Exploring the Border between Concerted and Two-Step Pathways of 1,3-Dipolar Cycloadditions of Organic Azides to Cyclic Ketene N,X-Acetals. – Synthesis and ^{15}N-NMR Spectra of Zwitterions and Spirocyclic Cycloadducts[1]

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Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

Cyclic ketene N,X-acetals **1** are electron-rich dipolarophiles that undergo 1,3-dipolar cycloaddition reactions with organic azides **2** ranging from alkyl to strongly electron-deficient azides, *e.g.*, picryl azide (**2L**; $R^1 = 2,4,6\text{-}(NO_2)_3C_6H_2$) and sulfonyl azides **2M**–**O** ($R^1 = XSO_2$; *cf. Scheme 1*). Reactions of the latter with the most-nucleophilic ketene N,N-acetals **1A** provided the first examples for two-step HOMO(dipolarophile)–LUMO(1,3-dipole)-controlled 1,3-dipolar cycloadditions *via* intermediate zwitterions **3**. To set the stage for an exploration of the frontier between concerted and two-step 1,3-dipolar cycloadditions of this type, we first describe the scope and limitations of concerted cycloadditions of **2** to **1** and delineate a number of zwitterions **3**. Alkyl azides **2A**–**C** add exclusively to ketene N,N-acetals that are derived from 1*H*-tetrazole (see **1A**) and 1*H*-imidazole (see **1B**,**C**), while almost all aryl azides yield cycloadducts **4** with the ketene N,X-acetals (X = NR, O, S) employed, except for the case of extreme steric hindrance of the 1,3-dipole (see **2E**; $R^1 = 2,4,6\text{-}(^tBu)_3C_6H_2$). The most electron-deficient paradigm, **2L**, affords zwitterions **16D**,**E** in the reactions with **1A**, while ketene N,O- and N,S-acetals furnish products of unstable intermediate cycloadducts. By tuning the electronic and steric demands of aryl azides to those of ketene N,N-acetals **1A**, we discovered new borderlines between concerted and two-step 1,3-dipolar cycloadditions that involve similar pairs of dipoles and dipolarophiles: 4-Nitrophenyl azide (**2G**) and the 2,2-dimethylpropylidene dipolarophile **1A** (R, R = H, ^{t}Bu) gave a cycloadduct **13H**, while 2-nitrophenyl azide (**2H**) and the same dipolarophile afforded a zwitterion **16A**. Isopropylidene dipolarophile **1A** (R = Me) reacted with both **2G** and **2H** to afford cycloadducts **13G**,**J**) but furnished a zwitterion **16B** with 2,4-dinitrophenyl azide (**2I**). Likewise, **1A** (R = Me) reacted with the isomeric encumbered nitrophenyl azides **2J** and **2K** to yield a cycloadduct **13L** and a zwitterion **16C**, respectively. These examples suggest that, in principle, a host of such borderlines exist which can be crossed by means of small structural variations of the reactants. Eventually, we use ^{15}N-NMR spectroscopy for the first time to characterize spirocyclic cycloadducts **10**–**14** and **17** (*Table 6*), and zwitterions **16** (*Table 7*).

1. Introduction. – *Huisgen*'s seminal and profound work on 1,3-dipolar cycloadditions has opened up a continent of concertedness which is bordered by two conceivable two-step pathways *via* zwitterionic intermediates which remained *terra incognita* for many years, however [1]. Almost 20 years ago, one of these borderlines has been crossed for the first time by *Huisgen* and co-workers when they investigated

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[1]) Most of the results are parts of the Ph. D. Theses by *M. Ach* (1992), *T. Hergenröther* (1992), and *D. Regnat* (1990), and the Diploma Thesis (1990) and unpublished results (1991–92) by *J. Balthasar*, Universität Würzburg.

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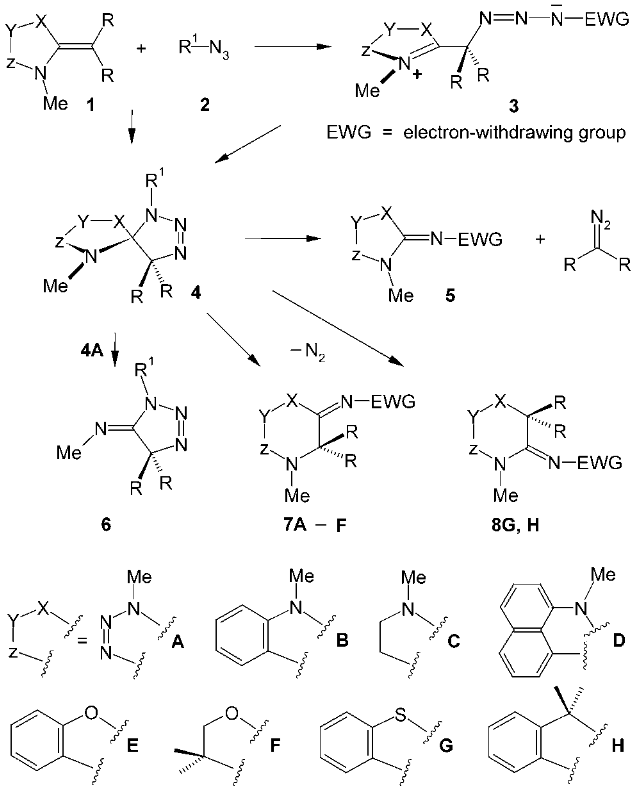
the HOMO(1,3-dipole) – LUMO(dipolarophile)-controlled cycloaddition of very electron-rich 1,3-dipoles, *viz.* thiocarbonyl ylides (= alkylidenesulfonium ylides), to acceptor-substituted ethenes [2]. Several years later, a second crossing of this borderline has been discovered by *Sauer* and co-workers who observed loss of configurational integrity in the cycloaddition of an electron-poor azomethine imine to an enamine [3].

Serendipity triggered crossing of the opposite borderline [4a] after we had come across HOMO(dipolarophile) – LUMO(1,3-dipole)-controlled cycloadditions of the extremely electron-rich dipolarophiles **1A** to methyl azide [5]. Subsequently, we studied the reactions of cyclic ketene N,X-acetals **1** with organic azides **2** more generally to contribute to the rich chemistry that has evolved from 1,3-dipolar cycloadditions of organic azides to C=C bonds [6] (*Scheme 1*): cycloadducts **4** may undergo [3 + 2] cycloreversions [7] into components **1** and **2** [8] or imines **5** and diazoalkanes [4][9]. Those of type **4A** may be cleaved in yet another [3 + 2] cycloreversion reaction affording an azide and dihydro-1*H*-triazolimines **6** [7][10]. Loss of N_2 from the dihydro-1*H*-triazole ring of **4** (R^1 = electron-withdrawing group (EWG)) is accompanied by 1,2-shifts to furnish ring-expanded imines **7A – F** and **8G**,**H** [4][8][9][11].

