in the early 1980s.

INTRODUCTION

Among heteroaromatic *N*-ylides – widely known as cycloimmonium ylides[1–4] – azolium representatives constitute a major subdivision. While the first members became already known in the 1960s,[1] derivatives of 1,2,3-triazoles and tetrazoles were not prepared until the 1980s. Since the ylides of these azoles did not receive adequate attention by recent reviewers,[3,4] they will be featured in the present report. Structures to be dealt with are gathered in Chart 1, which exhibits four classes of 1,2,3-triazolium ylides (**A–D**) besides

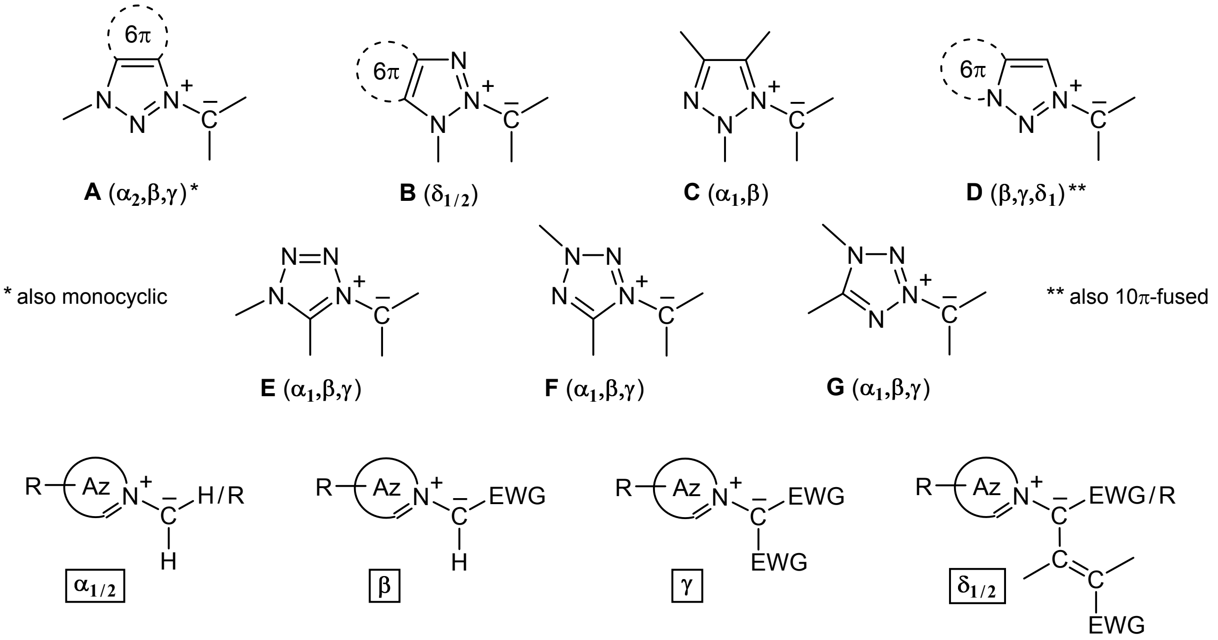
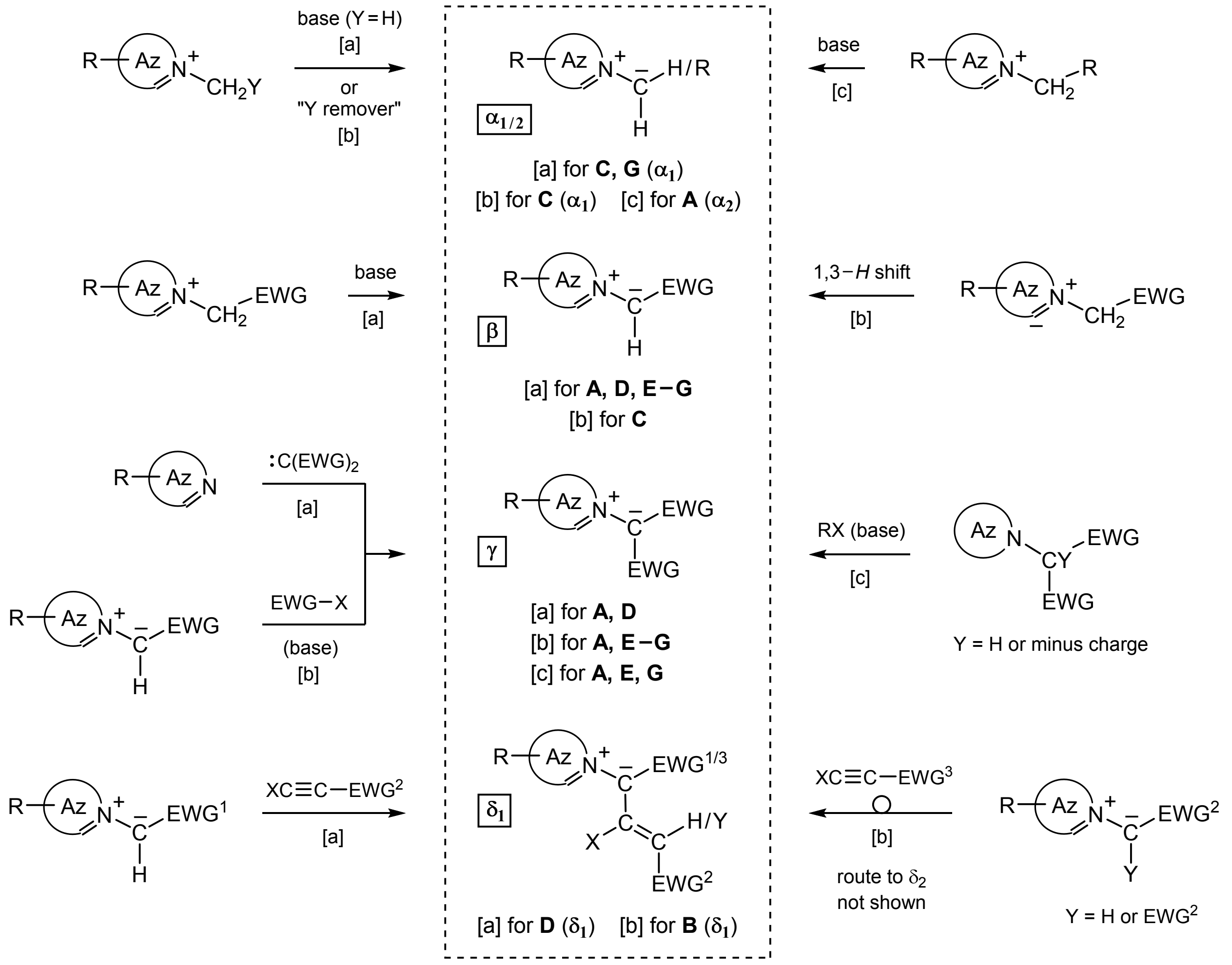


Chart 1. Reported title systems [with indication of ylide types (α – δ)]

[§] **Dedicated to the late Professor Alan R. Katritzky.**



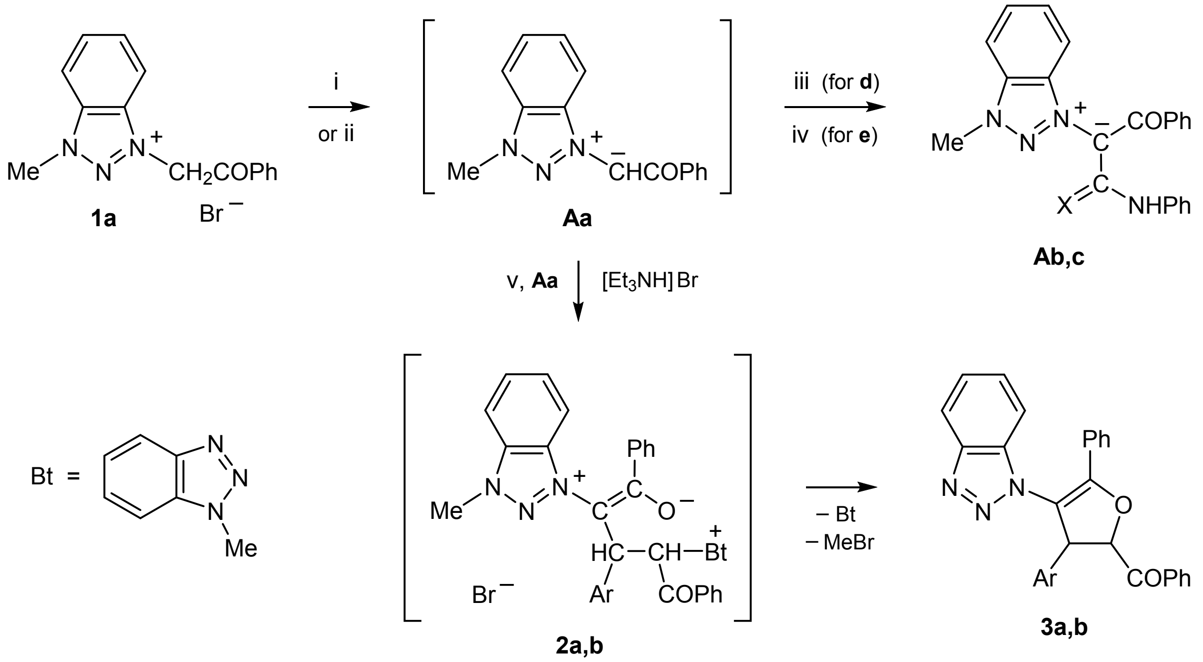
Scheme 1. Entries to ylides (**A**–**G**) arranged by type (α–δ)

three categories of tetrazolium ylides (**E**–**G**), moreover indicating the occurrence of a particular ylide type (α–δ; internal classification). The preparative access is outlined in Scheme 1. This graphic, however, does not display whether a given ylide constitutes an isolable material or an unstable intermediate. Such details (including the transformations of those species) will be disclosed in the chapters to the single classes.

1) *N*-YLIDES OF 1,2,3-TRIAZOLES

a) Class (A)

Following the classical Kröhnke route, treatment of the benzotriazolium salt (**1a**) with alkali carbonate produced the ylide (**Aa**) (Scheme 2).[5] This β-type species (said to be stable in solution[6]) was not isolated and reacted with phenyl isocyanate and isothiocyanate to give the derivatives (**Ab,c**) in reasonable yield.[5] Most interestingly, generation of **Aa** with triethylamine in the presence of benz- or *p*-tolualdehyde caused a 2 : 1 reaction to occur: After attack of the aldehyde on the ylide carbon the resultant adduct coupled to a second molecule of **Aa** to give the species (**2a,b**) which, through expelling 1,3-dimethylbenzotriazolium, furnished the poly-substituted 2,3-dihydrofurans (**3a,b**).[6] – Beyond the unexpected aldehyde-mediated dimerization of **Aa**, this ylide is capable of undergoing cycloadditions with acetylenic esters. As this leads to the new ylide class (**B**), the process will be detailed in the appropriate chapter [see Section (1b)].



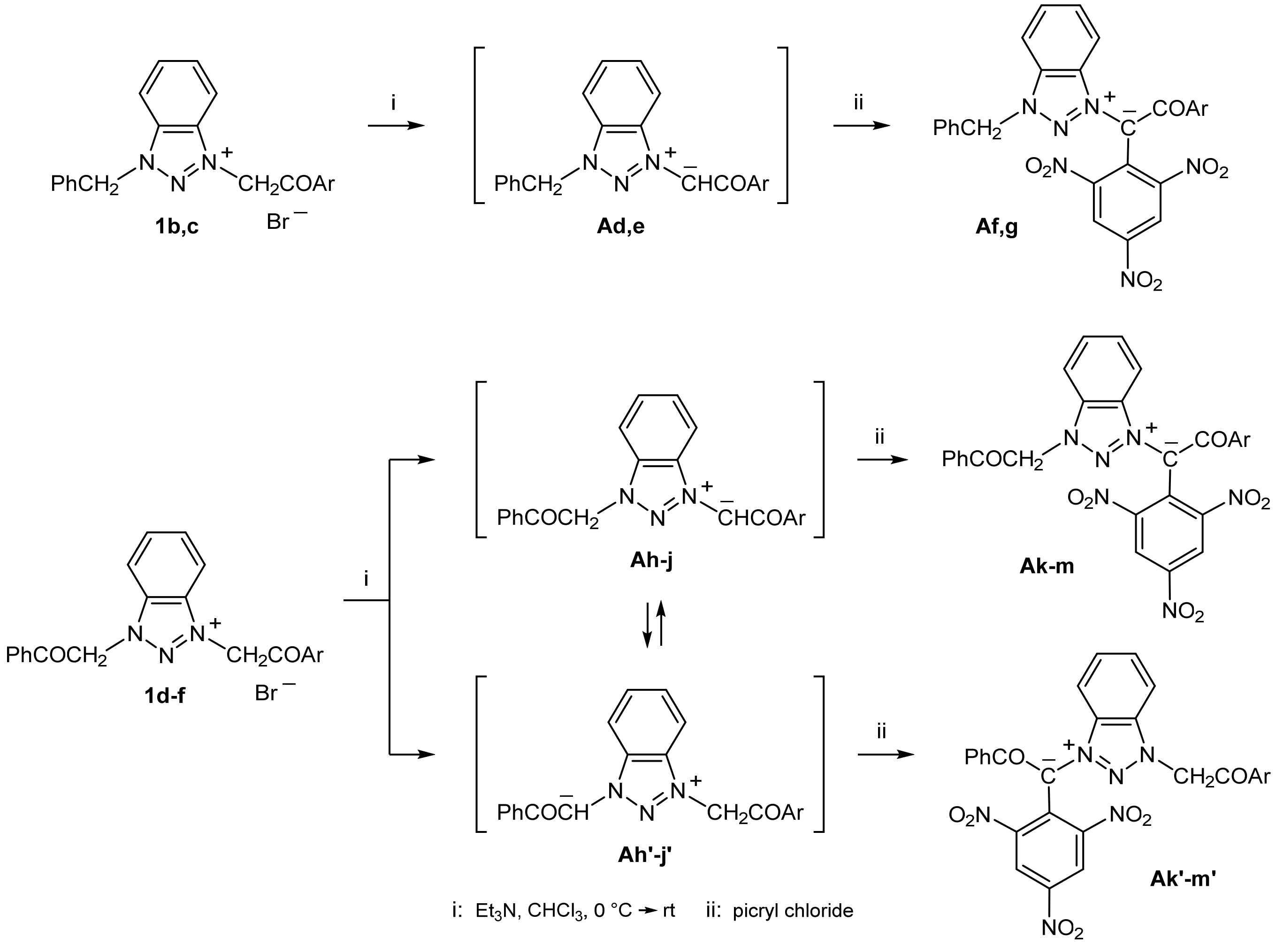
i: K_2CO_3, MeCN or CH_2Cl_2 / H_2O, rt ii: Et_3N, THF, Δ iii: PhNCO iv: PhNCS v: ArCHO

A	X	yield (%)	mp (°C)	$\tilde{\nu}_{CO}$ (cm^{-1}) [a]	δ_{NH} (ppm) [b]	3	Ar	yield (%)	mp (°C)
b	O	54	238−240	1640	12.51	**a**	Ph	25	201−203
c	S	81	188−189	1595	14.51	**b**	4-MeC_6H_4	22	121−123

[a] KBr. [b] DMSO-d_6.

Scheme 2

Much work has been spent on benzotriazolium ylides derived from the salts (**1b-f**) (Scheme 3).[7,8] Two categories should be discerned: substrates having one phenacyl group (**1b,c**) and those bearing two such groups (**1d-f**). With **1b,c** deprotonation takes place regiospecifically with formation of the ylides (**Ad,e**). These species were trapped with picryl chloride to afford the stable γ-type ylides (**Af,g**).[7a] By contrast, with the salts (**1d-f**) either side chain is susceptible to proton loss such as to give mixtures of ylides like **Ah**/**Ah'**, **Ai**/**Ai'**, and **Aj**/**Aj'**, the composition of which is determined by the substituent at the Ar ligand. As expected, the chloro and nitro groups favour the formation of **Ah** and **Aj**, respectively, but the electron-releasing methoxy group should shift the equilibrium toward the isomeric ylide (**Ai'**). Yet, the authors, obviously misunderstanding the meaning of the $\sigma_{p\text{-OMe}}$ constant (which was quoted without the minus sign!), failed to realize this, although their energy studies either uniformly[7a,8a] (AM1 method) or partly[8a] (PM3 method) point to the ylide (**Ai'**) as the predominant species.[9] Thus, the original ratio (75/25) of the products (**Al**/**Al'**) obtained with picryl chloride[7a,8a] should read 25/75 instead. In a complementary (UV spectrometry-based) study of the pK_a values of the two phenacyl groups of **1d-f** the authors found: 9.71/10.53 (**1d**), 10.38/11.82 (**1e**), and 7.21/9.62 (**1f**).[10] Regarding **1e**, again their wrong notion of the $\sigma_{p\text{-OMe}}$ constant (*cf.* above) led them to assign the lower value to the ylide (**Ai**) – an error that follows independently from the reported pK_a values of 1-(4-methoxyphenacyl)-4-phenyl-4*H*-1,2,4-triazolium[11] and 1-(4-methoxyphenacyl)pyridinium.[12]



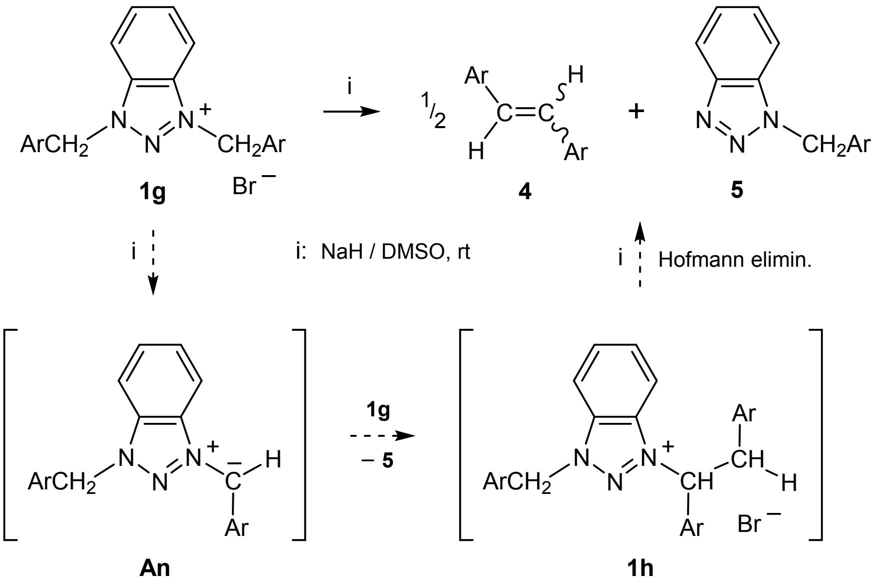
i: Et$_3$N, CHCl$_3$, 0 °C → rt ii: picryl chloride

1	A	Ar	A	yield (%)	ratio	mp (°C)	$\tilde{\nu}_{CO}$ (cm^{-1}) [c]	δ_H (ppm) [d]: MeO; CH$_2$; picryl
b	**d**	4-ClC$_6$H$_4$	**f**	61		119−120	1665, 1569	
c	**e**	4-MeOC$_6$H$_4$	**g**	55		139−140	1603, 1558	
d	**h / h'**	4-ClC$_6$H$_4$	**k / k'**	72 [a]	76 / 24			6.95 / 6.93; 8.60 / 8.64
e	**i / i'**	4-MeOC$_6$H$_4$	**l / l'**	56 [a]	25 / 75 [b]			3.71 / 3.90; 6.87 / 6.94; 8.61 / 8.58 [e]
f	**j / j'**	4-NO$_2$C$_6$H$_4$	**m / m'**	65 [a]	89 / 11			6.92 / 6.94; 8.72 / 8.61

[a] Mixture of both ylides. [b] Ratio corrected (see text). [c] KBr. [d] CDCl$_3$. [e] Values adapted to corrected ratio.

Scheme 3

Benzotriazolium salts like **1g** have recently proved to be useful sources for symmetrical (*E*)-stilbenes (**4**) (Scheme 4).[13] Under the influence of a strong base these salts undergo homocoupling, which commences with formation of the respective ylide (**An**). This species is attacked by a second molecule of **1g** to give, after loss of **5**, the intermediate (**1h**). The latter stabilizes *via* Hofmann elimination to provide, besides further **5**, the desired olefin (**4**). As apparent from the list of examples prepared by this procedure, both electron-releasing and -withdrawing groups at the benzyl ligand have a detrimental effect on the yield.

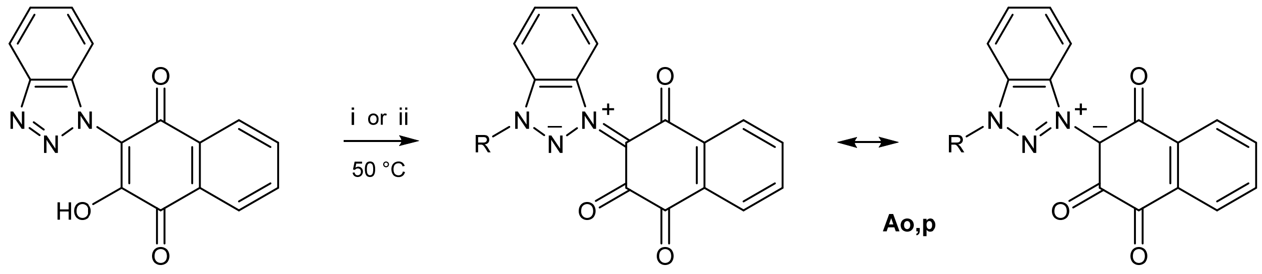


Ar	**4**: yield (%)	*E* : *Z*
Ph	91	100 : 0
2/3/4-MeC$_6$H$_4$	72 / 70 / 73	100 : 0 (all)
3-MeOC$_6$H$_4$	64	100 : 0
2/3/4-ClC$_6$H$_4$	59 / 57 / 61	90 : 10 / 86 : 14 / 98 : 2
4-BrC$_6$H$_4$	64	95 : 5
4-FC$_6$H$_4$	65	100 : 0

Scheme 4

While the aforementioned ylide preparations are two-step procedures that require isolation of a quaternary salt as the immediate precursor, this route is abridged in the case of the ylides (**Ao,p**) (Scheme 5).[14] When the hydroxyquinone-substituted benzotriazole (**6**) was reacted with benzoyl as well as benzenesulfonyl chloride, the products of quaternization are acidic to such an extent as to deprotonate *in situ* once they were formed [for a similar approach to ylides of the class (**E**) and (**G**), *cf.* Section (2b) and (2c)].

A short entry of the 'reverse order' constitutes the direct insertion of the ylide function into an azole. This has been achieved with 1-ethyl-1,2,3-triazole and two 1-substituted benzotriazoles (Scheme 6). Treatment of these compounds with tetracyanoethylene oxide gave rise to the dicyanomethylides (**Aq,r**)[15] and (**As**).[17]



6

Ao,p

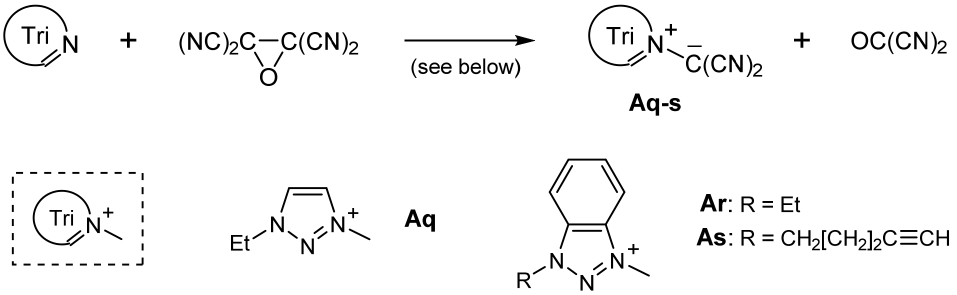
i: PhCOCl / pyridine ii: $PhSO_2Cl$ / pyridine

A	R	yield (%)	mp (°C)	$\tilde{\nu}_{PhCO}$ (cm^{-1}) [a]
o	PhCO	59	181−182	1805
p	$PhSO_2$	63	231−232	

[a] KBr.

Scheme 5

The regioselectivity of this process is consistent with the rules that govern the quaternization of azoles; hence, an ylide of the class (**B**) cannot arise in this case. Whereas the procedure works also well with 1,2,4-triazoles,[15] it fails with 2-methylbenzotriazole[15] (and likewise tetrazoles[18]) because of insufficient nucleophilicity of these substrates. – For the chemical behaviour of **Ar,s**, see Section (1b).



Aq-s

Aq

Ar: R = Et
As: R = $CH_2[CH_2]_2C\equiv CH$

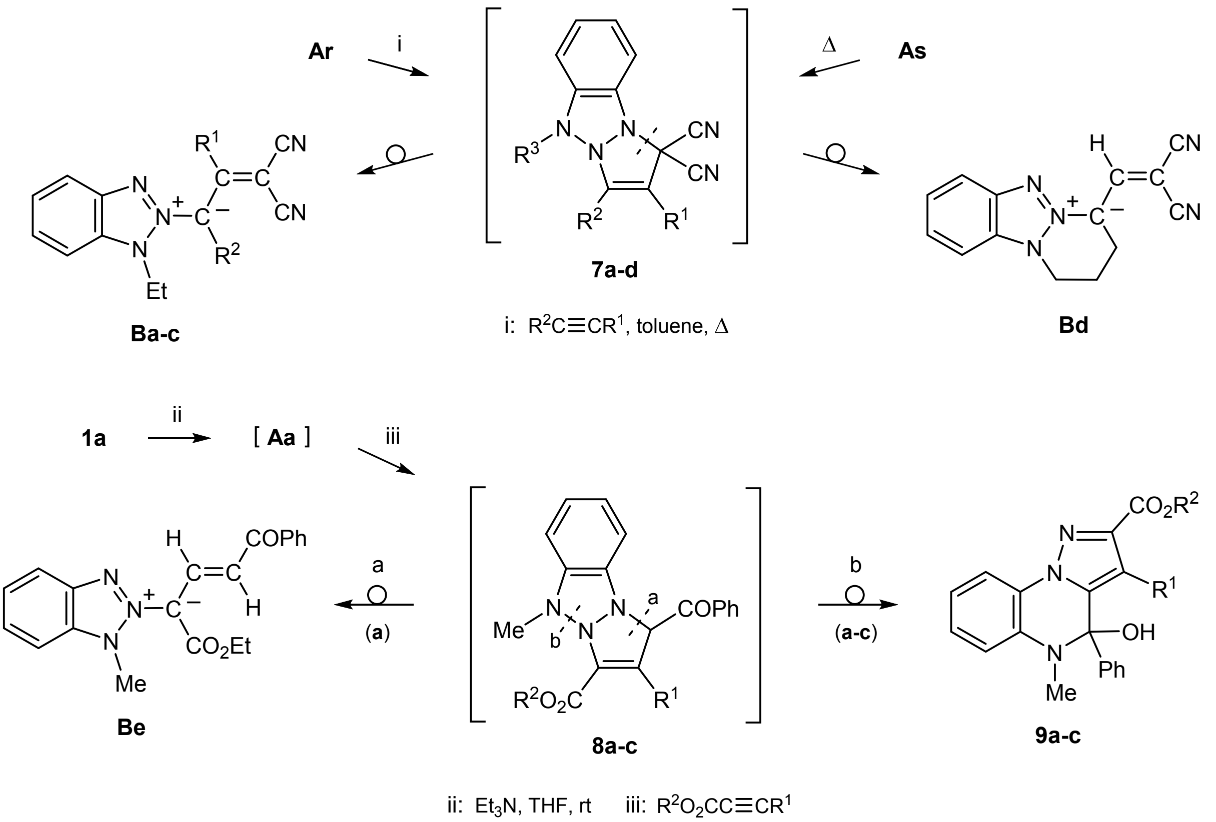
A	yield (%)	conditions	mp (°C)	λ_{max} (nm) [a]	$\tilde{\nu}_{C\equiv N}$ (cm^{-1}) [b]	δ_{C^-} (ppm) [c]	ref.
q	73	AcOEt, 0 °C	176−177		2190, 2160	51.1	15, 16 [d]
r	21	Et_2O, rt	160−161		2190, 2150		15
s	56	Et_2O, rt	161	446	2180, 2150		17

[a] CH_2Cl_2. [b] KBr. [c] DMSO-d_6. [d] Ref.[16] for δ_{C^-} only.

Scheme 6

b) Class (B)

Since ylides of the preceding class contain an azomethine imine unit, they were envisaged as candidates for 1,3-dipolar cycloadditions. Indeed, reactions of the derivative (**Ar**) with alkynes in an apolar solvent gave cycloadducts like **7a-c**, according to the predicted regioselectivity (Scheme 7).[19a] But – apparently not recognized at first[19a] – these species eluded isolation: they underwent cleavage of the N–$C(CN)_2$ bond to give members of a novel ylide class, *viz.* the compounds (**Ba-c**) [representing the δ_1 type ('allylide')].[19b] Later, an intramolecular example of this kind of cycloaddition, *i.e.* **As** → **7d** → **Bd**, was also reported.[17]



i: $R^2C{\equiv}CR^1$, toluene, Δ

ii: Et_3N, THF, rt iii: $R^2O_2CC{\equiv}CR^1$

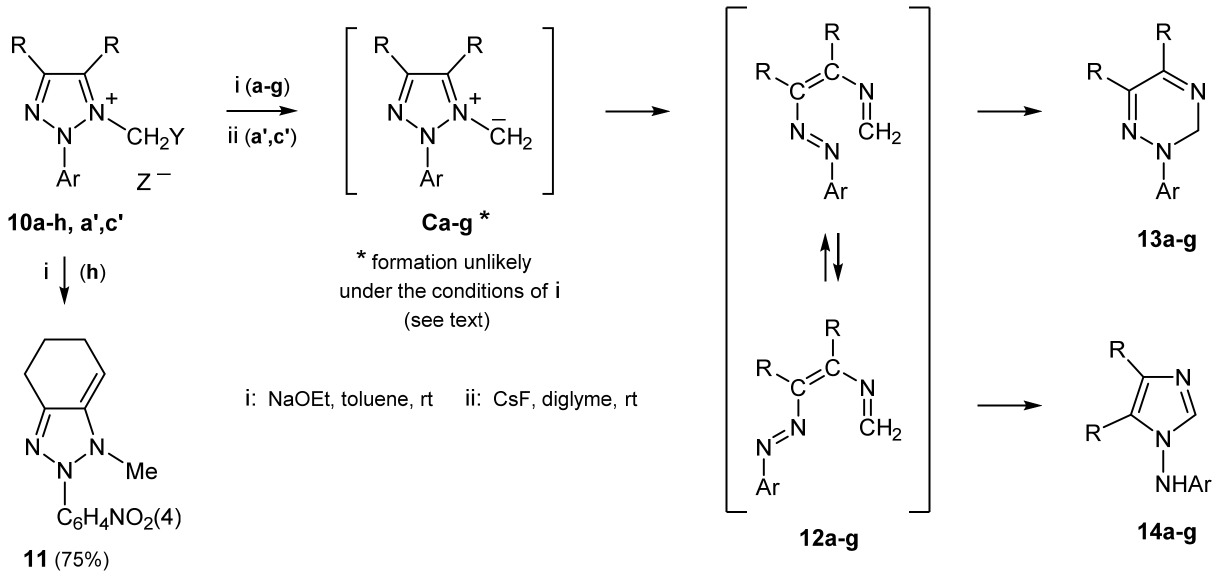
7, B	R^1	R^2	R^3	Δ time (h)	yield (%)	mp (°C)	8, 9	R^1	R^2		yield (%)	mp (°C)
a	H	CO_2Me	Et	15	37	196−198				Be	30	162
b	CO_2Me	CO_2Me	Et	15	34	203−204	a	H	Et	9a	52	194−196
c	Ph	CO_2Et	Et	480	14	179−180	b	CO_2Me	Me	b	25	175−177
d	H	$-[CH_2]_3-$		48	42	239	c	Ph	Et	c	20	197−199

Scheme 7

Surprisingly, cycloadducts obtained from the ylide (**Aa**), *viz.* the derivatives (**8a-c**), tend to ring-open in a different way: here fission of the triazole half-ring predominates (step b), followed by a new ring closure through engagement of the MeN unit and the benzoyl group to afford pyrazolo[1,5-*a*]quinoxalines like **9**.[6] Only with **8a** cleavage of the pyrazole half-ring (step a) took place too (→ **Be**), but also here the tricycle (**9a**) was obtained as the major product. Extending the experiments to dimethyl butynedioate and ethyl phenylpropiolate, the analogues (**9b,c**) were the sole materials found. The structure of these unexpected heterocycles was confirmed by X-ray diffraction.[6] – No direct access to **B** seems to have been reported till now, *e.g.*, quaternization of 2*H*-1,2,3-triazoles (or -benzotriazoles) having an α-CH-acidic group at N(2).

c) Class (C)

The majority of cited members of this class belong to the α_1 type (Chart 1). The search for these species commenced around 1990 in pursuit of previous work on the analogous *N*-aminides and *N*-oxides;[20] their behaviour as 1,3-dipoles was the proper incentive. First efforts to generate **C** started from the *N*-methyl- (**10a-h**) and *N*-(silylmethyl)triazolium salts (**10a',c'**) (Schemes 8).[21,22] When the former were treated with triethylamine or butyllithium, the base removed the methyl group, but employing sodium ethoxide, proton abstration could be effected. Apart from **10h** which was attacked at the six-membered ring to furnish **11**,[22]

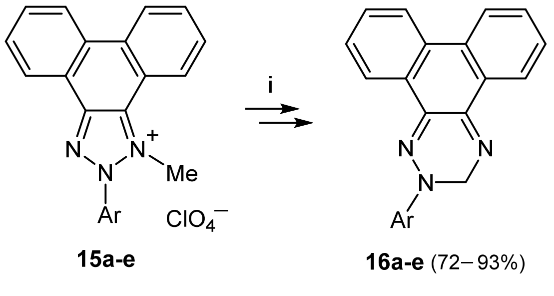


* formation unlikely under the conditions of **i** (see text)

i: NaOEt, toluene, rt   ii: CsF, diglyme, rt

10 [a], **C**, **12**	Y	Z	R	Ar		yield (%) [b]	mp (°C)		yield (%) [b]	mp (°C)
a / a'	H / $SiMe_3$	ClO_4 / CF_3SO_3	Ph	Ph	**13a**	73 / 72	87−89	**14a**	15 / 15	153−155
b	H	ClO_4	Ph	4-BrC_6H_4	**b**	57	104−106	**b**	25	211−213
c / c'	H / $SiMe_3$	ClO_4 / CF_3SO_3	Ph	4-$NO_2C_6H_4$	**c**	45 / 45	196	**c**	44 / 45	279
d	H	ClO_4	Ph	4-MeC_6H_4	**d**	78	98 −100	**d**	10	173−175
e	H	ClO_4	Ph	4-$MeOC_6H_4$	**e**	83	107−109	**e**	trace	
f	H	ClO_4	Me	4-BrC_6H_4	**f**	trace		**f**	83	153−155
g	H	ClO_4	Me	4-$NO_2C_6H_4$	**g**	5	120−122	**g**	85	223−225
h	H	ClO_4	[c]	4-$NO_2C_6H_4$						

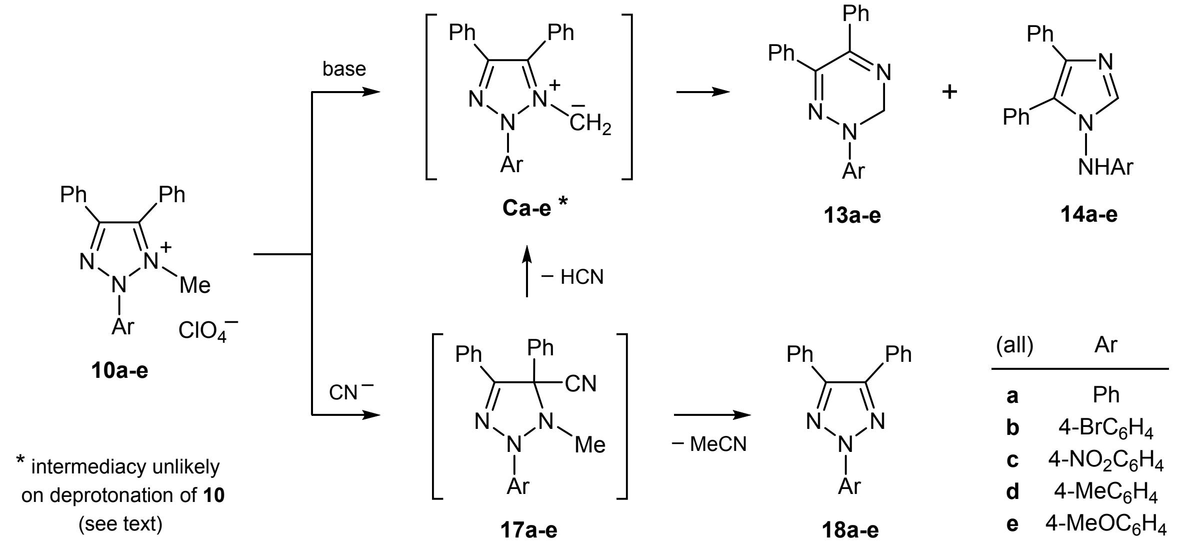
[a] Because of high lability, **10a',c'** (formed on treatment of the appropriate 2*H*-1,2,3-triazoles with trimethylsilylmethyl triflate) were used unpurified. [b] Product balance (**13**, **14**) was made up by recovered substrate (**10**). [c] R,R = $[CH_2]_4$.