Scheme 1



As much as these reactions may have been studied, however, neither scope and limitations of the synthesis of cycloadducts **4** nor the border between the concerted and two-step formation have been addressed so far. Therefore, the present paper explores areas of concerted and two-step HOMO(dipolarophile) – LUMO(1,3-dipole)-controlled cycloadditions of azides **2**, and eventually the borders between them. Toward this end, we describe stable, isolable zwitterions **3A** that have been reported briefly in a communication [4a], and 1,3-dipolar cycloadducts **4**. Subsequently, we use members of the most-reactive ketene N,N-acetals **1A** and nitroaryl azides **2** with different steric and electronic demand to uncover new transgressions of the borders between the two mechanistic alternatives. A number of zwitterions **3A** and cycloadducts **4** were characterized by ^{15}N-NMR spectroscopy for the first time.

2. Results and Discussion. – After the first evidence for intermediate zwitterions [2], *Huisgen* and co-workers demonstrated in studies of 1,3-dipolar cycloadditions of thiocarbonyl ylides to electron-deficient ethenes that, besides appropriate frontier-orbital energies, the extent of steric hindrance at one terminus of the thiocarbonyl ylide decided whether the concerted or the two-step pathway was followed [12]. These results suggested a similar strategy for the present study of an electronic counterpart to the thiocarbonyl ylide/electron-deficient ethene reactions. Accordingly, the dipoles **2** varied strongly with respect to both steric and electronic demand. Alkyl azides **2A** – **C** and azides with electron-withdrawing groups, like picryl azide (**2L**) [13] and sulfonyl azides **2M** – **O**, were used as extreme paradigms on the azide-LUMO-energy scale. In addition, aromatic azides were employed whose 1,3-dipolar reactivity was tuned by means of the substitution pattern [14].

R^1—N_3

2

	R^1		R^1
2A	Me	**2I**	2,4-$(NO_2)_2C_6H_3$
2B	^{t}BuCH_2	**2J**	2,6-Me_2(4-NO_2)C_6H_2
2C	^{t}Bu	**2K**	4,6-Me_2(2-NO_2)C_6H_2
2D	Ph	**2L**	2,4,6-$(NO_2)_3C_6H_2$
2E	2,4,6-^{t}Bu$_3C_6H_2$	**2M**	$MeSO_2$
2F	2,6-$Me_2C_6H_3$	**2N**	4-$MeC_6H_4SO_2$
2G	4-$NO_2C_6H_4$	**2O**	Me_2NSO_2
2H	2-$NO_2C_6H_4$		

Although ketene N,X-acetals **1**, including enamine **1H**, cover a range of dipolarophilic reactivity, all possess high-lying HOMOs and hence react under HOMO(dipolarophile) – LUMO(1,3-dipole) control. Comparison of the HOMO energies of the isopropylidene dipolarophiles **9** (*Table 1*) shows that the most-likely candidates for two-step cycloadditions are expected among ketene N,N-acetals **1A** – **C**[3]). This follows also from high electron densities at the C=C-bonded exocyclic C(α) atoms of **1** [15 – 17]. These resonate at much higher field than the ring C(2) atoms, at highest field for ketene N,N-acetals (see δ(C(α)) of **9A**,**B** [15] and **9C** [16] in *Table 1*). Therefore, highly dipolar, ylide-like structures have been attributed to such ketene

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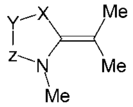
[3]) We recall that it is not meaningful to compare ionization potentials unless the corresponding orbital energies refer to the same type of orbitals. Thus, only the HOMO energies of **9A**,**C**, and of **9B**,**E**,**G**,**H** should be compared.



9 for X-Y-Z, see *Scheme* 1

Table 1. *HOMO Energies* [eV], *as Determined by Photoelectron Spectroscopy, and* ^{13}*C-NMR Chemical Shifts* δ [ppm] *of the Exocyclic C(α) Atom of Cyclic Ketene N,X-Acetals* **9A** – **G** *and Enamine* **9 H** [15]3)

	HOMO energy	δ(C(α))		HOMO energy	δ(C(α))
9A	6.90	63.7	**9B**	6.33	71.0
9C	7.06	84.1	**9E**	6.85	75.3
9D		110.7	**9G**	6.76	95.8
9F		77.9	**9 H**	6.84	102.1

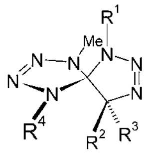
N,N-acetals [16–18]. On the other hand, ketene N,N-acetal **9D** with a six-membered ring is expected to be rather reluctant toward azides, at least according to the δ(C) criterion. Besides ring size and heteroatoms of **1**, we varied the substituents of **1A** and **1B**.

The first border between concerted and two-step HOMO(dipolarophile)–LUMO(1,3-dipole)-controlled cycloadditions has been discovered 15 years ago, as reported briefly in a communication [4a]. Crystallized zwitterions of type **3A** of different thermal stability arose when ketene N,N-acetals **1A** were allowed to react with picryl azide (**2L)** or sulfonyl azides **2M** – **O** at low temperatures. These zwitterions **16** are characterized here by IR, UV/VIS, and NMR spectroscopy, including ^{15}N-NMR. By contrast to ketene N,N-acetals **1A** – **C**, ketene N,X-acetals **1D** – **G** and **1H** reacted with these electron-deficient azides to afford N_2 and ring-expanded imines **7D** – **F** and **8G**,**H**, respectively. Attempts to detect intermediate zwitterions **3** or 1,3-dipolar cycloadducts **4** by recording NMR spectra at temperatures as low as – 78° met with failure. This indicates that the lifetimes of conceivable elusive intermediates – if they exist at all – are shorter than the duration of the NMR experiments [9]. We note that this operational criterion for the absence or presence of intermediates, which we also employed in the present work, is simplistic and much less stringent than the use of stereochemical probes [1]. Unfortunately, these are not feasible, however, due to the present lack of pairs of diastereomeric ketene N,X-acetals **1** [15–18]. Given the reliability of the NMR criterion, these results suggest that, for strongly electron-deficient azides, the borderline separating the mechanistic alternatives runs between the reactions of ketene N,N-acetals **1A** – **C** and those of ketene N,X-acetals **1D** – **G** and **1H**.

Only two 1,3-dipolar cycloadducts **10A**,**B** of an alkyl azide, *viz.* methyl azide (**2A**), to a ketene N,N-acetal **1A** have been reported so far [5]. This reaction is quite general for alkyl azides provided that cyclic ketene N,N-acetals with a five-membered ring, **1A** – **C**, are employed as dipolarophiles. All cyclic ketene N,X-acetals used have already been described [5][15–17][19], except for 1,4-diethyl-5-isopropylidene-4,5-dihydro-1*H*-tetrazole, the precursor to **13E**,**I**,**K** (see **21** in the *Exper. Part*). Preparative experiments were performed by allowing **2** to react with distilled ketene N,X-acetals **1** in solutions in inert solvents (*Method A*) or with solutions of **1** that were obtained by deprotonation with NaH or KH of the corresponding heterocyclic quaternary salts (*Method B*). In some cases, deprotonation was carried out in the presence of the azide

(*Method C*), either for the sake of convenience or because the ketene N,N-acetal had to be trapped *in situ* (→**10D**) to avoid decomposition of the dipolarophile [17]. Isopropylidene dipolarophiles **9** = **1A** (R = Me) were preferred because their cycloadducts are stable toward base. By contrast, cycloadducts of 2,2-dimethylpropylidene dipolarophiles **1A** (R, R = H, ^{t}Bu) are prone to base-mediated ring-opening elimination to yield 1*H*-1,2,3-triazol-5-amines [5][6a].

Disappearence of the yellow color of alkylidenedihydrotetrazoles **1A** allowed rough estimates of the rates of cycloadditions. Reactions of colorless ketene N,X-acetals were monitored by recording NMR spectra. Since these ketene N,X-acetals **9B** – **G** and enamine **9H** are more or less reluctant toward alkyl azides, neat mixtures of dipolarophile and an excess of **2A** were used without solvent. The isolated cycloadducts of alkyl azides **2A** – **C** are listed in *Table 2* (see **10** – **12**). All are colorless, low-melting, crystalline solids which were sublimed under vacuum or recrystallized from nonpolar solvents. The structures are based on elemental analysis and spectroscopic evidence.



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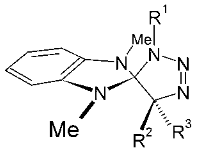

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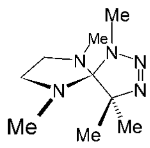

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	R^1	R^2	R^3	R^4
10A, **11A**	Me	Me	Me	Me
10B, **11B**	Me	^{t}Bu	H	Me
10C	Me	Ph	Me	Me
10D	Me	–CH$_2$—CH$_2$–		Me

	R^1	R^2	R^3	R^4
10E	^{t}BuCH$_2$	Me	Me	Me
10F, **11F**	^{t}BuCH$_2$	^{t}Bu	H	Me
10G	^{t}Bu	Me	Me	Me
10H	Me	Me	Me	Ph

Table 2. *Methods and Reaction Conditions, Yields of 1,3-Dipolar Cycloadducts* **10** – **12** *of Alkyl Azides* **2A** – **C** *to Ketene N,N-Acetals* **1A** – **C**, *and Physical Data*

	Method^a)	Solvent	Temp. [°]	Period [d]	Yield [%]^b)	M.p. [°]^b)	IR (KBr) [cm^{-1}]
10C	*B* (3 h)	Et$_2$O	5	5	60	101 – 102 (petr. ether/AcOEt)	1600, 1490
10D	*C*	THF/pentane (1 : 1)	70 → 5	0.5	30	103 – 104 (hexane; subl. 50 – 60°/0.01 Torr)	
10E	*A*	toluene	20 – 25	0.7	90	90 – 91 (hexane)	
10F	*A*	toluene	20 – 25	1.6	78	139 – 140 (hexane)	
10G	*A*	toluene	20 – 25	1.5	80	88 – 90 (Et$_2$O)	
10H	*B* (18 h)	Et$_2$O	5	4	63	80 – 81 (AcOEt)	1600, 1495, 1480
11A	*A*	toluene	2	0.6	81	71 – 72 (pentane/Et$_2$O 4 : 1, – 20°)	1602, 1502
	B (4 d)	THF	2	0.6	60		
11B	*A*	benzene	2	0.6	56	123 – 125 (pentane)	1602, 1501
11F	*A*	benzene	2	1	50	113 – 114 (Et$_2$O)	
12	*A*	benzene	2	21	78	59 – 61 (subl. 50 – 60°/0.1 Torr)	

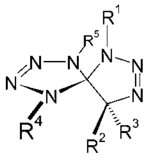
^{a}) *Method:* see text. The period of time given for *Method B* is the duration of the deprotonation step. ^{b}) Yields and m.p. after recrystallization.

Some have been studied by X-ray-diffraction analyses, *viz.*, **11B** [20], **13A** [21], **14J** [22], and **15D** [23].

Alkylidenedihydrotetrazoles **1A** add alkyl azides faster than other ketene N,N-acetals (**1B**,**C**). The dipolarophile **9C** required no less than three weeks for the cycloaddition of **2A**. While primary azides **2A**,**B** add to the isopropylidene dipolarophile **9A** = **1A** (R = Me) and the corresponding 2,2-dimethylpropylidene dipolarophile **1A** (R, R = H, ^{t}Bu) with similar rates, *tert*-butyl azide (**2C**) reacted more slowly with **9A** and failed to add to **1A** (R, R = H, ^{t}Bu), probably due to steric hindrance. Steric strain appears also to cause the equilibration of **10G** with the components **2C** and **9A** at temperatures as low as 70° [8]. Phenyl substitution of the alkylidenedihydrotetrazole **1A**, as in **1A** (R, R = Me, Ph) and **1A** (X = PhN, R = Me), also retards the cycloaddition of **2A** relative to the alkyl compounds **1A**.

Methyl azide did not add to ketene N,N-acetal **9D** nor to N,X-acetals **9E**–**G** or enamine **9H** during extended periods of time (up to several months). This shows that the size of the HOMO–LUMO energy gaps limits the scope of cycloadditions to **1** in the first place. Steric hindrance comes into play with **2C**, while it is not clear whether the steric or the electronic effect of phenyl groups in **1A** plays the major role in slowing down the cycloaddition. The results indicate that crossing of the border between concerted and two-step 1,3-dipolar cycloadditions is not feasible with encumbered alkyl azides and even the most reactive ketene N,N-acetals **1A**.