15, 16	Ar
a	Ph
b	4-BrC_6H_4
c	4-ClC_6H_4
d	4-$MeOC_6H_4$
e	4-MeC_6H_4

Scheme 8

the salts (**10a-g**) reacted at the desired position to eventually give mixtures of the dihydro-1,2,4-triazines (**13a-g**) and the 1-aminoimidazoles (**14a-g**), the ratio of which depended on the substituents. Identical findings, *i.e.* **13a,c** and **14a,c**, resulted on treatment of the salts (**10a',c'**) with cesium fluoride.[22] On the other hand, the alkoxide-caused ring transformation of the phenanthrotriazolium salts (**15a-e**) only gave the dihydrotriazines (**16a-e**) (Scheme 8).[23] A complementary study of the behaviour of **10a-e** toward other bases including cyanide ion allowed additional insights into the formation of **13** and **14**, in particular as regards the proportions (Schemes 9).[24] These heterocycles, the structures of which had been confirmed by



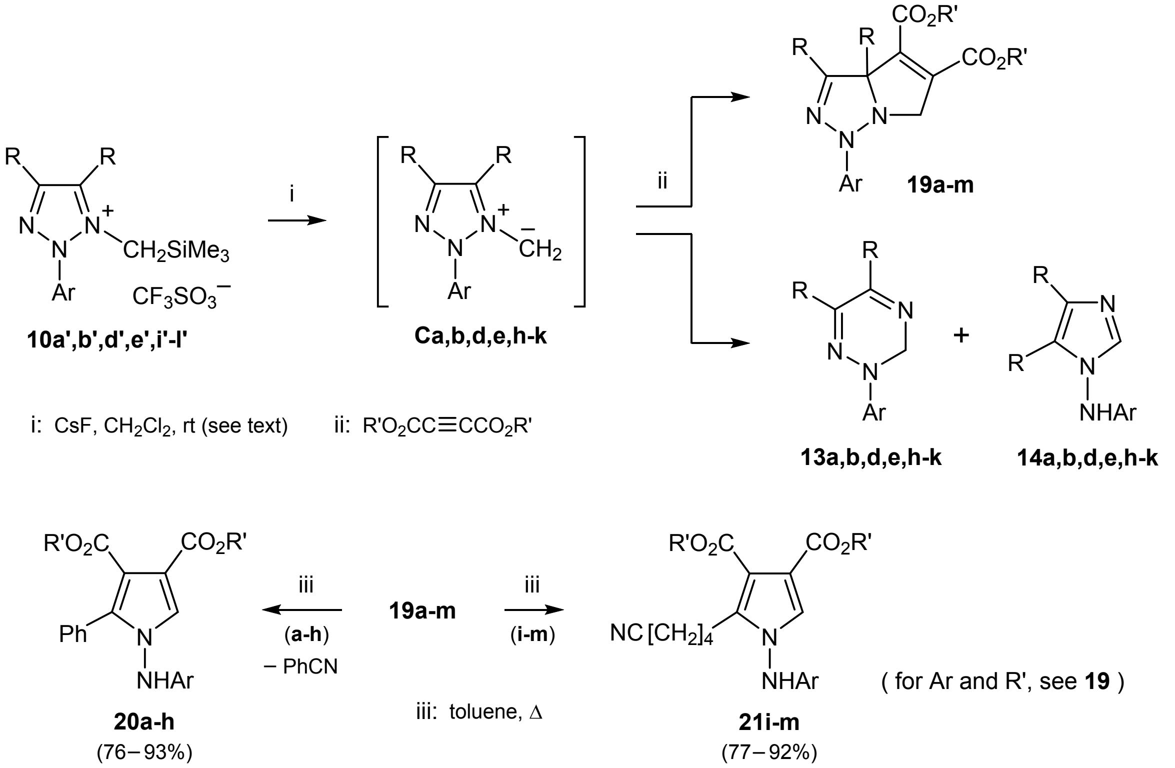
substrate	base [a]	**13**	[b]	**14**	[b]	**18**	[b]	[c]	substrate	base [a]	**13**	[b]	**14**	[b]	**18**	[b]	[c]
10a	NaOEt	**a**	69	**a**	14			8	**10b**	NaOEt	**b**	26	**b**	11			50
	KOBu-*t*	**a**	18	**a**	6			70		KOBu-*t*	**b**	31	**b**	16			49
	LiN(Pr-*i*)$_2$	**a**	69	**a**	13			18		LiN(Pr-*i*)$_2$	**b**	46	**b**	23			30
	KCN	**a**	8	**a**	7	**a**	10	73		KCN [d]	**b**	13	**b**	12	**b**	17	68
10c	NaOEt	**c**	24	**c**	20			54	**10d**	NaOEt	**d**	56	**d**	13			30
	KOBu-*t*	**c**	23	**c**	19			49		KOBu-*t*	**d**	40	**d**	14			40
	LiN(Pr-*i*)$_2$	**c**	23	**c**	20			43		LiN(Pr-*i*)$_2$	**d**	52	**d**	13			34
	KCN	**c**	12	**c**	12	**c**	5	66		KCN	**d**	12	**d**	4	**d**	5	77
10e	NaOEt	**e**	83	**e**	trace			9	**10e**	KCN	**e**	9	**e**	7	**e**	6	67

[a] Using 1.1 mol in toluene (rt); exception with LiN(Pr-*i*)$_2$: solvent THF. [b] Conversion (%). [c] Recovery of **10** (%). [d] Reaction at 45 °C.

Scheme 9

the X-ray method,[22] arose by a 6π-electrocyclic process of the triazatrienes (**12a-g**) (Scheme 8). The latter species were shown by *ab initio* 3-21G calculations to be thermodynamically preferred over the ylides (**Ca-g**) (the opposite applies to the related *N*-oxides, while the *N*-aminides are borderline).[21] This meant: Does an ylide (**C**) form at all in the *base*-induced reactions? Considering that the trienes (**12**) can arise directly from **10** through a Hofmann-type degradation and, second, that interception of the ylides with

1,3-dipolarophiles failed, the occurrence of **C** appeared doubtful.[21] Under divergent conditions, however, ylide formation did take place: (i) on decomposition of the above adducts (**17**), namely β-elimination of hydrogen cyanide,[24] and (ii) on desilylation of the side chain of the specialized triazolium salts (**10'**).[25–28] This will be evidenced below (Scheme 10):

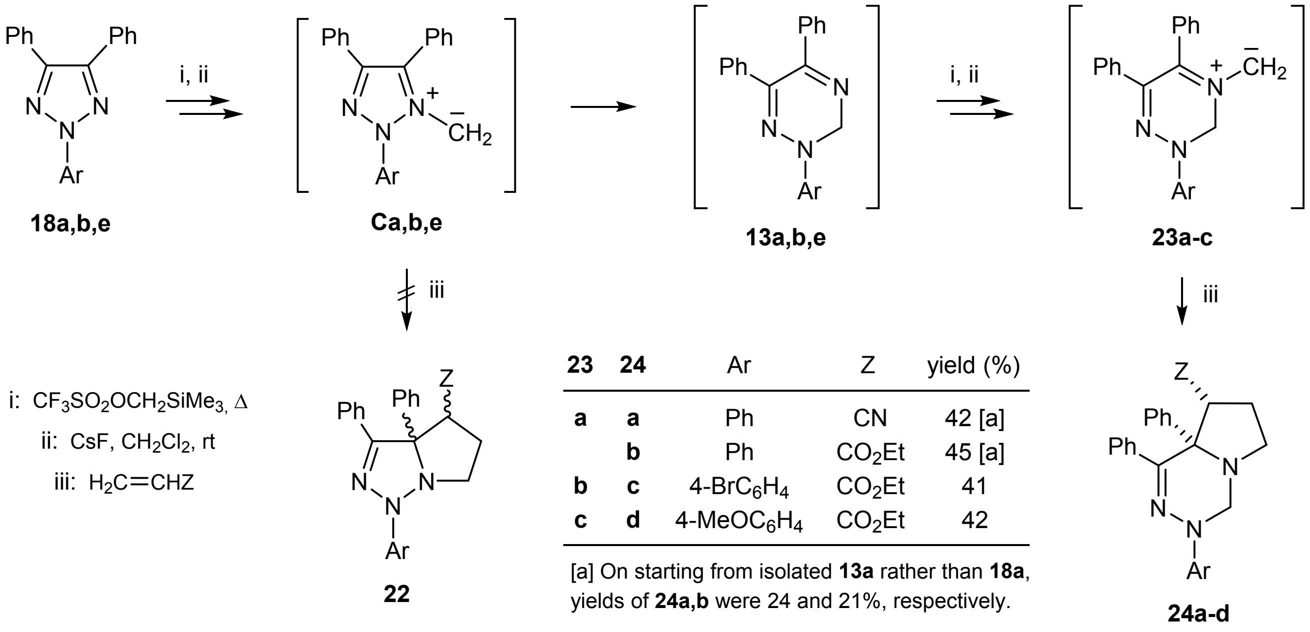


10 [a]	**C**	R	R	Ar	R'		yield (%)	mp (°C)		yield (%)
a'	**a**	Ph	Ph	Ph	Me / Et	**19a** / **e**	50 / 40	129–130 / 123–125	**13, 14a**	23.5 / 9.5, 8.5 / 4
b'	**b**	Ph	Ph	4-BrC_6H_4	Me / Et	**b** / **f**	49.5 / 39.5	142–144 / 108–110	**b**	25 / 17, 7.5 / 4
d'	**d**	Ph	Ph	4-MeC_6H_4	Me / Et	**c** / **g**	52.5 / 34	171–173 / 126–128	**d**	21 / 17.5, 7.5 / 5
e'	**e**	Ph	Ph	4-MeOC_6H_4	Me / Et	**d** / **h**	47.5 / 36	154–156 / 124–125	**e**	22.5 / 16, 8 / 5
i'	**h**	–$[CH_2]_4$–		Ph	Me / Et	**i** / **j**	40 / 35	129–131 / 79–81	**h**	10 / 25, 12 / 27
j'	**i**	–$[CH_2]_4$–		4-BrC_6H_4	Me	**k**	31	128–130	**i**	13, 42
k'	**j**	–$[CH_2]_4$–		4-MeC_6H_4	Me	**l**	42	130–132	**j**	14, 20
l'	**k**	–$[CH_2]_4$–		4-MeOC_6H_4	Me	**m**	28	106–108	**k**	8, 43

[a] Substrates (**10**) were used unpurified (*cf.* Scheme 8).

Scheme 10

Treatment of the diphenyl-substituted triazolium salts (**10a',b',d',e'**) with cesium fluoride in the presence of dimethyl/diethyl butynedioate gave the pyrrolotriazole derivatives (**19a-h**);[25,26] accordingly, trapping of the ylide (**Cb**) that originated from **17b** (*cf.* Scheme 9) led to **19b** (27%).[24] Side products of **19** are the above compounds (**13**) and (**14**). These materials result from ring opening of **C** – a reaction that could not be fully avoided, even if the dipolarophile was present before the cesium fluoride was added. Extending the alkyne-based experiments to the bicyclic ylides (**Ch-k**), which were generated from the salts (**10i'-l'**), the derivatives (**19i-m**) were isolated.[27] All of these cycloadducts proved surprisingly stable, in striking contrast to those formed from the analogous *N*-oxides and *N*-aminides which rearrange *in* situ.[20] Only prolonged heating in toluene effected degradation of **19**; the process, however, took a different course in that the original ylide bond was retained and 1-aminopyrroles (**20**/**21**) were formed. While **19a-h** extruded benzonitrile to afford **20a-h**,[25,26] double ring opening of the tricyclic substrates (**19i-m**) led to compounds like **21i-m**, the side chain of which originates from the former six-membered ring.[27] Of these materials, the derivatives (**19e**) and (**20e**) have been characterized by X-ray crystallography.[25,26]



i: $CF_3SO_2OCH_2SiMe_3$, Δ
ii: CsF, CH_2Cl_2, rt
iii: $H_2C{=}CHZ$

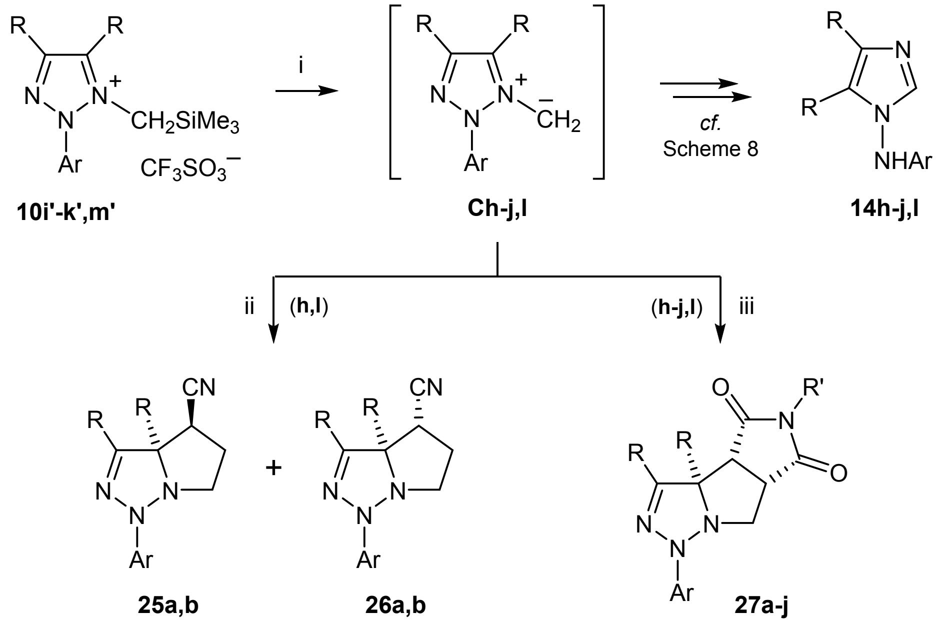
23	24	Ar	Z	yield (%)
a	a	Ph	CN	42 [a]
	b	Ph	CO_2Et	45 [a]
b	c	4-BrC_6H_4	CO_2Et	41
c	d	4-$MeOC_6H_4$	CO_2Et	42

[a] On starting from isolated **13a** rather than **18a**, yields of **24a,b** were 24 and 21%, respectively.

Scheme 11

While interception of the diphenyl-substituted ylides (**Ca,b,d,e**) worked well with alkynes, experiments using alkenes (namely acrylonitrile and ethyl acrylate) failed to afford the envisaged cycloadducts (**22**) (Scheme 11).[26] Rather, starting from the triazoles (**18a,b,e**), a reaction cascade led to another kind of cycloadducts, *viz.* the pyrrolotriazines (**24a-d**). Here the authors observed that, quite remarkably, the *in situ* quaternization of **13** (to be followed by desilylation giving **23**) did not take place in the absence of the dipolarophile, even if the quaternizing reagent was used in excess.