By contrast to alkyl azides, phenyl azide (**2D**) reacted with all types of ketene N,X-acetals **1** to afford 1,3-dipolar cycloadducts in high yields (→ **13**–**15**, *Table 3*). In accord with the estimated reactivities inferred from the data listed in *Table 1*, the isopropyl-



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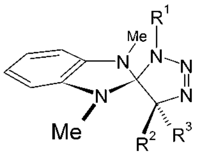

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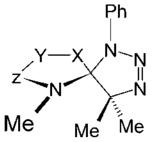
	R^1	R^2	R^3	R^4	R^5
13A, **14A**	Ph	Me	Me	Me	Me
13B, **14B**	Ph	^{t}Bu	H	Me	Me
13C	Ph	Ph	Me	Me	Me
13D	Ph	Me	Me	Ph	Me
13E	Ph	Me	Me	Et	Et
13F	2,6-$Me_2C_6H_3$	Me	Me	Me	Me
13G	4-$NO_2C_6H_4$	Me	Me	Me	Me
13H	4-$NO_2C_6H_4$	^{t}Bu	H	Me	Me
13I	4-$NO_2C_6H_4$	Me	Me	Et	Et
13J, **14J**	2-$NO_2C_6H_4$	Me	Me	Me	Me
13K	2-$NO_2C_6H_4$	Me	Me	Et	Et
13L	2,6-Me_2(4-NO_2)C_6H_2	Me	Me	Me	Me



15C - **H** for X-Y-Z, see *Scheme* 1

Table 3. *Methods and Reaction Conditions, Yields of 1,3-Dipolar Cycloadducts* **13**–**15** *of Aryl Azides to Cyclic Ketene N,X-Acetals* **1**, *and Physical Data*

	Method[a])	Solvent	Temp. [°]	Period	Yield [%]	M.p. [°][b])	IR (KBr) [cm^{-1}]
13A	*A*	benzene	0–5	0.2 h	86	114–115 (hexane)	1600, 1485
13B	*A*	toluene	0–5	0.2 h	65	106–107 (toluene)	
13C	*B* (3 h)	Et$_2$O	20–25	15 h	82	128–129 (hexane)	1600, 1485
13D	*C*	Et$_2$O	−5		80	102–103 (hexane)	1595, 1495, 1485
13E	*A*	Et$_2$O	0	1 h	67	87 (pentane)	
	C	Et$_2$O	20	3 h	31		
13F	*A*	CH$_2$Cl$_2$	$-30 \rightarrow 0$	1 h	78	77–80 (Et$_2$O)	
13G	*A*	toluene	0–5	1 h	89	147–148 (toluene)	1595, 1495, 1515, 1335 (NO$_2$)
13H	*A*	toluene	0–5	1 h	71	109–111 (AcOEt/Et$_2$O)	1590, 1515, 1340 (NO$_2$)
13I	*C*	Et$_2$O	20	3 h	62	124 (dec.; hexane)	
13J	*A*	toluene	$0 \rightarrow 20$	2 h	90	118–120 (Et$_2$O)	
13K	*C*	Et$_2$O	20	3 h	44	98–99 (hexane)	
14A	*A*	benzene	25	0.25 h	75	112–114 (pentane)	1600, 1513, 1501
14B	*A*	benzene	25	0.25 h	75	116–118 (pentane)	1601, 1515, 1505
14J	*A*	toluene	5	0.25 h	70	95–96 (pentane)	
15C	*A*	benzene	25	0.25 h	56	56–57 (pentane)	1596, 1491, 1475
15D	*A*	benzene	60	30 d	80	193 (dec.; AcOEt)	
15E	*A*	benzene	25	0.25 h	79	80–82 (pentane)	1600, 1501, 1489
15F	*A*	benzene	25	0.25 h	79	79–80 (pentane)	1598, 1487
15G	*A*	benzene	25	10 d	73	60–62 (dec.; pentane)	1630, 1598, 1485
15H	*A*	CD$_3$CN	1) 25 2) 60	20 d 10 d	89	93–94 (pentane)	1600, 1489

[a]) *Method:* see text. The period of time given for *Method B* is the duration of the deprotonation step.

idene dipolarophiles **9A**–**C**,**E**,**F** reacted rapidly at room temperature or below, while **9D**,**G**,**H** required many days or even heating of the reaction mixture (**9H**).

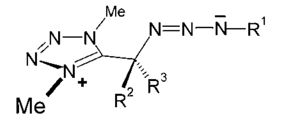
Since picryl azide (**2L**) has permitted isolation of stable zwitterions [4a,b], combinations of less electron-deficient nitrophenyl azides **2** with cyclic ketene N,N-acetals **1** that are shielded by bulky groups promised prospects of seeing new frontiers. This hope was confirmed by *Huisgen*'s [2][12a–d] and *Heuschmann*'s results [24] who demonstrated that intermediate zwitterions in two-step cycloadditions may be detected provided that – besides the presence of favorable HOMO/LUMO energy gaps – at least one terminus of a reactant is encumbered owing to steric hindrance. In fact, these results are mirrored in the propensity of zwitterions **3** to undergo cyclization to the cycloadducts **4**. Zwitterions **3** (R, R = H, ^{t}Bu) require much higher temperatures than **3** (R = Me) [4a,b]. Since even **2L** gave zwitterions only with the most-reactive ketene N,N-acetals **1A**–**C** but not with N,X-acetals **1D**–**G**, only members of the former group, **1A**, were chosen for the present study. The existence of possible labile zwitterions was probed by recording NMR spectra of frozen solutions of the components that were allowed to thaw and mix at low temperatures in the cavity of the spectrometer.

Not unexpectedly, 2,4,6-tri(*tert*-butyl)phenyl azide (**2E**) was completely inert toward **9A**. The two *ortho*-positioned ^{t}Bu groups force the azido group to adopt a conformation perpendicular to the plane of the aromatic ring and thus prohibit any conjugative interaction [25]. Two *ortho*-positioned Me groups as in 2,6-dimethylphenyl azide (**2F**) did not preclude cycloaddition to **9A** but rendered the reaction slow and reversible already at room temperature [8]. A zwitterion could not be detected by recording NMR spectra for solutions of the equilibrating components.

The 4-nitrophenyl azide (**2G**) gave high yields of cycloadducts to **1A**, *i.e.*, **13G–I** (*Table 3*), just like **2D**, except that it reacted already at temperatures as low as –40°. Since zwitterions of type **16** (see below) could not be detected by NMR experiments at low temperatures, all three cycloadditions of **2G** appear to be concerted, irrespective of the different steric requirements of the dipolarophiles **1A**. This contrasts strikingly with the reactions of the same dipolarophiles with 2-nitrophenyl azide (**2H**), whose NO_2 group exerts both, an electron-withdrawing *and* a steric effect. In fact, different steric requirements of the dipolarophiles **1A** translated in different mechanistic pathways.

The 2-nitrophenyl azide (**2H**) reacted with isopropylidenedihydrotetrazole **9A** at –60° to afford cycloadduct **13J** (*Table 3*) which slowly decomposed at room temperature but could be kept at 0°. A zwitterion intermediate of type **16** (see below) was not detectable by NMR experiments at low temperatures nor any other products. Exchange of the Me groups at the dihydrotetrazole ring of **9A** for Et groups did not alter the course of the cycloaddition of **2H** (→**13K**). However, encumbering the electron-rich terminus of the dipolarophile with a ^{t}Bu group as in **1A** (R, R = H, ^{t}Bu) dramatically changed the result: a single product was formed from **2H** and **1A** (R, R = H, ^{t}Bu) in CD_2Cl_2 solution at –30°. It survived several hours at room temperature but could not be isolated due to consecutive reactions, which have not yet been elucidated, however.

Reliable criteria for the distinction between 1,3-dipolar cycloadducts **13** and zwitterions **16** are found in NMR chemical shifts that are listed in *Table 4*. Equivalent H- and C-atoms absorb at similar and characteristic fields irrespective of the substitution pattern R^1, R^2, and R^3 of the skeletons. Due to the positive charge on the heterocyclic ring of zwitterions **16**, the H- and C-atoms of ring MeN groups resonate at lower fields than corresponding nuclei in cycloadducts **13**. According to these criteria, the product of **2H** and **1A** (R, R = H, ^{t}Bu) has the zwitterionic structure **16A**. This assignment was corroborated by the rest of the ^{1}H- and ^{13}C-NMR data. Provided that **16A** cyclizes to a 1,3-dipolar cycloadduct, as it has been demonstrated for other zwitterions [4a,b], a borderline between a concerted and a two-step cycloaddition has been crossed, *viz*. for **2H** between **9A** = **1A** (R = Me) and **1A** (R, R = H, ^{t}Bu).



16

	R^1	R^2	R^3
16A	$2\text{-}NO_2C_6H_4$	^{t}Bu	H
16B	$2,4\text{-}(NO_2)_2C_6H_3$	Me	Me
16C	$4,6\text{-}Me_2(2\text{-}NO_2)C_6H_2$	Me	Me
16D	$2,4,6\text{-}(NO_2)_3C_6H_2$	Me	Me
16E	$2,4,6\text{-}(NO_2)_3C_6H_2$	^{t}Bu	H
16F	$MeSO_2$	^{t}Bu	H
16G	$4\text{-}MeC_6H_4SO_2$	Me	Me
16H	$4\text{-}MeC_6H_4SO_2$	^{t}Bu	H
16I	Me_2NSO_2	^{t}Bu	H

The results described in the foregoing paragraph suggested that increase of the electron demand of the nitrophenyl azides **2G,H** by a second nitro group as in 2,4-dinitrophenyl azide (**2I**) might stabilize the zwitterion relative to the spirocyclic structure and thus allow observation of a zwitterion also in the reaction with the (non-

Table 4. *Selected* ^{1}*H- and* ^{13}*C-NMR Chemical Shifts* δ [ppm] *of 1,3-Dipolar Cycloadducts* **13** *and Zwitterions* **16**

Cycloadduct	$\mathrm{C}\mathit{H}_3\mathrm{N}$	$\mathit{C}\mathrm{H}_3\mathrm{N}$	$\mathrm{R_2}\mathit{C}\mathrm{(R_3)(=C(}\alpha\mathrm{))}$	Spiro-C	Solvent	Ref.
13A	2.51	34.3	79.7	101.5	C_6D_6	[a])
13B	2.40	31.5	81.9	101.1	C_6D_6	[a])
	2.55	33.9				
13F	3.04	34.9	76.6	101.4	$CDCl_3$	[a])
13G	2.95	34.6	80.6	101.2	$CDCl_3$	[a])
13H	2.23	31.3	82.0	101.0	C_6D_6	[a])
	2.42	33.6				
13I	–		78.8	101.3	CD_3CN	[a])
13J	2.96	35.1	79.3	103.2	CD_3CN	[a])
13K	–		78.3	102.2	CD_3CN	[a])
13L	3.21				CD_2Cl_2 [b])	[a])
Zwitterion	$\mathrm{C}\mathit{H}_3\mathrm{N}$	$\mathit{C}\mathrm{H}_3\mathrm{N}$	$\mathrm{R_2}\mathit{C}\mathrm{(R_3)(=C(}\alpha\mathrm{))}$	$\mathrm{MeN^+{=}}\mathit{C}\mathrm{{-}NMe}$		
16A	3.96	37.4	61.7	151.8	CD_2Cl_2[c])	[a])
	4.21	38.4				
16B	3.80				CD_2Cl_2[c])	[a])
16C	3.97				CD_2Cl_2[d])	
16D[e])	4.28	40.0	63.7	156.2	(D_6)DMSO	[4a]
16E	3.99	37.7	61.4	152.0	(D_6)DMSO	[a])
	4.33	38.8				
16F	4.07	37.3	62.0	153.5	(D_6)DMSO	[a])
	4.32	38.3				
16G	3.89	37.9	56.1	155.5	$CDCl_3$ [c])	[4a]
16H	3.61	37.5	62.2	153.6	(D_6)DMSO	[a])
	4.32	38.5				
16I[f])	4.01	37.0	60.7	153.1	(D_6)DMSO	[a])
	4.21	38.6				

[a]) This work. [b]) At −50°. [c]) At −30°. [d]) At −75°. [e]) The ^{1}H-NMR spectrum was recorded in CD_3CN. [f]) The ^{1}H-NMR spectrum was recorded in $CDCl_3$.

encumbered) isopropylidene dipolarophile **9A**. Indeed, **2I** reacted cleanly with **9A** in CD_2Cl_2 solution at −40° to afford a short-lived intermediate which was quantitatively transformed to the known 4,6-dihydrotetrazine-5(1*H*)-imine of type **7A** [11] on warming of the reaction mixture. This conversion could be monitored conveniently by ^{1}H-NMR spectroscopy. Although a ^{13}C-NMR spectrum was not recorded due to the fleeting existence of the intermediate, its ^{1}H-NMR spectrum allowed to reject a spirocyclic structure in favor of the zwitterionic structure **16B**. This result shows that the second nitro group in **2I** tips the balance toward the two-step mechanism in the 1,3-dipolar cycloaddition at **9A**.