In contrast to the diphenyl-substituted ylides (**Ca,b,e**) the tetramethylene and dimethyl derivatives (**Ch,l**) could be trapped with acrylonitrile (Scheme 12). The extent of this cycloaddition, however, was modest; mixtures of the *endo*- (**25a,b**) and *exo*-tetrahydropyrrolotriazoles (**26a,b**) arose, with the former isomers predominating. Major side products were the aminoimidazoles (**14h**) and (**14l**). Employing *N*-substituted maleimides as dipolarophiles, the ylides (**Ch-i**) furnished the tricyclic adducts (**27a-c**), (**27e**), and (**27g-i**), respectively, while from the congener (**Cl**) the analogues (**27d,f,j**) were obtained. All of these derivatives



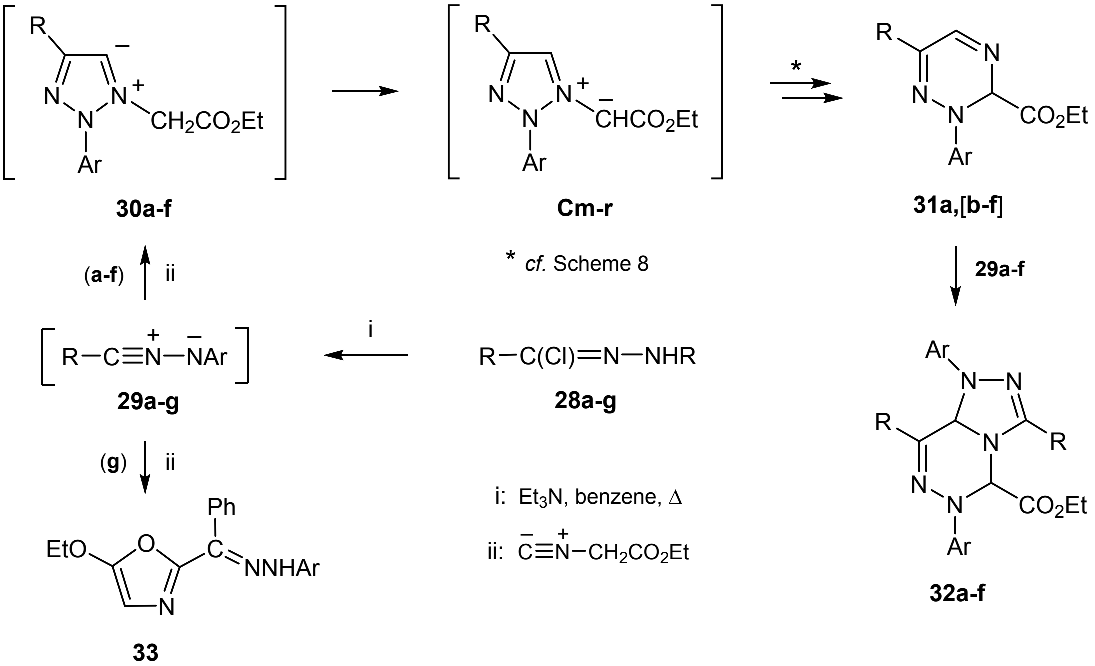
i: CsF, CH_2Cl_2, rt (see text) ii: $H_2C{=}CHCN$ iii: *N*-R'-maleimide

10	C	R R	Ar	R'		yield (%)	mp (°C)	besides (%)
i'	**h**	$-[CH_2]_4-$	Ph		**25a**	8	127–129	**14h** (70)
m'	**l**	Me Me	Ph		**b**	10	gum	**l** (80)
i'	**h**	$-[CH_2]_4-$	Ph		**26a**	5	100–102	–
m'	**l**	Me Me	Ph		**b**	5	gum	–
i'	**h**	$-[CH_2]_4-$	Ph	Ph	**27a**	20	172–174	**h** (57)
j'	**i**	$-[CH_2]_4-$	$4\text{-}BrC_6H_4$	Ph	**b**	17	177–179	**i** (76)
k'	**j**	$-[CH_2]_4-$	$4\text{-}MeC_6H_4$	Ph	**c**	29	171–173	**j** (55)
m'	**l**	Me Me	Ph	Ph	**d**	19	153–154	**l** (75)
i'	**h**	$-[CH_2]_4-$	Ph	*t*-Bu	**e**	20	133–136	**h** (69)
m'	**l**	Me Me	Ph	*t*-Bu	**f**	17	gum	**l** (58)
i'	**h**	$-[CH_2]_4-$	Ph	Me	**g**	22	132–133	**h** (73)
j'	**i**	$-[CH_2]_4-$	$4\text{-}BrC_6H_4$	Me	**h**	11	133–134	**i** (65)
k'	**j**	$-[CH_2]_4-$	$4\text{-}MeC_6H_4$	Me	**i**	30	gum	**j** (65)
m'	**l**	Me Me	Ph	Me	**j**	21	133–135	**l** (65)

Scheme 12

display *exo*-stereochemistry – a finding that has been rationalized *via* the transition state. As with the experiments using acrylonitrile, major amounts of the respective aminoimidazoles (**14**) were formed.[28]

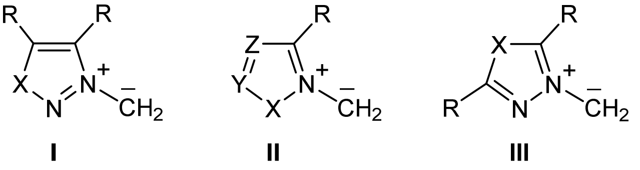
The occurrence of β-type ylides (**C**) has been invoked to explain the formation of triazines (**31**) during base-induced reactions starting from hydrazonoyl chlorides (**28**) and ethyl isocyanoacetate (Scheme 13).[29] The multistep process commenced with the generation of the nitrilimines (**29a-f**) which combined with the isocyanide to form the triazolium structures (**30a-f**) – according to a principle detected in the 1980s.[30] Owing to the acidic side chain, rapid proton transfer led to the ylides (**Cm-r**) which in turn ring-expanded to the triazines (**31a-f**) (*cf.* Scheme 8). Since the latter are highly prone to cycloadd to the nitrilimine (**29**), the bicycles (**32b-f**) were obtained instead. An exception to the formation of **30** constitutes the behaviour of the initial (*i.e.* linear) adduct of nitrilimine (**29g**) and isocyanide: Due to the electron-withdrawing nitro group, ring closure by N–N bond building was severely hampered so as to lead exclusively to the oxazole (**33**). In the experiments with **28a-f**, however, analogues of (**33**) were observed in minor amounts only.[29]



C	28−32	R	Ar		yield (%)	mp (°C)
m	a	Ph	Ph	32a	51	110−113
n	b	4-MeOC$_6$H$_4$	Ph	b	43	167−170
o	c	Ph	4-MeOC$_6$H$_4$	c	31	109−112
p	d	COMe	Ph	d	54	133−136
q	e	COMe	4-MeC$_6$H$_4$	e	56	134−137
r	f	CO$_2$Et	4-BrC$_6$H$_4$	f	69	109−113
	g	Ph	4-NO$_2$C$_6$H$_4$	33	87	202−206

Scheme 13

Addendum: In pursuit of the work on α$_1$-type ylides of class (**C**), several analogues have been studied. These systems are shown in Chart 2; their treatment, however, falls outside the scope of this review.

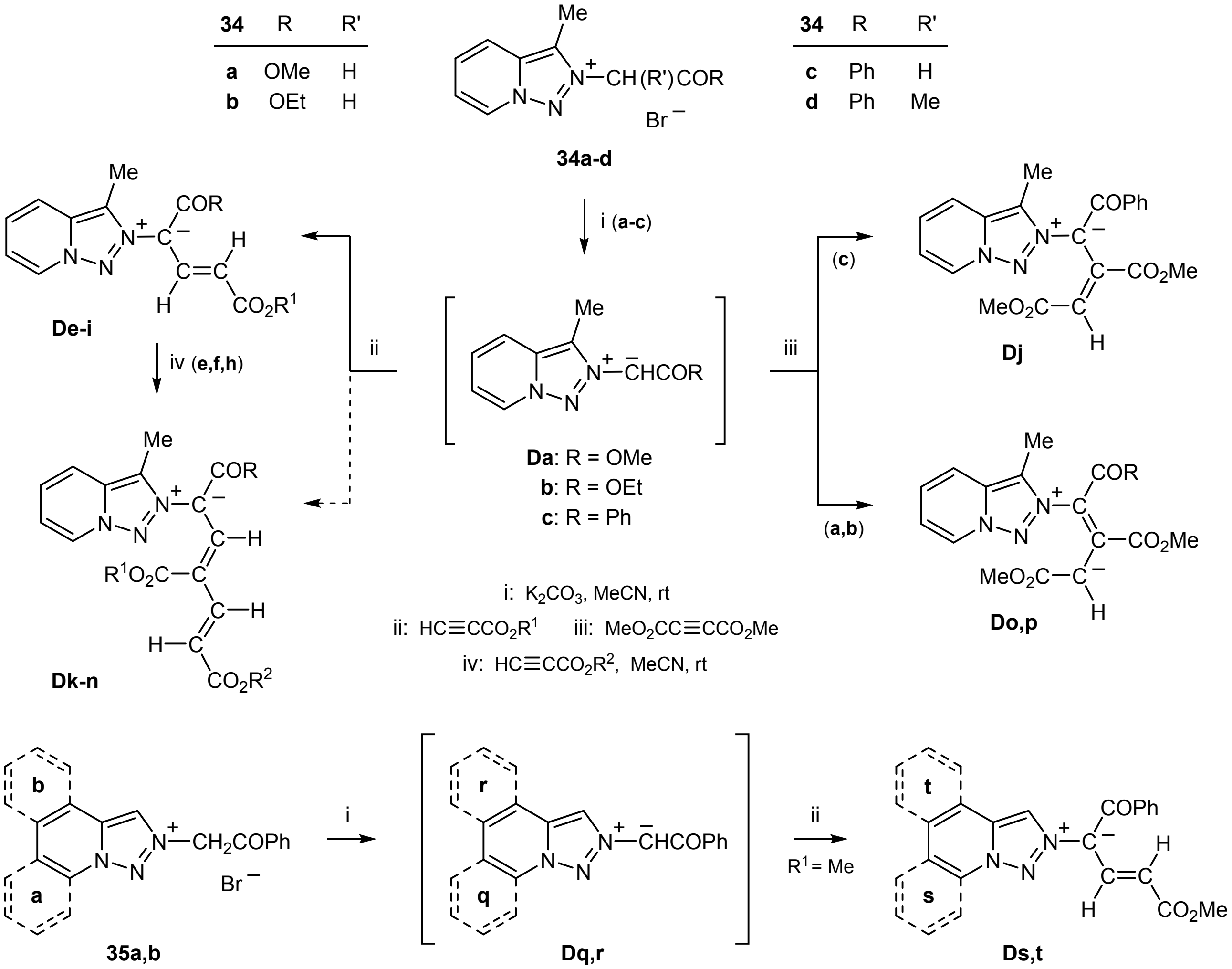


I: X	ref.	**II**: X	Y	Z	ref.	**III**: X	ref.
S	31	O	N	CR	33	O	35
Se	32	S	N	CR	34	S	36
		S	CR	N	34		

Chart 2. α$_1$-Type azolium *N*-ylides showing behaviour of class (**C**)

d) Class (D)

These ylides might be looked at as mere derivatives of class (**A**), but since a number of reactions proceed with triazole ring opening (due to the fused heterocycle), system (**D**) stands apart. Most attention has been paid to the behaviour towards electron-poor alkynes and alkenes, showing that the results strongly depend on the conditions. When the ylides (**Da-c**) – generated from **34a-c** – reacted with an alkyl propiolate in a *polar* solvent, Michael adducts like **De-i** arose (Scheme 14); a pyrazolotriazole analogous to **7**/**8** (Scheme 7)

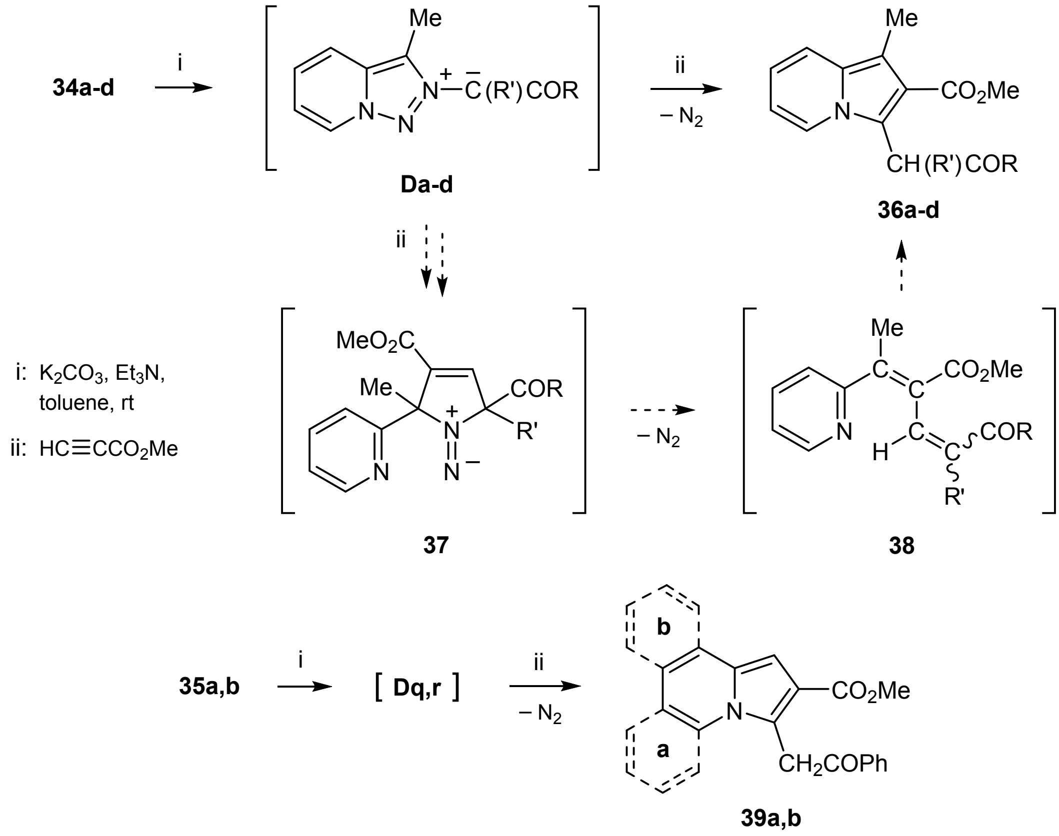


D	R	R^1	yield (%)	mp (°C)	δ_{C^-} (ppm) [a]	D	R	R^1	R^2	yield (%) [b]	mp (°C)	δ_{C^-} (ppm) [a]
e	OMe	Me	65	80−82	90.96	k	OMe	Me	Me	16 / 100	194−195	96.02
f	OEt	Me	82	95−96	91.38	l	OEt	Me	Me	6 / 100	153−155	96.56
g	Ph	Me	43	170−173	106.2	m	OMe	Et	Et	30 / 100	154−155	95.87
h	OMe	Et	63	144−145	90.87	n	OMe	Me	Et	100	156−158	95.92
i	Ph	Et	80	210−211	106.43	o	OMe			52	147−148	84.53
j			70	188−189	100.76	p	OEt			61	184−185	79.06
s			52	221−223	109.69	t				48 [c]	177−179	108.67

[a] $CDCl_3$ (except **Dj,o,p**: DMSO-d_6). [b] Yields of **Dk,l,m**: left, directly from intermediary ylides (**Da,b,a**), respectively; right, from isolated ylides (**De,f,h**), respectively. [c] Besides 11% **39b** (see Scheme 15).

Scheme 14

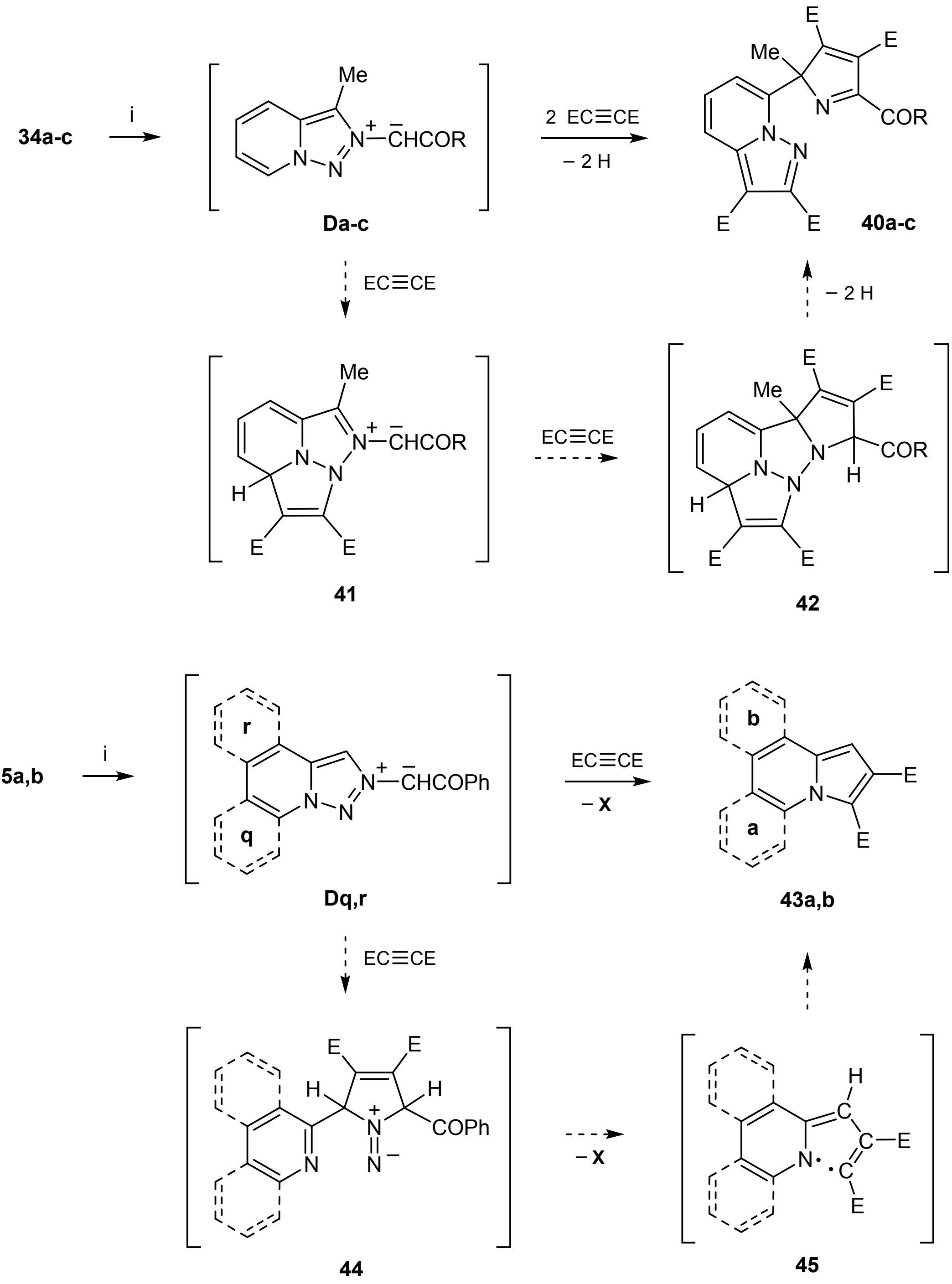
was excluded, *inter alia* because of the orange colour.[37] These new ylides can add another alkyne unit to form dienic ylides like **Dk-n** (confirmed by X-ray analysis of **Dk**). Hence, starting from the salts (**34a,b**), the derivatives (**Dk-m**) occurred as side products of **De,f,h**. But applying dimethyl butynedioate, only 1:1 adducts like **Dj** and **Do,p** were found (the mesomeric structures of **Do,p** were suggested by spectroscopy). Turning to the quinoline- and isoquinoline-fused ylides (**Dq**) and (**Dr**), these species (made from **35a,b**) reacted with methyl propiolate to give the adducts (**Ds,t**) – in close analogy to the process (**Dc** → **Di**).[38]



D, 36	R	R'		yield (%)	mp (°C)		yield (%)	mp (°C)
a	OMe	H	36a	82	110−111	39a	64	170−172
b	OEt	H	b	82	121−122	b	54	174−176
c	Ph	H	c	65	190−191			
d	Ph	Me	d	90	103−105			