Eventually, it was intriguing to adorn the nitrophenyl azides **2G**,**H** with *ortho*-Me groups to study the effect of steric hindrance of the 1,3-dipoles. Both *ortho*-Me-substituted nitrophenyl azides **2J**,**K** reacted with **9A** = **1A** (R = Me) at low temperatures to afford each a single product. Unfortunately, both primary products decomposed in an undefined way already above *ca.* −30° thus precluding unambiguous characterization by means of ^{13}C-NMR spectra recorded on the available 50-MHz spectrometer. However, on the basis of 200-MHz ^{1}H-NMR spectra, we tentatively assign the spirocyclic structure **13L** to the product of **2J** and the zwitterionic structure

16C to the product of **2K**. Apparently, the border between the mechanisms of the reactions of the encumbered 1,3-dipoles **2J**,**K** with **1A** (R = Me) parallels the mechanistic border for the reactions of the parent nitrophenyl azides **2G**,**H** with the encumbered dipolarophile **1A** (R, R = H, ^{t}Bu).

The results of the present search for new borderlines between the concerted and the two-step mechanism of HOMO(dipolarophile) – LUMO(dipole)-controlled 1,3-dipolar cycloadditions are briefly summarized in *Table 5*. They should be considered with caution, however, in view of our simplistic NMR criterion (see above). Scrutiny of the *bona fide* concerted 1,3-dipolar cycloadditions of the nitroaryl azides in the left column to the dipolarophiles in the central column with the help of more-stringent probes may well uncover that these cycloadditions are actually not concerted but follow a two-step mechanism. Furthermore, a zwitterion must be established to be an intermediate en route to the cycloadduct before its existence can attest to a two-step cycloaddition. This is not unlikely in case of **16A**,**C** but should not be taken for granted.

Table 5. *Nitroaryl Azides* (left and right column) *That Afford Different Primary Products in Reactions with the Same Dipolarophile Listed in the Central Column*

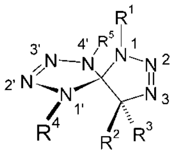
Product = 1,3-dipolar cycloadduct[a])	Dipolarophile	Product = zwitterion
2G $R^1 = 4\text{-}NO_2C_6H_4$	**1A** R, R = H, ^{t}Bu	**2H** $R^1 = 2\text{-}NO_2C_6H_4$
2G $R^1 = 4\text{-}NO_2C_6H_4$	**1A** R = Me	**2I** $R^1 = 2,4\text{-}(NO_2)_2C_6H_3$
2H $R^1 = 2\text{-}NO_2C_6H_4$	**1A** R = Me	**2I** $R^1 = 2,4\text{-}(NO_2)_2C_6H_3$
2J $R^1 = 2,6\text{-}Me_2(4\text{-}NO_2)C_6H_2$	**1A** R = Me	**2K** $R^1 = 4,6\text{-}Me_2(2\text{-}NO_2)C_6H_2$

[a]) Zwitterions could not be detected by NMR spectroscopy at low temperatures.

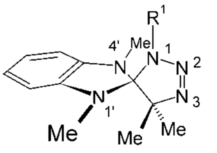
^{15}N-NMR Spectra. ^{15}N-NMR Spectroscopy is a powerful tool for the characterization of N-compounds in general and N-heterocycles in particular [26]. Surprisingly, however, only a single ^{15}N-NMR study of 4,5-dihydro-1*H*-1,2,3-triazoles has been published [27], except for a few examples scattered in the literature, despite the great importance of this group of heterocycles for many areas. Therefore, the ^{15}N-NMR spectra recorded for the cycloadducts **4** not only served for their characterization but also offer welcome additions to the ^{15}N-NMR data base of 1*H*-1,2,3-triazoles and 1*H*-tetrazoles. ^{15}N-NMR Spectra for zwitterions of type **3** are reported here for the first time.

The assignment of the ^{15}N-NMR signals for **10A**,**D**,**E**,**G**, **11A**, **12**, **13A**,**E**,**G** and **14A** was straightforward owing to molecular symmetry (*Table 6*; for **14A**, *cf.* values of **17**, which was available from previous work [28]). Their dihydro-1*H*-tetrazole rings give rise to two N-signals with about twice the intensity of the dihydro-1*H*-triazole N-signals. The saturated N-atoms N(1) and N(1′)/N(4′), absorb at highest fields (arbitrary numbering of the N-atoms). The shifts of the N(1) signals depend strongly on the nature of the alkyl groups at N(1) while the shifts of N(1′)/N(4′) are much less affected. Consequently, the differential influence of the N(1) substituents allowed unequivocal assignment of the N(1) signals. The remaining two N-signals were assigned to N(2) and N(3) by comparison with similar dihydro-1*H*-triazoles [27].

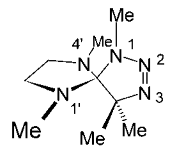
The dihydro-1*H*-tetrazole spirocycles **10B**,**F** and **13B** – **D** lack molecular symmetry and, therefore, show seven N-signals. Their assignment is exemplified for **10B**. The



10, 13



11A, 14A



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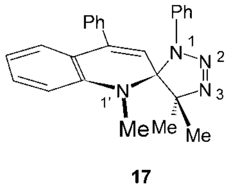

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Table 6. ^{15}*N-NMR Chemical Shifts* δ [ppm] *of 1,3-Dipolar Cycloadducts of Azides to Cyclic Ketene N,N-Acetals.* Arbitrary numbering.

	N(1)	N(2)	N(3)	N(1′)/N(4′)	N(3′)/N(2′)
10A	– 197.9	38.9	– 9.3	– 230.2	– 31.8
10B	– 189.5	45.1	– 25.1	– 227.0	– 32.8
				– 234.7	– 36.9
10D	– 201.3	38.2	– 29.3	– 228.0	– 37.9
10E	– 184.1	43.2	– 4.9	– 231.1	– 35.5
10F	– 172.3	50.0	– 22.1	– 226.9	– 37.0
				– 238.1	43.5
10G	– 170.3	39.4	– 23.0	– 230.9	– 39.8
11A	– 196.0	39.3	– 11.0	– 318.1	
12	– 194.7	45.8	– 9.4	– 344.8	
13A	– 172.6	30.0	– 5.4	– 231.8	– 35.5
13B	– 163.9	37.0	– 19.0	– 227.6	– 37.0
				– 235.0	– 38.9
13C	– 167.4	37.7	– 7.1	– 223.6	– 30.3
				– 227.1	– 34.9
13D	– 170.2	34.4	0.0	– 201.5	– 30.2
				– 226.8	– 42.4
13E	– 163.9	34.6	– 1.1	– 213.0	– 32.6
13G[a])	– 164.9	32.8	– 8.9	– 226.9	– 30.6
14A	– 168.0	34.5	– 0.8	– 313.6	
17	– 166.2	30.3	– 7.8	– 310.0	

[a]) $\delta(NO_2)$ 10.3. This signal and the signal for N(3) may be exchanged.

INEPT ^{15}N-NMR spectrum showed enhancement of all N-signals when the delays were optimized for long-range coupling constants (^2J and ^3J) of *ca.* 4 Hz. The ^{15}N,^{1}H-heteronuclear COSY plot that was recorded by using the optimized coupling information (*Fig.*) shows seven cross-peaks: *H*–C(4) is coupled to N(1′), N(4′), N(2), and N(3); *Me*–N(4′) is correlated with N(3′); *Me*–N(1) shows a cross-peak with N(2), and *Me*–N(1′) one with N(2′). The correlation of *Me*–N(1) with N(2) supports the assignment of the δ(H) 2.93 to *Me*–N(1). The assignment of the H-signals was completed by homonuclear NOE difference spectroscopy (strong NOE (13%) for ^{t}Bu/H−C(4), weak NOE (1%) for ^{t}Bu/*Me*−N(1′)). The completely assigned ^{1}H-NMR spectrum allowed us to assign the δ(N) of N(3), N(2′), and N(3′). Negative NOEs cause diminished ^{15}N-NMR signals, especially for saturated N-atoms during broad-band decoupling. This effect was employed to distinguish N(1′) and N(4′) by selective ^{1}H-decoupling experiments. Irradiation of the frequencies of *Me*−N(1′) or ^{t}*Bu*−C(4) decreased the N(1′) signal, while irradiation of *Me*−N(4′) or *H*−C(4) weakened the N(4′) signal.

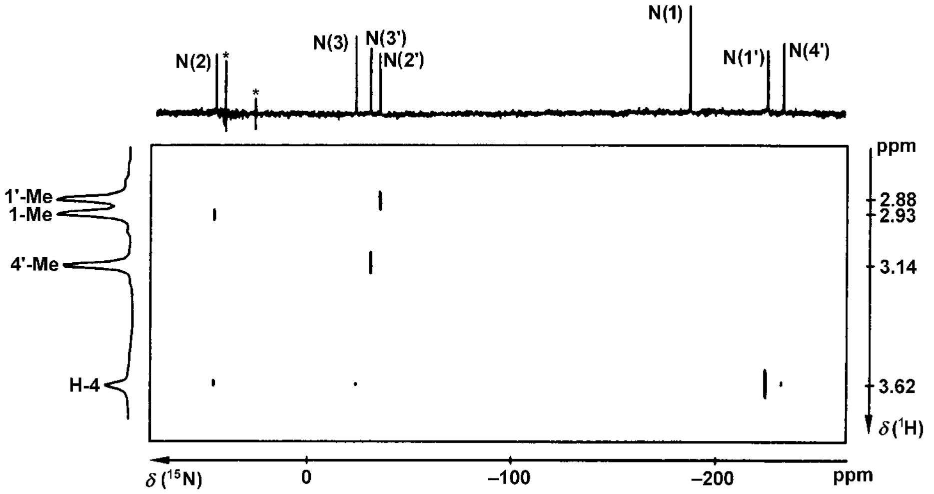
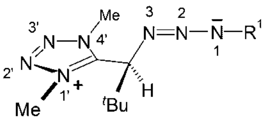


Figure. *^{15}N,^{1}H-Heteronuclear COSY plot of the spirocyclic dihydro-1*H*-1,2,3-triazole* **10B**. The asterisk * indicates noise artifacts which were specific to the spectrometer employed. H-4,4′-Me, *etc.*, are short forms of *H*−C(4), *Me*−N(4′), *etc.* Arbitrary numbering.

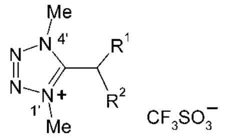
The influence of different substituents on the ^{15}N-NMR chemical shifts (*Table 6*) can be interpreted on the basis of established rules [26]. Exchange of the Me group at N(1) for a branched alkyl group (**10A** → **10E**,**G**; **10B** → **10F**) or a phenyl group (**10A** → **13A**; **10B** → **13B**) results in down-field shifts of the N(1) signal as known from amines [29]. Replacement of the geminal Me groups at C(4) with a ^{t}Bu group and a H-atom (**10A** → **10B**; **10E** → **10F**; **13A** → **13B**) shifts the signals of N(1) and N(2) to lower and that of N(3) to higher field than expected from well-known β and γ effects [26].

Zwitterions **3** that arise from ketene N,N-acetals **1A**–**C** and strongly electron-deficient azides [4] have not yet been studied by ^{15}N-NMR spectroscopy. We report here ^{15}N-NMR data for two examples, **16F**,**H**, which were chosen on the grounds of solubility, stability, and the absence of NO_2 groups (*Table 7*). The comparison of their ^{15}N-NMR chemicals shifts, which differ significantly from those of **10** and **13**, with those of the 1*H*-tetrazolium salts **18** supports the assignment of the ring N-atoms. The terminal N(1) and N(3) atoms of the triazenide moiety (arbitrary numbering of the N-atoms), which each bear a negative partial charge, resonate at much higher field than the central N(2) atom, whose signal appears at lowest field and thus may be used as diagnostic criterion for the distinction of zwitterions **3** from 1,3-dipolar cycloadducts **4**. The nonequivalence of the ^{15}N-NMR signals of N(1′) and N(4′) as well as of N(2′) and

N(3′), and of the ^{1}H- and ^{13}C-NMR signals for the two *Me*N groups, indicates that rotation around the single bond C(5′)−CH^{t}Bu of **16F,H** is slow on the different NMR time scales. As shown for the solid state by X-ray-diffraction analyses, zwitterion **16F** [4a] and the analogous benzimidazole zwitterion [4b] adopt a conformation with the CH−^{t}Bu bond perpendicular to the plane of the heterocyclic ring.