Scheme 15

Experiments in a *non-polar* solvent, however, took a different course. Using methyl propiolate, the ylides (**Da-d**) and (**Dq,r**) were transformed into the indolizine derivatives (**36a-d**)[39] and (**39a,b**),[38] respectively (Scheme 15). This conversion was believed to proceed *via* the diazene (**37**) which arose by a concerted process involving cycloaddition and triazole fission. Subsequent extrusion of molecular nitrogen led to a diradical that was stabilized to the diene (**38**) which in turn cyclized.[39] Still more surprising did appear the



i: K_2CO_3, Et_3N, toluene, rt

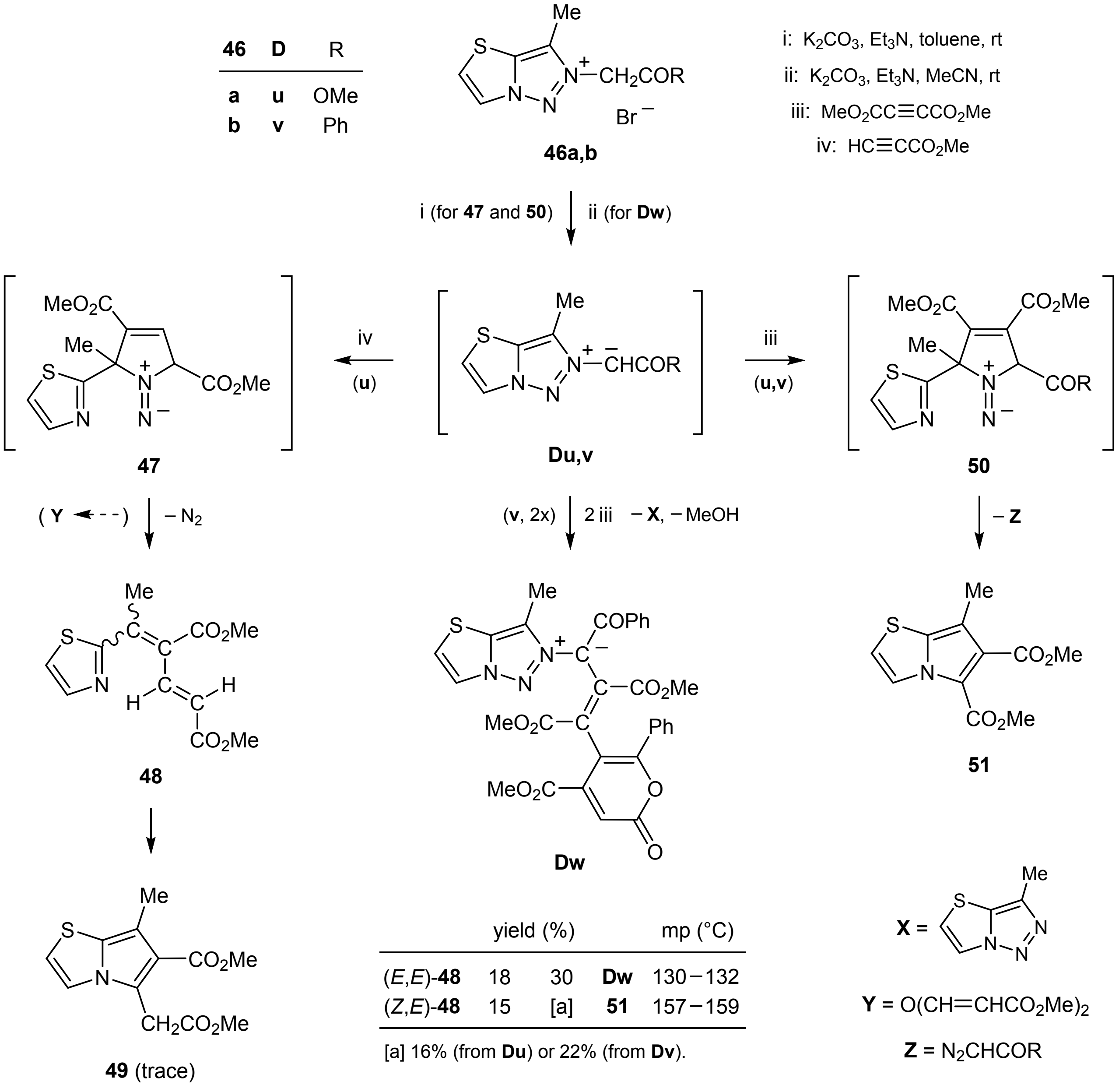
E = CO_2Me **X** = $N_2CHCOPh$

D, 40	R		yield (%)	mp (°C)		yield (%)	mp (°C)
a	OMe	**40a**	82	137−138	**43a**	13 [a]	[c]
b	OEt	**b**	65	132−134	**b**	9 [b]	157−159
c	Ph	**c**	73	130−131			

[a] Besides 59% [1,2,3]triazolo[1,5-*a*]quinoline (see Scheme 22: **68a**). [b] Besides 63% [1,2,3]triazolo[5,1-*a*]isoquinoline (**68b**). [c] Not reported.

Scheme 16

reactions with dimethyl butynedioate (Scheme 16). The ylides (**Da-c**) took up this alkyne in a 1:2 ratio to yield the pyrazolopyridines (**40a-c**).[40] Of the two mechanisms the authors put forward, the alternative that suggests the cyclazine (**41**) as the *primary* intermediate is presented here; after cycloaddition (→ **42**) the sequence was terminated by triazole ring opening and dehydrogenation. The peculiar structure of the products was confirmed by X-ray diffraction of the derivative (**40c**). A deviating route, however, was followed by the ylides (**Dq,r**).[41] While the major reaction was simple defunctionalization to leave the parent triazoloquinoline (59%) and -isoquinoline (63%), a side process led to compounds like **43a,b**. Their formation is believed to involve **44** (a species analogous to **37**). But instead of extruding nitrogen, the molecule split out diazoacetophenone to give the diradical (**45**) which cyclized to the final product.



46	D	R
a	u	OMe
b	v	Ph

i: K_2CO_3, Et_3N, toluene, rt
ii: K_2CO_3, Et_3N, MeCN, rt
iii: $MeO_2CC{\equiv}CCO_2Me$
iv: $HC{\equiv}CCO_2Me$

	yield (%)			mp (°C)
(*E*,*E*)-**48**	18	30	**Dw**	130−132
(*Z*,*E*)-**48**	15	[a]	**51**	157−159

[a] 16% (from **Du**) or 22% (from **Dv**).

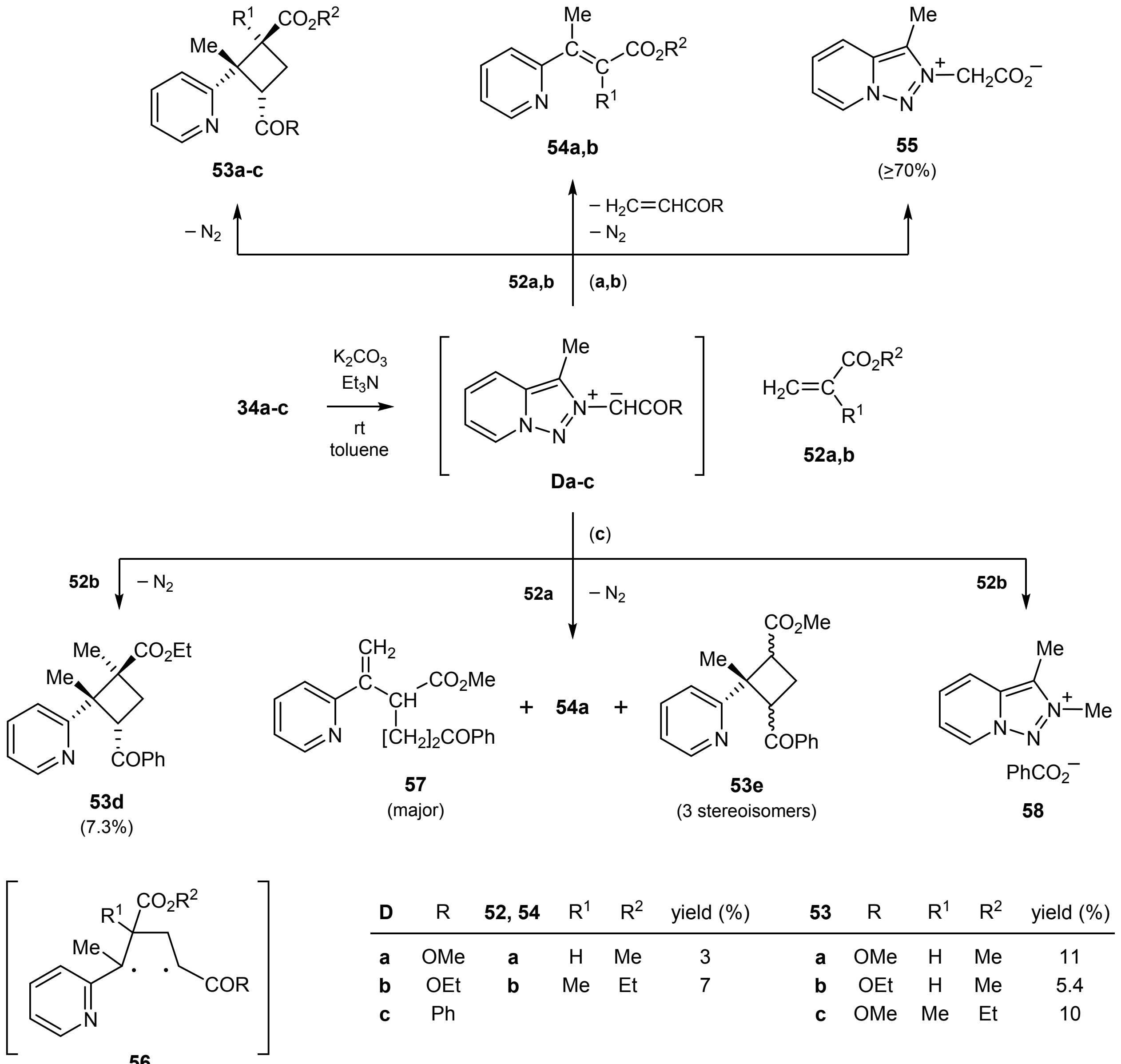
X =

Y = $O(CH{=}CHCO_2Me)_2$

Z = N_2CHCOR

Scheme 17

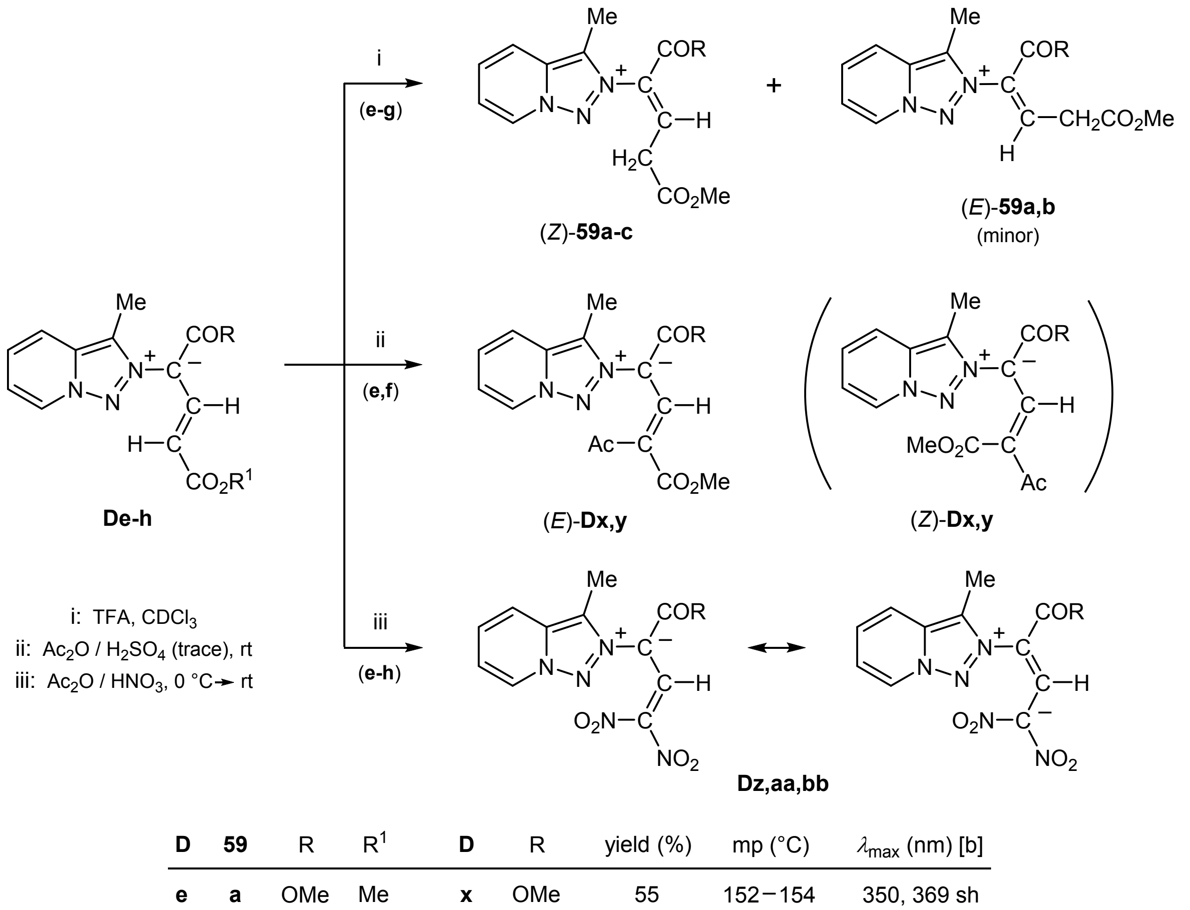
Reactions of thiazole-fused ylides with dipolarophilic alkynes largely follow the pattern described above. Generated from the salt (**46a**), the ylide (**Du**) was reacted with methyl propiolate to afford – besides some ether (**Y**) – the dienes (**48**), which were formed *via* **47** (Scheme 17).[42] Previously, the existence of such dienes, *i.e.* **38** (*cf.* Scheme 15), was postulated, but the species were not isolated.[39] The formation of compound (**49**) was negligible and could not be enforced by heating of the isolated dienes. Employing dimethyl butynedioate, only one equivalent was taken up to convert the ylides (**Du,v**) *via* **50** into **51**.[42] While this reaction differs from the process (**Da-c** → **40a-c**) (*cf.* Scheme 16), it resembles the conversion (**Dq,r** → **43a,b**). Changing to acetonitrile, again linear addition occurred, as exemplified with the ylide (**Dv**). But instead of forming an analogue of adduct (**Dj**) (*cf.* Scheme 14), a multistep dimerization process with extrusion of the bicycle (**X**) and pyrone ring closure occurred to give the red-coloured ylide (**Dw**).[42]



D	R	52, 54	R^1	R^2	yield (%)	53	R	R^1	R^2	yield (%)
a	OMe	a	H	Me	3	a	OMe	H	Me	11
b	OEt	b	Me	Et	7	b	OEt	H	Me	5.4
c	Ph					c	OMe	Me	Et	10

Scheme 18

Reactions with alkenes are on the whole more complicated. When the ester-functionalized ylides (**Da,b**) were treated with the acrylates (**52a,b**), the cyclobutanes (**53a-c**) and the pyridylacrylates (**54a,b**) were obtained – apart from major amounts of the product of simple hydrolysis (**55**) (Scheme 18).[43] As a direct precursor to **53** and **54**, the diradical (**56**) has been proposed; it either expelled the unit ($H_2C{=}CHCOR$) to yield **54** or cyclized to **53**. Note that the ester group in the compounds (**54**) originates from the reagent, not the ylide; thus, using methyl acrylate, both **Da** and **Db** gave the compound (**54a**). – Partly divergent results came from the phenacylide (**Dc**):[43] (i) Employing methyl acrylate (**52a**), a complex mixture arose that contained the alkene (**57**), the derivative (**54a**), and several stereoisomers of the cyclobutane (**53e**); also compound (**57**) was explained as arising *via* species (**56**); and (ii) applying ethyl methacrylate (**52b**), the ylide (**Dc**) gave the cyclobutane (**53d**), some pyridylacrylate (**54b**), and a substantial quantity of the quaternary salt (**58**). The formation of the latter matches Kröhnke's classical 'acid-splitting'[44] (not referred to by the authors[43]) – a kind of conversion also tetrazolium ylides can undergo [see Section (2c)].[45]



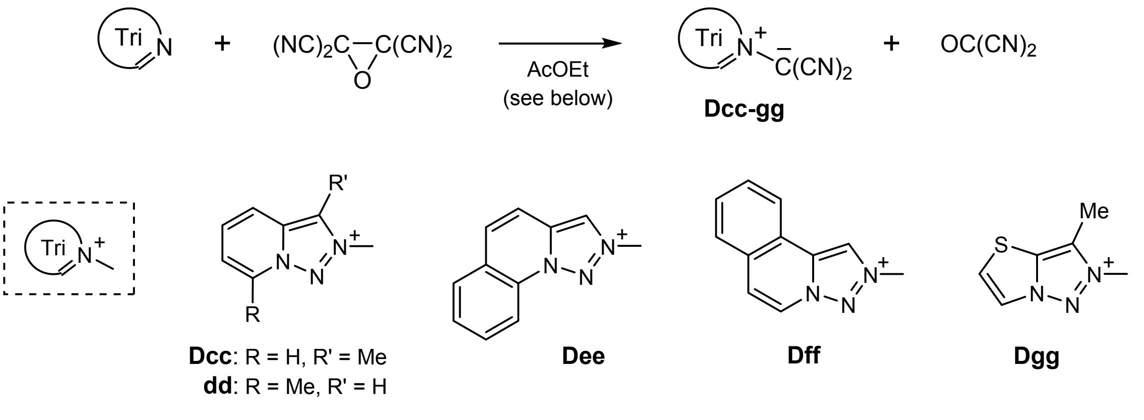
D	59	R	R^1	D	R	yield (%)	mp (°C)	λ_{max} (nm) [b]
e	**a**	OMe	Me	**x**	OMe	55	152−154	350, 369 sh
f	**b**	OEt	Me	**y**	OEt	82	178−179	343
g	**c**	Ph	Me	**z**	OMe	60 [a]	215−216	401
h		OMe	Et	**aa**	OEt	55	214−215	378
				bb	Ph	30	270−273	398

[a] This yield also from **Dh**. [b] Absol. EtOH.

Scheme 19

Regarding reactions with electrophiles, examples are available from the ylides (**De-h**) (Scheme 19).[46] It was found that attack took place at the end of the side chain. Thus, protonation of the substrates (**De-g**) gave alkenes like **59a-c**, with the *Z* isomers predominating. Similarly, acetic anhydride (plus mineral acid) converted the substrates (**De,f**) into the new ylides (**Dx,y**); these compounds occurred exclusively in the *E* form. On treating the ylides (**De-h**) with acetic anhydride and nitric acid, the nitryl cation also replaced the terminal ester group such as to form dinitro derivatives like **Dz**, **Daa**, and **Dbb**. The structure of these materials was not fully recognized by means of spectroscopy, but could be established *via* X-ray analysis of **Dz**; the crystal data, however, did not point to a particular charge localization.[46]

Known γ-type ylides of class (**D**) are limited to derivatives having a dicyanomethylide group (Scheme 20). Access to representatives like **Dcc,dd**,[47] **Dee,ff**,[38] and **Dgg**[41] followed the procedure applied for class (**A**) [see Section (1a)] and turned out to be a straightforward process. Of these stable ylides, the derivatives (**Dcc**) and (**Ddd**) gave interesting EI mass spectra: While **Dcc** is characterized by stepwise loss of the ylide function, molecular nitrogen, and hydrogen to afford a (2-pyridyl)vinyl ion [*m/z* 104 (100%)], the congener (**Ddd**) undergoes triazole cleavage with formation of a three-membered ring followed by loss of nitrogen and a methyl hydrogen to give the [6-(2,2-dicyanovinyl)-2-pyridyl]methyl ion [*m/z* 168 (91%)]. It may be added that these findings, contrary to the authors' assumption,[47] do not constitute the first MS data to have been reported on cycloimmonium ylides [*cf.* Section (2c): Tables within Schemes 25 and 28].



Dcc-gg

Dcc: R = H, R' = Me
dd: R = Me, R' = H

Dee

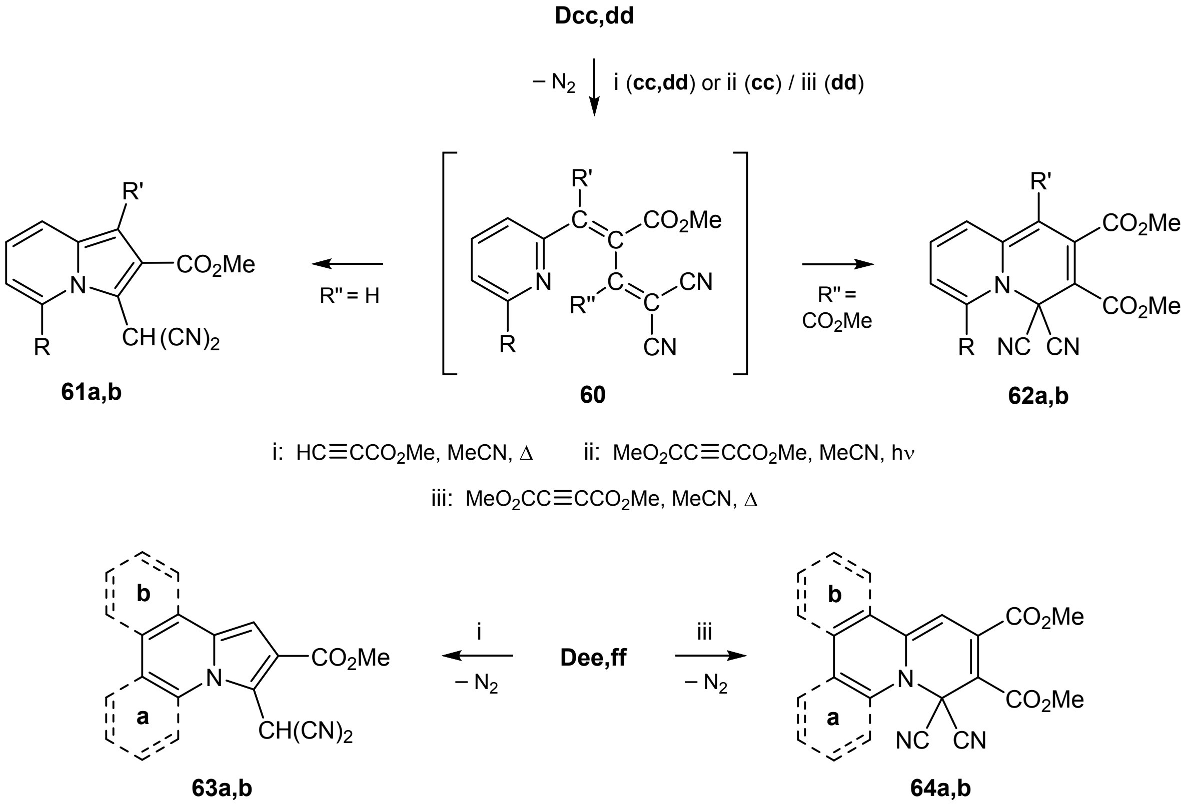
Dff

Dgg

D	yield (%)	conditions	mp (°C)	λ_{max} (nm) [a]	$\tilde{\nu}_{C\equiv N}$ (cm^{-1}) [b]	*m/z* [c]	δ_{C^-} (ppm) [d]	ref.
cc	66	rt	175−176	362	2188, 2158	197 [e,f]	45.97	47
dd	68	rt	265−268	361	2188, 2151	197 [f,g]	52.54	47
ee	52	rt	302−305	385	2189, 2152	233 [g]	53.15	38
ff	66	rt	295−297	378	2190, 2150	233 [g]	52.98	38
gg	29	0 °C	191−193		2183, 2143		45.00	41

[a] EtOH. [b] KBr. [c] EI. [d] DMSO-d_6. [e] M$^+$, 57%. [f] Isomers (**Dcc**) and (**Ddd**) fragment in a different way. [g] M$^+$, 100%.

Scheme 20



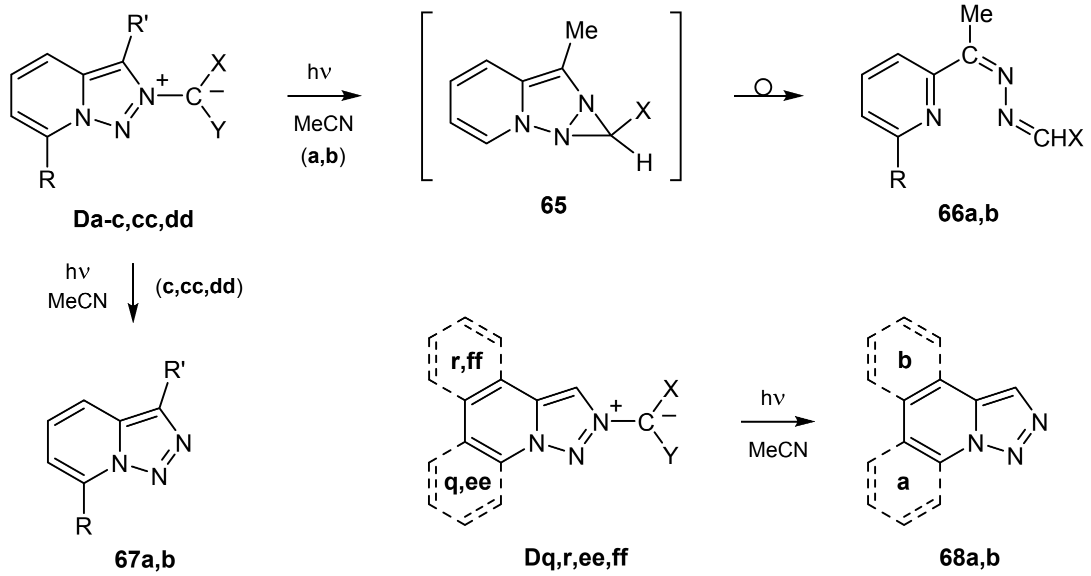
61, 62	R	R'		yield (%)	mp (°C)		yield (%)	mp (°C)
a	H	Me	**61a**	73	190−193	**63a**	56	210−212
b	Me	H	**b**	58	146−147	**b**	48	170−172
			62a	52	183−185	**64a**	61	144−146
			b	62	144−145	**b**	59 [a]	[b]

[a] Besides 12% **43b**; *cf.* Scheme 16: formation of this compound from species (**44**) having CN / CN (instead of H / COPh) through loss of $N_2C(CN)_2$. [b] Not reported.

Scheme 21

Investigating the behaviour of the dicyanomethylides (**Dcc-ff**) toward electron-poor alkynes, it was found that **Dcc,dd** as well as **Dee,ff** gave two classes of compounds, depending on the reagent (Scheme 21). While methyl propiolate yielded indolizines like **61a,b**[47] and **63a,b**,[38] dimethyl butynedioate gave rise to quinolizines like **62a,b**[47,48] and **64a,b**.[41] Both reactions proceed *via* species (**60**) or its benzologues; note that the formation of **62a** – divergent from **62b** – requires irradiation.[48] The route to the compounds (**61**) and (**63**) resembles the path to **36** and **39** (*cf.* Scheme 15); the formation of **62** and **64**, however, is owing to the $C(CN)_2$ group, if one compares the products (**40**) and (**43**) from **Da-c** and **Dq,r** and the *same* alkyne (*cf.* Scheme 16). – Experiments performed with the ylide (**Dgg**) did not produce identifiable materials.[41]

Photochemical investigations have been conducted with both the isolable ylides (**Dcc-ff**) and the transient congeners (**Da-c,q,r**) (Scheme 22).[48] Not unexpectedly, most of these substrates suffered loss of the ylide



D	66	67	R	R'	X	Y	product	yield (%)
a	**a**		H	Me	CO_2Me	H	**66a**	73
b	**b**		H	Me	CO_2Et	H	**66b**	59
c			H	Me	COPh	H	**67a**	88 [a]
q					COPh	H	**68a**	91 [a]
r					COPh	H	**68b**	90 [a]
cc		**a**	H	Me	CN	CN	**67a**	90
dd		**b**	Me	H	CN	CN	**67b**	88
ee					CN	CN	**68a**	95
ff					CN	CN	**68b**	83

[a] Besides 2% 1,4-diphenylbutane-1,4-dione and 3% 3-benzoyl-1,5-diphenylpentane-1,5-dione.

Scheme 22

Table 1. Photochemical reactions of ylides (**D**) with methyl propiolate (**1**) and dimethyl butynedioate (**2**) [a]

D	products from (**1**)	yield (%)	D	products from (**2**)	yield
a	**67a** (*22*) / **De** (*14*) / **Dk** (*14*) / **36a** (*15*)	14 / 59 / 1 / 22	**a**	**67a** (*22*)	76
b	**67a** (*22*) / **Df** (*14*) / **Dl** (*14*) / **36b** (*15*)	30 / 46 / 2 / 5	**b**	**67a** (*22*)	69
c	**67a** (*22*) / **Dg** (*14*) / **36c** (*15*)	15 / 68 / 3	**c**	**67a** (*22*)	91
q	**Ds** (*14*) / **39a** (*15*)	60 / 5	**q**	**68a** (*22*)	73
r	**Dt** (*14*) / **39b** (*15*)	48 / 39	**r**	**68b** (*22*)	77
cc	**67a** (*22*)	54	**cc**	**62a** (*21*)	52
dd	**67b** (*22*)	81	**dd**	**62b** (*21*)	39
ee	**68a** (*22*)	80	**ee**	**64a** (*21*)	51
ff	**68b** (*22*)	64	**ff**	**68b** (*22*)	59

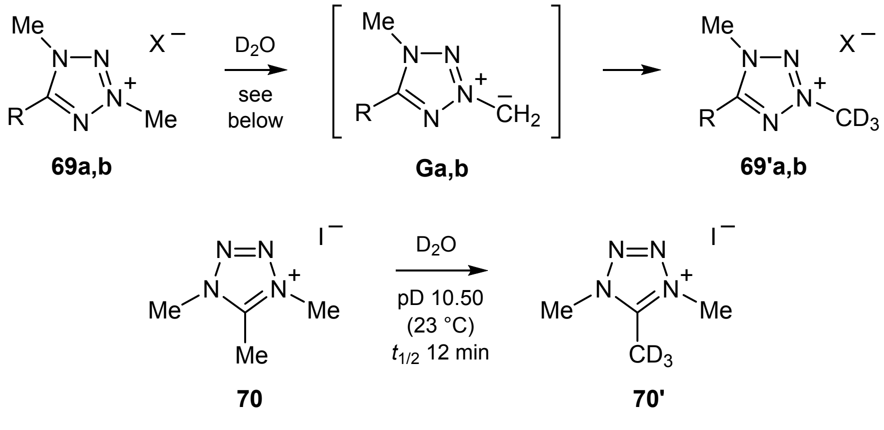
[a] Conditions: acetonitrile, rt, 2–3 h. Products: numerals in *italics* refer to Schemes where structures are shown.

function to leave the parent heterocycles (**67a,b**) and (**68a,b**). But an interesting exception was observed with the ester-functionalized ylides (**Da,b**). These materials gave alkylidenehydrazones like **66a,b**; their formation was rationalized to proceed *via* a diaziridine stage (**65**). Complementary photoreactions were performed in the presence of alkynes that had been used before under thermal conditions. Employing methyl propiolate, the behaviour of the two series (**Da-c,q,r**) and (**Dcc-ff**) differed in that the former did not lose the ylide group, but gave mixtures of compounds known from preceding experiments (Table 1). Reversely, using dimethyl butynedioate, the ylides (**Da-c,q,r**) were defunctionalized throughout, whereas the majority of the dicyano congeners, *viz.* the substrates (**Dcc-ee**), were transformed into the quinolizines (**62a,b**) and (**64a**), respectively. Of these products, the derivative (**62a**) was not obtained under thermal conditions (*cf.* preceding paragraph).[48]

2) *N*-YLIDES OF TETRAZOLES

a) Introductory studies

Prior to preparation of the first ylides of this series it has been observed that the tetrazolium salt (**69a**) in basic deuterium oxide underwent H/D exchange at the 3-methyl group (in addition to position 5) to afford the species (**69'a**), supposedly with involvement of the ylide (**Ga**) (Scheme 23).[49] Later, a similar result was obtained with the salt (**69b**), whereas the 4-methyl group of the isomer (**70**) was found unaffected.[50] These different kinetic acidities were rationalized by comparing classical resonance structures (Chart 3).[51] Considering the delocalization of the anionoid lone pair in the ylides (**Ea**), (**Fa**), and (**Ga**), the latter ylide



69a,b **Ga,b** **69'a,b**

70 **70'**

69 / G / 69'	R	X	pD	°C	$t_{1/2\ (H \rightarrow D)}$ (min)
a	H / H / D	Cl	11.15 [a]	60	130 ± 10 [b]
b	Me / Me / CD_3	I	13.50 [c]	23	26 [b]

[a] 5-H/5-D half exchange at pD 4.40 (25 °C) in 60 ± 5 min. [b] *N*-Me/*N*-CD_3
[c] 5-Me/5-CD_3 half exchange at pD 11.05 (23 °C) in 3115 min (at pD 13.50 too fast to be measured).

Scheme 23

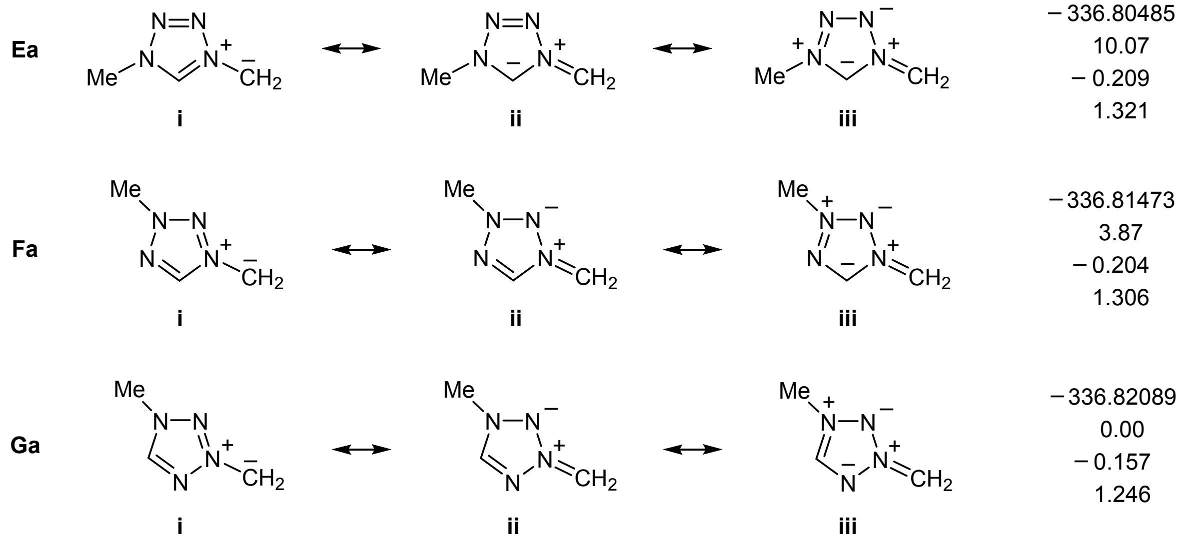
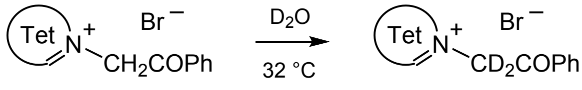
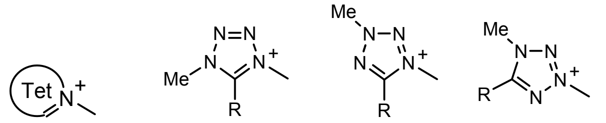


Chart 3. Resonance structures of the α_1-type ylides (**Ea**), (**Fa**), and (**Ga**).[51] Right: absolute minima (a.u.), relative energies (kcal/mol), atomic charges and π-electron densities of ylide carbon; calculated at the B3LYP/6-31G** level (gas phase)[53,54]

is preferred energetically, since structure (**Ga/iii**) has *both* negative charges on the more electronegative nitrogen atoms, whereas **Ea/iii** and **Fa/iii** each have one formal negative charge on carbon. Moreover, the comparison reveals that the electron-withdrawing influence exerted by the three tetrazolium systems decreases in the order 1-R-tetrazolium-3-yl > 3-R-tetrazolium-1-yl > 1-R-tetrazolium-4-yl. This gradation can likewise be inferred from: (i) an inspection of INDO[51] and CNDO/2[52] atomic charges for 1,3- and 1,4-dimethyltetrazolium cations including the ylides (**Fa**) and (**Ga**),[51] and (ii) DFT calculations of **Ea**, **Fa**, and **Ga** (Chart 3; see columns on right).[53,54] Extending these studies to phenacyltetrazolium salts (**71–73**), kinetic and also thermodynamic acidities were found fully in line with the above results; in addition, both kinds of data show a close correlation (Scheme 24).[45]



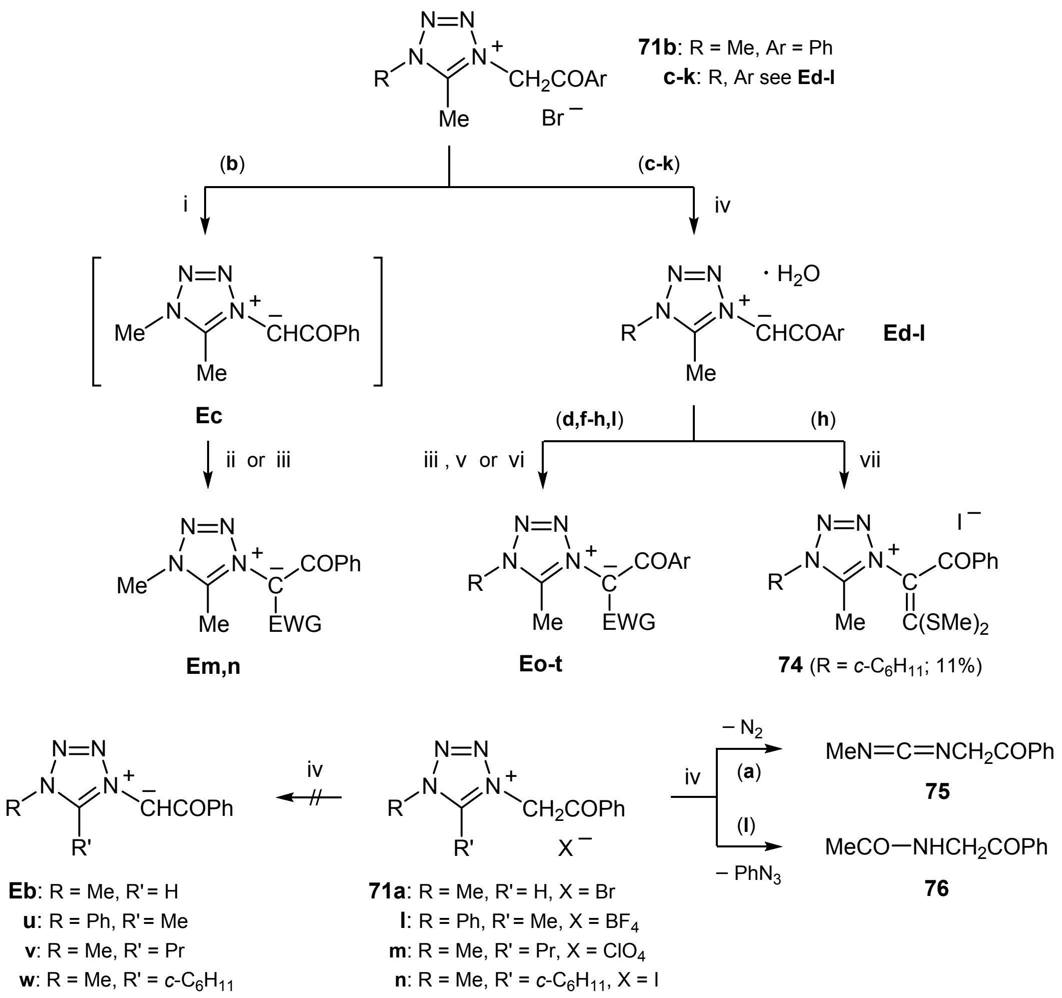
71b−73b **71'b−73'b**



	(**71, 71'**)	(**72, 72'**)	(**73, 73'**)	R
pK_a [a]	9.64	8.98	8.45	H (**a**)
	10.17	9.64	9.05	Me (**b**)
$t_{1/2\ (H \rightarrow D)}$ (min)	60	17	6	Me (**b**)

[a] Values by potentiometric titration with 0.01 M NaOH in water.

Scheme 24



i: Et_3N (see text) ii: Ac_2O, rt iii: $(PhCO)_2O$, 45 °C iv: K_2CO_3, H_2O, 0 °C v: PhNCO, 0 °C → rt vi: PhNCS, rt
vii: K_2CO_3, H_2O, CS_2, MeI, rt

E	R	Ar	EWG	yield (%)	mp (°C) [a]	λ_{max} (nm) [b]	$\tilde{\nu}_{CO}$ (cm^{-1}) [c]	*m*/*z* [d]	$\delta_{\bar{C}H/C^-}$ (ppm) [e]
d	Pr	Ph		79	62–65	299	1535	245 [h]	6.43 / 87.4
e	*i*-Pr	Ph		77	61–63	295	1540		6.44 / 87.0
f	*i*-Bu	Ph		83	68–70	303	1545		6.45 / 87.2
g	CH_2Bu-*t*	Ph		93	69–73	302	1540		6.50 / 87.1
h	*c*-C_6H_{11}	Ph		91	89–91 [f]	296	1530	285 [h]	6.40 / 86.7
i	Me	4-BrC_6H_4		87	50–53	300	1530		6.45 / 87.2
j	Me	4-$NO_2C_6H_4$		92	71–77	350	1555		6.59 / 88.8
k	*c*-C_6H_{11}	4-BrC_6H_4		92	96–98	299	1530		6.43 / 86.9
l	*c*-C_6H_{11}	4-$NO_2C_6H_4$		83	83–87	349	1550		6.56 / 88.6
m			COMe	61	127–128		1525	230 [i]	111.5 [k]
n			COPh	15	112–115 [g]		1505		
o	Pr	Ph	COPh	33	117		1520	320 [j]	110.6 [k]
p	*i*-Bu	Ph	COPh	49	119–120	307.5	1520, 1505		110.5 [k]
q	*c*-C_6H_{11}	Ph	COPh	50	127–129 [g]	307.5	1495		110.6 [k]
r	*c*-C_6H_{11}	4-$NO_2C_6H_4$	COPh	37	138–139		1535, 1520		
s	*c*-C_6H_{11}		CONHPh	88	121–123		1645, 1520		98.0 [l,m]
t	CH_2Bu-*t*		CSNHPh	87	113–114		1565, 1515		108.2 [l,n]

[a] Decomp. [b] 0.1 M NaOH (**Ed-l**); H_2O (**Ep,q**). [c] KBr. [d] FAB, glycerol (**Ed,h**); 70 eV (**Em,o**). [e] MeOH unless otherwise stated. [f] Ref.[18] 87–89 °C. [g] Hemihydrate. [h] $[M+H]^+$, 100%. [i] $[M-28]^+$, 8%. [j] $[M-28]^+$, 17%. [k] $CDCl_3$. [l] DMSO-d_6. [m] δ_{NH} 12.10 ppm. [n] δ_{NH} 14.17 ppm.

Scheme 25

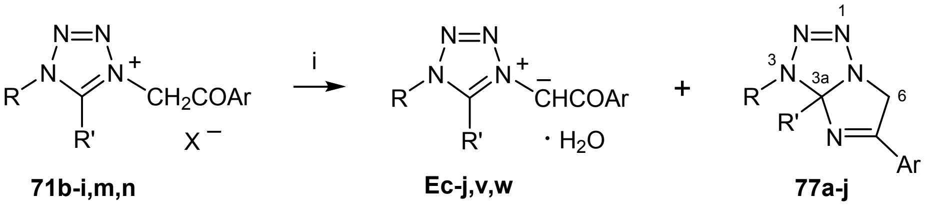
b) Class (E)

Applying the classical Kröhnke method, treatment of the tetrazolium salts (7**1b-k**) with alkali carbonate produced the corresponding β-type ylides (**Ec-l**) (Scheme 25).[55] Save the derivative (**Ec**), all compounds were obtained as solids; their stability decreases with the *N*-substituent becoming smaller. An essential feature that distinguishes these ylides from their analogues of class (**F**) and (**G**) is the presence of crystal water; it apparently stabilizes the negative charge, as attempts of dehydration resulted in decomposition. Also aprotic solvents are detrimental, which limits the investigation of certain spectroscopic phenomena such as the (negative) solvatochromism typical of the 'ylide band' [see Section (2c)].

Expectedly, the new ylides exhibit appreciable reactivity towards electrophiles. For practical reasons, the labile substrate (**Ec**) was treated *in situ*: joint action of (neat) acid anhydrides and excess base on the salt (**71b**) gave the crystalline γ-type ylides (**Em**) or (**En**); note that acetic anhydride, to a minor extent, can acylate the 5-methyl group instead of the ylide function – with the consequence of forming small amounts of pyrrolotetrazoles.[55,56] In contrast to **Ec**, the stable ylides (**Ed-l**) were reacted after their isolation and, again using neat reagents, were transformed into the products (**Eo-t**); only the ketene thioacetal (**74**) was made directly from the respective salt (**71g**).[55]

Regarding the scope of the Kröhnke route, ylides could not be prepared from salts having 5-H for 5-Me (such as **71a**) or having 1-phenyl for 1-alkyl (such as **71l**). Substrates of this kind, instead of giving **Eb** or **Eu**, fragmented into molecular nitrogen and a carbodiimide (**75**) or were hydrolyzed to phenyl azide and *N*-phenacylacetamide (**76**),[45] *i.e.* they followed reaction patterns that had previously been observed with related structures (cited in ref.[45]). Likewise, attempts to obtain ylides bearing bulkier groups at C(5) such as propyl and cyclohexyl remained unrewarded (*cf.* below).[55]

Complementary experiments with the salts (**71**) were carried out with concentrated ammonia (instead of potassium carbonate) (Scheme 26).[57,58] Surprisingly, it was found that this reagent not only acts as a base, but also as a nucleophile. As a consequence, ylides (**E**) and/or bicycles of the type (**77**) were obtained, depending on the substituents. From the list of examples it is apparent that salts (**71**) having small R rests favour the formation of **77** (see **a,i,j**), regardless of the size of the R' residue. However, when the R ligand is becoming bulkier, the ylides (**E**) will arise (see **d-h**), while the yields of the bicycles (**77**) gradually decrease (see **b-f**). Ylides (**E**) also predominate in the case of substituted phenacyl groups (see **i,j**). These observations were rationalized as follows: (i) The folded geometry of **77**, which was studied by the X-ray method performed with **77a**, implies that sterically demanding substituents are hindered when attached to N(3), but not when residing at the bridgehead C(3a); (ii) on the other hand, ylides (**E**) having larger R residues or substituted phenacyl groups are sparingly soluble in water and separate once the base had been added, thereby reducing the stock of **71** for the (much slower) production of **77**; the latter explains why the ylides (**Ei,j**) predominate, whilst, arguing sterically, the formation of **77g,h** should be preferred.

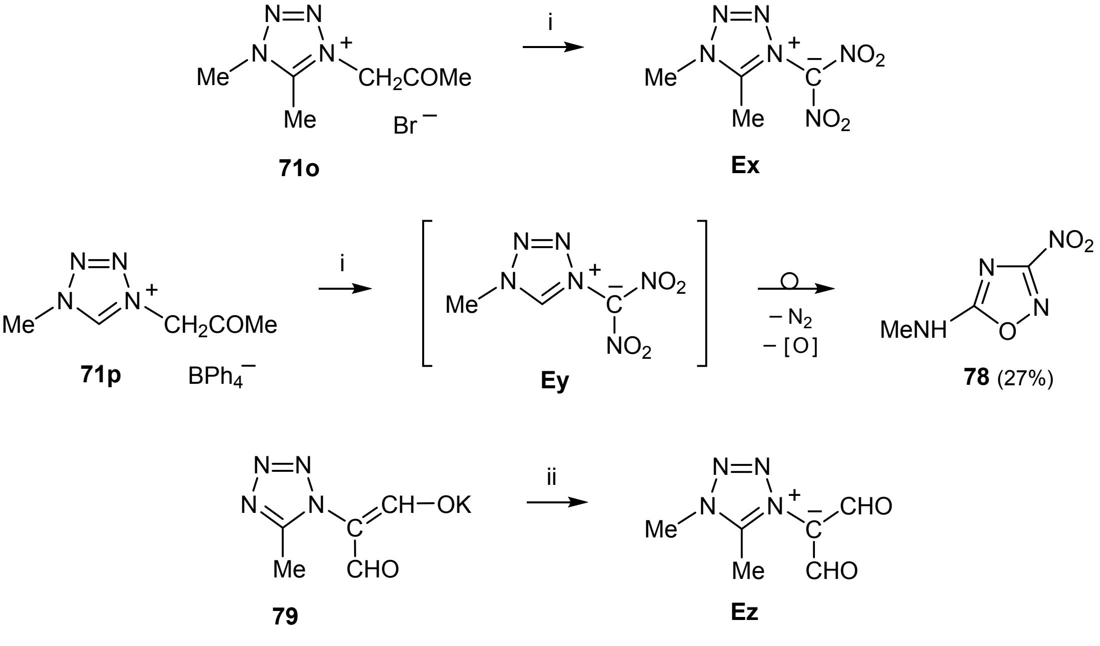


i: 13−14 M NH_3, ⩽0 °C

71	E	77	R	R'	Ar	X	yield **E** / **77** (%) [a]
b	**c**	**a**	Me	Me	Ph	Br	− / 95
c	**d**	**b**	Pr	Me	Ph	Br	60 / 32
d	**e**	**c**	*i*-Pr	Me	Ph	Br	79 / 13
e	**f**	**d**	*i*-Bu	Me	Ph	Br	80 / 10
f	**g**	**e**	CH_2Bu-*t*	Me	Ph	Br	90 / 2
g	**h**	**f**	*c*-C_6H_{11}	Me	Ph	Br	92 / − [b]
h	**i**	**g**	Me	Me	4-BrC_6H_4	Br	83 / 4
i	**j**	**h**	Me	Me	4-$NO_2C_6H_4$	Br	89 / − [b]
m	**v**	**i**	Me	Pr	Ph	ClO_4	− / 90
n	**w**	**j**	Me	*c*-C_6H_{11}	Ph	I	− / 91

[a] Data from ref.[57a] unless otherwise stated. [b] From ref.[59]

Scheme 26



i: HNO_3 / H_2SO_4 / H_2O, Δ ii: FSO_2OMe, MeCN; then EtOH; then aq. $KHCO_3$, rt

	yield (%)	λ_{max} (nm) [a]	$\tilde{\nu}_{\bar{C}(NO_2)_2}$ (cm^{-1}) [b]	$\delta_{CH(NO_2)_2}$ (ppm) [c]	pK_a [d]
Ex	30	332	1501, 1285	8.70	−3.4
Ez	80 [e]	258 [e]			

[a] H_2O. [b] KBr. [c] H_2SO_4. [d] $H_2O-H_2SO_4$. [e] From ref.[63c]

Scheme 27

In addition to the plethora of ylides (**E**) shown in Scheme 25, two representatives exist that distinguish from those examples either by structure and/or way of access (Scheme 27).

(i) In conjunction with the synthesis of azolium and azinium dinitromethylides the tetrazolium derivative (**Ex**) has been made [for an analogue of class (**G**), see Section (2.c)].[60] The method implies a destructive nitration of the acetonyl side chain of the starting compound (**71o**), which occurred in a nitrating medium containing sufficient water. The two nitro groups were sequentially introduced *via* addition of the nitryl cation to the enolic intermediates followed by hydrolysis of the acetyl group. Later, employing substrates having an uncharged cycle, the mechanism has been studied in more detail.[61] In contrast to the ylide (**Ex**), a 5-unsubstituted congener like **Ey** could not be obtained, even at 0–20 °C. However, heating the reaction mixture at 50–70 °C, the respective salt (**71p**) was converted into an oxadiazole like **78**.[62] Its formation partly resembles the process (**71a** → **75**) (*cf.* Scheme 25); yet, the linear species which resulted from loss of dinitrogen underwent cyclization involving one nitro group to give an *N*-oxide that was deoxygenated.

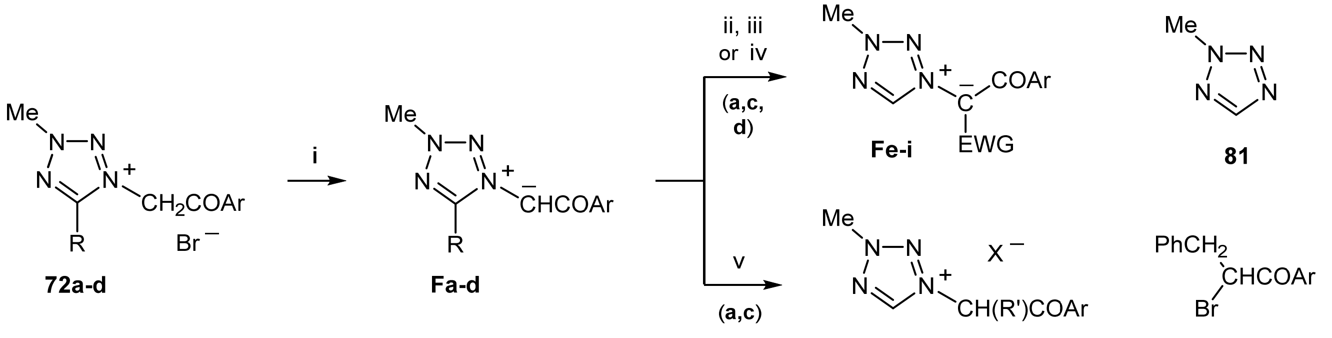
(ii) Methylation of the tetrazolyl-substituted malonaldehyde (**79**) with methyl fluorosulfate to be followed by treatment with a weak base gave the diformylmethylide (**Ez**)[63] (according to ref.[63c] an unstable oil). Usually, quaternization of 1*H*-tetrazoles leads to isomers, which in the present case might have produced also some ylide (**F**). In addition to the ylide (**Ez**), the preparation of its *N*-ethyl analogue was claimed, but without giving experimental details and characterization data.[63a,c]

c) Classes (F) and (G)

Investigations of ylides (**F**) have been conducted as part of a comparative study including the isomers (**G**) (Scheme 28).[45] It seems therefore appropriate to treat both classes jointly.

Following the classical Kröhnke route, action of potassium carbonate on the salts (**72a-d**) and (**73a-d**) afforded the ylides (**Fa-d**) and (**Gc-f**) in excellent yield. These compounds crystallize in anhydrous form, in contrast to their β-type congeners (**Ed-l**) (*cf.* Scheme 25). Derivatives having an unsubstituted ring carbon are stable as well. Considering the stronger electron-withdrawing influence exerted by the azolium system in **G** [*cf.* Section (2a)], reactions of the ylides (**F**) with electrophiles should proceed more readily. This is borne out as follows:

(i) While aroylation of the salts (**72a**) and (**73a**) under Schotten-Baumann conditions gave the ylides (**Fe**) and (**Gg**) in similar yield, the formation of **Fe** occurred much more rapidly; accordingly, experiments with the nitrophenacyl salts (**72d**) and (**73d**) succeeded only with the former (→ **Ff**); (ii) employing phenyl isocyanate, the conversion of the ylides (**Fa,c**) into the carbamoylated derivatives (**Fg,h**) was distinctly faster (about four times) than the analogous process (**Gc,e** → **Gh,i**); (iii) attempts to thiocarbamoylate the ylides (**Fd**) and (**Gf**) failed with the latter.



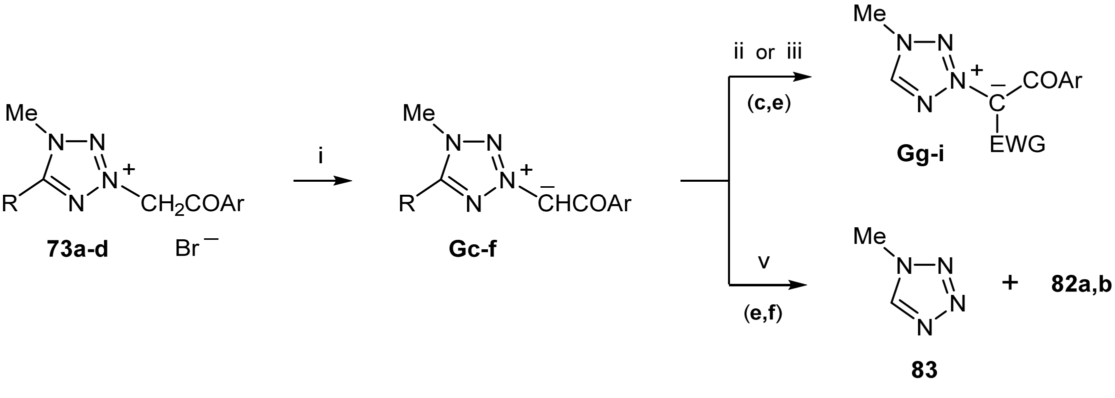
80a: R' = Me, Ar = Ph, X = I (35%)
b: R' = CH_2Ph, Ar = 4-BrC_6H_4, X = Br (21%)

82a: Ar = 4-BrC_6H_4
b: Ar = 4-$NO_2C_6H_4$

i: K_2CO_3, H_2O, 0 °C   ii: Ar'COCl, K_2CO_3, $H_2O-CH_2Cl_2$, 0 °C
iii: PhNCO, rt   iv: PhNCS, rt
v: MeI or $PhCH_2Br$, DMF, rt

72, F	R	Ar	EWG	yield (%)	mp (°C) [a]	λ_{max} (nm) [b]	$\tilde{\nu}_{CO}$ (cm^{-1}) [c]	*m/z* [d]	$\delta_{\bar{C}H/C^-}$ (ppm) [e]
a	H	Ph		98	121–124	371	1520	202 [j]	7.33
b	Me	Ph		96	132–135		1525	216 [k]	7.47 [m] / 87.3 [n]
c	H	4-BrC_6H_4		96	144–147 [h]	373	1525	282/280 [l]	7.47
d	H	4-$NO_2C_6H_4$		93	160–161	390	1550		7.65
e		Ph	COAr' [f]	56 [g]	174–176		1515		
f		4-$NO_2C_6H_4$	COAr' [f]	51 [g]	202–205 [h]		1530		
g		Ph	CONHPh	96	134–135		1625, 1530		100.2 [o]
h		4-BrC_6H_4	CONHPh	93	145–147 [i]		1640, 1530		[p]
i		4-$NO_2C_6H_4$	CSNHPh	43	166–168		1515, 1505		[q]

[a] Decomp. [b] H_2O. [c] KBr. [d] 70 eV. [e] DMSO-d_6 unless otherwise stated. [f] Ar' = 4-MeC_6H_4. [g] Made without isolation of **Fa** and **Fd**, respectively. [h] Hemihydrate. [i] Adduct with 0.5 mol CH_2Cl_2. [j] M^+, 56% (please note: no M^+ peak from **Gc**). [k] M^+, 100% (no M^+ peak from **Gd**). [l] M^+, 7% (no M^+ peak from **Ge**). [m] MeOH: $\delta_{\bar{C}H}$ 6.41 ppm (ref.[59]). [n] MeOH (ref.[59]). [o] δ_{NH} 12.05 ppm ($CDCl_3$). [p] δ_{NH} 11.96 ppm ($CDCl_3$). [q] δ_{NH} 14.1 ppm.

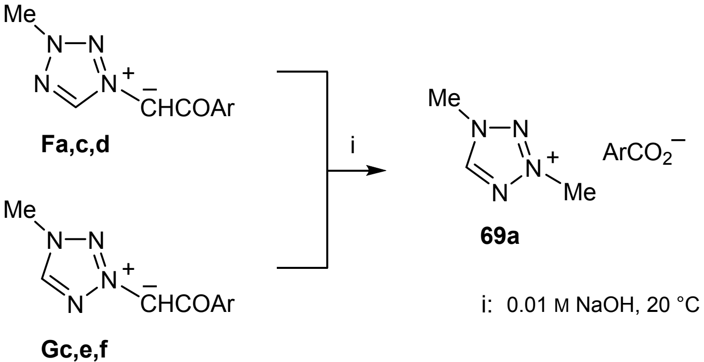


73	G	R	Ar	EWG	yield (%)	mp (°C) [a]	λ_{max} (nm) [b]	$\tilde{\nu}_{CO}$ (cm^{-1}) [c]	$\delta_{\bar{C}H/C^-}$ (ppm) [d]
a	**c**	H	Ph		99	124–127	376	1535	7.52
b	**d**	Me	Ph		93	154–155		1535	7.40 [h] / 96.1 [i]
c	**e**	H	4-BrC_6H_4		95	153–155	378	1535	7.43
d	**f**	H	4-$NO_2C_6H_4$		95	171–174	393	1555	7.54
	g		Ph	COAr' [e]	53 [f]	194–196		1535	
	h		Ph	CONHPh	93	109–112 [g]		1635, 1535	(12.05) [j] / 105.3
	i		4-BrC_6H_4	CONHPh	92	167–168 [g]		1635, 1530	(12.10) [j]

[a] Decomp. [b] H_2O. [c] KBr. [d] DMSO-d_6 unless otherwise stated (**Gh,i**; values in brackets: NH). [e] Ar' = 4-MeC_6H_4. [f] Made without isolation of **Gc**. [g] Hemihydrate. [h] MeOH: $\delta_{\bar{C}H}$ 7.14 ppm (ref.[59]). [i] MeOH (ref.[59]). [j] $CDCl_3$.

Scheme 28

Alkylation studies with methyl iodide or benzyl bromide revealed that desired products could be obtained only from the isomers (**F**), *i.e.* salts of the type (**80**). But since the derivative (**80b**) was accompanied by 2-methyltetrazole (**81**) and the α-bromodihydrochalcone (**82a**), an inherent lability of the C–N bond of **80** became apparent. This weakness turned out to be even more pronounced with salts that were expected from: benzyl bromide and (a) **Fd** / (b) **Ge** / (c) **Gf**, because in these cases only mixtures of (a) **81** + **82b** / (b) **83** + **82a** / (c) **83** + **82b** were isolated.



Fa,c,d

Gc,e,f

69a

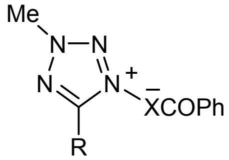
i: 0.01 M NaOH, 20 °C

F / G	Ar	$t_{1/2}$ (F / G → 69a) (min)
a / c	Ph	175.4 / 3.9
c / e	4-BrC_6H_4	93.5 / 1.9
d / f	4-$NO_2C_6H_4$	15.9 [a] / 1.0

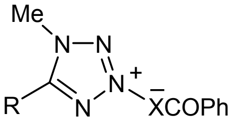
[a] Plot linear over 1 half-life.

Scheme 29

Most significant is a comparison of Kröhnke's 'acid splitting', *i.e.* the action of alkali hydroxide on the pairs of isomers (**Fa/Gc**), (**Fc/Ge**), and (**Fd/Gf**) (Scheme 29): it was found that all compounds (**G**) have a much higher proclivity for giving the benzoate salt (**69a**). This nicely matches the results in Section (2a).



Fa: X = CH, R = H
84: X = N, R = Me



Gc: X = CH, R = H
85: X = N, R = Me

solvent	i.c.t. band [λ_{max} (nm)] **Fa**	**Gc**	**84**	**85**
H_2O	371	376		
$HO[CH_2]_2OH$	384	384		
MeOH	387	386	268	294
EtOH	390	387	269	298
i-PrOH	396	388	274	300
t-BuOH	398	390		
MeCN			293	306
MeCOMe	416	395		
$CHCl_3$	420	400	302	316
CH_2Cl_2	420	400	306	315
dioxane			309	318

correlation between transition energy E_T // E'_T (i.c.t. band) and empirical solvent polarity Z^{66} // E_T^{67}

Fa: $E_T = 0.294\ Z + 49.4$ ($n = 8$, $r = 0.998$) [a]

Gc: $E_T = 0.142\ Z + 62.5$ ($n = 7$, $r = 0.992$) [b]

//

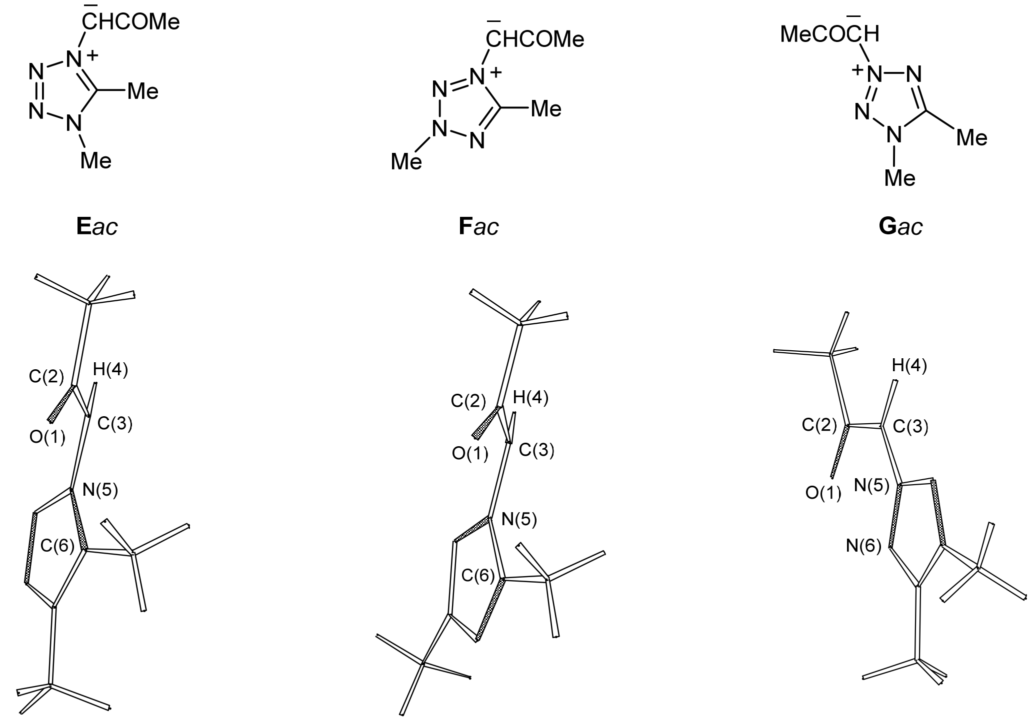
84: $E'_T = 0.841\ E_T + 61.1$ ($n = 7$, $r = 0.955$) [c]

85: $E'_T = 0.413\ E_T + 74.5$ ($n = 7$, $r = 0.983$) [c]

[a] *t*-BuOH neglected. [b] *t*-BuOH and MeCOMe neglected. [c] Correlation with E_T values in close analogy to ref.[68]

Chart 4. UV/Vis spectral behaviour of the ylides (**Fa**), (**Gc**) and the aminides (**84**), (**85**)

A prominent spectroscopic evidence for the stronger electron-withdrawal of the tetrazolium moiety in system (**G**) was provided by the less pronounced (negative) solvatochromism of the visible absorption band (intramolecular charge-transfer band) of the phenacylide (**Gc**) compared to the ylide (**Fa**) (Chart 4); a plot of the transition energies E_T of these i.c.t. bands against the empirical solvent polarity *Z* revealed linear relationships.[45] Later, similar findings were made with the isosteric *N*-aminides (**84**) and (**85**).[64]

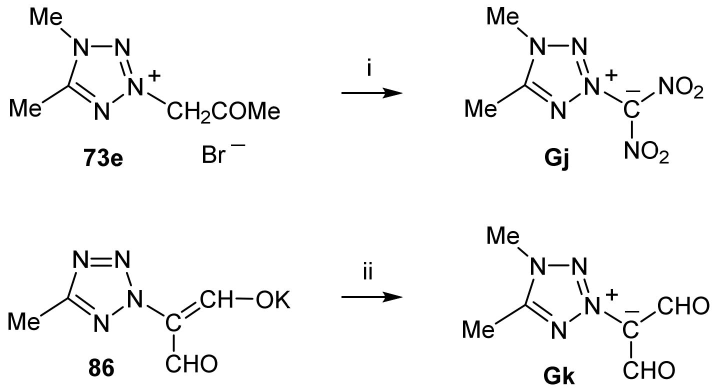


O(1)-C(2)-C(3)-H(4)	164.4	O(1)-C(2)-C(3)-H(4)	162.3	O(1)-C(2)-C(3)-H(4)	−180.0
O(1)-C(2)-C(3)-N(5)	3.1	O(1)-C(2)-C(3)-N(5)	1.3	O(1)-C(2)-C(3)-N(5)	0.0
C(2)-C(3)-N(5)-C(6)	−41.0	C(2)-C(3)-N(5)-C(6)	−43.0	C(2)-C(3)-N(5)-N(6)	0.0
−544.81396		−544.81559		−544.81405	
1.02		0.00		0.97	

Figure 1. Structures of the acetylides (**E***ac*), (**F***ac*), and (**G***ac*); below: dihedral angles (°), absolute minima (a.u.), and relative energies (kcal/mol); calculated at the B3LYP/6-31G** level (gas phase)[53,54]

Comparing the lowest energy geometries of the acetylides (**F***ac*) and (**G***ac*) [including that of (**E***ac*)], it is most noteworthy that only the derivative (**G***ac*) shows a fully planar structure (Figure 1).[53,54] This has also been reported for the corresponding acetylaminides (N instead of CH) which, like **E***ac*–**G***ac*, exhibit a *Z* configured functional group throughout.[65]

Finally, outside the foregoing comparative study two scattered ylides of the class (**G**) deserve mention (Scheme 30): Along with the preparation of analogous ylides (**E**) (*cf.* Scheme 27), the compounds (**Gj**)[60] and (**Gk**)[63] have been made; their properties are essentially those of the isomers (**Ex**) and (**Ez**).



i: HNO_3 / H_2SO_4, Δ ii: FSO_2OMe, MeCN; then EtOH; then aq. $KHCO_3$, rt

	yield (%)	mp (°C)	λ_{max} (nm) [a]	$\tilde{\nu}_{C(NO_2)_2}$ (cm^{-1}) [b]	$\delta_{CH(NO_2)_2}$ (ppm) [c]	pK_a [d]
Gj	35		332	1500, 1305, 1285	8.78	−2.5
Gk	64	202−203	257, (320.5)	1500, 1305, 1285		

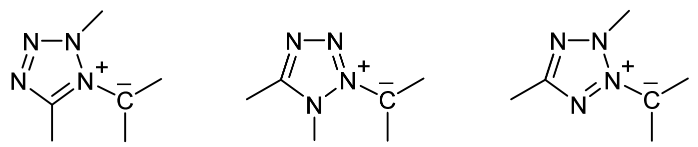
[a] H_2O. [b] KBr. [c] H_2SO_4. [d] $H_2O-H_2SO_4$.

Scheme 30

CONCLUSION

Reviewing the rich material on ylides (**A**–**G**) that has been accumulated in three decades, specific features emerged in great number. The most prominent ones are summarized as follows: (i) ylides (**A**) are capable of rearranging to allylides of class (**B**) *via* elusive cycloadducts; (ii) unsubstituted methylides (**C**) exhibit dichotomous reactivity towards ring expansion and cycloaddition; (iii) heteroring-fused ylides (**D**) are synthons for other heterocycles by virtue of a relatively weak N–N bond; (iv) isomeric tetrazolium ylides (**E**), (**F**), and (**G**) show properties that nicely reflect the different electronic influence exerted by the single ring systems.

However, despite much progress certain desiderata exist: (i) direct access to ylides (**B**) by depronotation of appropriate triazolium salts; (ii) generation (including cycloaddition reactions) of ylides (**E**) that are unsubstituted at C(5); (iii) approach to ylides (**H**–**J**) (below) by overcoming: a) the general inaccessibility of (monocyclic) 1,2-substitution patterns, and b) the difficulty of getting a 2,3-pattern with ligands other than aromatic.



H **I** **J**[69]

Chart 5. Unknown tetrazolium *N*-ylides

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