16F R^1 = MeSO$_2$
16H R^1 = 4-MeC$_6$H$_4$SO$_2$



18A R^1 = ^{t}Bu R^2 = H
18B R^1 = R^2 = Me

Table 7. *^{15}N-NMR Chemical Shifts δ* [ppm] *of Zwitterions* **16F,H** *and Tetrazolium Salts* **18A,B**. Arbitrary numbering.

	N(1)/N(3)	N(2)	N(1′)/N(4′)	N(2′)/N(3′)	Solvent	Temp. [°]
16F	− 54.25	+ 90.9	− 149.4	− 14.8	(D$_6$)DMSO	19
	− 76.8		− 152.2	− 15.75		
16H	− 49.9	+ 92.3	− 149.75	− 14.6	(D$_6$)DMSO	19
	− 75.4		− 153.1	− 16.1		
18A			− 145.0	− 13.9	CDCl$_3$	40
18B			− 146.2	− 17.0	(D$_6$)DMSO	19

3. Conclusions. – Cyclic ketene N,X-acetals **1** react with organic azides **2** covering a wide range of reactivity. The most electron-rich dipolarophiles **1** are ketene N,N-acetals **1A** – **C** that are derived from 1*H*-tetrazole and 1*H*-imidazole. They afford 1,3-dipolar cycloadducts **4** with most azides, even with alkyl azides. In contrast, picryl azide and sulfonyl azides – at the opposite end of the azide reactivity scale – react with **1A** – **C** to yield zwitterions **3**. By tuning the 1,3-dipolar reactivity of nitroaryl azides to that of **1A**, we discovered new border regions between the concerted and two-step worlds of HOMO(dipolarophile) – LUMO(1,3-dipole) controlled 1,3-dipolar cycloadditions. Crossing of the border was indicated by intermediate zwitterions that were observed by means of NMR spectroscopy at low temperatures.

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Experimental Part

1. *General.* FC = Flash chromatography. Instrumentation: see [4b] [9a] [27]. UV Spectra: $\lambda_{max}(\log \varepsilon)$ in nm. IR Spectra: in cm^{-1}. NMR Spectra: δ in ppm, *J* in Hz; δ(C) assignments supported by DEPT spectra. ^{15}N,^{1}H-Heteronuclear COSY (*Fig.*): *Bruker WH-400* spectrometer at 40.53 MHz; data acquisition with a spectral width of 14706 Hz (^{15}N) and 1260 Hz (^{1}H) as 2048 × 128 complex files in F_1 with 512 transients accumulated per t_1

increment; mixing time optimized to ^2J(N,H) and ^3J(N,H) of 4 Hz, according to previous results of ^{15}N-INEPT-NMR spectra; zero filling in F_1 afforded a final spectrum comprised of 1024 × 256 points with a digital resolution of 14.4 Hz (^{15}N) and 4.9 Hz (^{1}H).

2. *Cyclic Ketene N,X-Acetals.* For **1A**, see [5][17]; for **1B**, see [15]; for **9C**, see [16]; for **9D** – **G**, see [15]; for **9 H**, see [19].

3. *Azides* **2**. 3.1. *Alkyl Azides.* Methyl azide (**2A**) [5][30] was prepared from NaN$_3$ and immediately introduced into the soln. of the dipolarophile. For **2B**,**C**, see [30].

3.2. *Aryl Azides.* For **2D**, see [31]; for **2E**, see [25]. For **2F**, see [32], the crude product was distilled at 45 – 50° bath temp./1 Torr. FC (silica gel, petroleum ether (30 – 50°)) followed by distillation afforded a pale yellow oil, (53%, b.p. 49 – 50°/1 Torr). ^{1}H-NMR (CDCl$_3$. 400 MHz): 2.45 (*s*, 6 H); 7.05 – 7.12 (*m*, 3 H). ^{13}C-NMR (CDCl$_3$, 100.6 MHz): 18 (2 Me); 125.6 (CH); 128.8 (2 CH); 132.0 (2 quart. C); 136.9 (quart. C). For **2G**, **2H**, see [33][34]; for **2I**, see [11][35]; for **2L**, see [36].

2,6-Dimethyl-4-nitrophenyl Azide (*=2-Azido-1,3-dimethyl-5-nitrobenzene*; **2J**). According to the procedure described in [33], a soln. of NaNO$_2$ (46 mmol) in H$_2$O (10 ml) was added dropwise to a stirred soln. of 2,6-dimethyl-4-nitrobenzenamine (38 mmol) in a mixture of conc. HCl soln. (20 ml) and H$_2$O (35 ml) at – 5°. The mixture was stirred at 0° for 1 h. A soln. of NaN$_3$ (38 mmol) in H$_2$O (10 ml) was added dropwise to the cooled mixture so that the temp. did not exceed 5° (vigorous foaming). The mixture was stirred for 1 h at 0 – 5° and at 20 – 25° to produce a pale brown, light-sensitive precipitate (5.20 g, 71%; m.p. 56 – 58°). FC (silica gel, petroleum ether (30 – 50°)/AcOEt) yielded **2J** (4.90 g, 67%). Colorless crystals. M.p. 58 – 59°. IR (KBr): 2125 (N$_3$). ^{1}H-NMR (CD$_2$Cl$_2$): 2.47 (*s*, 6 H); 7.91 (*s*, 2 H). ^{13}C-NMR (CD$_2$Cl$_2$): 18.5 (2 Me); 124.2 (CH); 133.6, 143.3, 144.9 (quart. C). Anal. calc. for $C_8H_8N_4O_2$ (192.17): C 50.00, H 4.20, N 29.16; found: C 50.25, H 4.30, N 29.40.

4,6-Dimethyl-2-nitrophenyl Azide (*=2-Azido-1,5-dimethyl-3-nitrobenzene*; **2K**). As described for **2J**, with 4,6-dimethyl-2-nitrobenzenamine (38 mmol). The pale brown powder (5.05 g, 69%; m.p. 59 – 62°) was subjected to FC; **2K** (4.97 g, 68%). Colorless crystals. M.p. 64 – 65°. IR (KBr): 2135 (N$_3$). ^{1}H-NMR (CD$_2$Cl$_2$): 2.35 (*s*, 3 H); 2.38 (*s*, 3 H); 7.21 (1 H); 7.59 (1 H). ^{13}C-NMR (CD$_2$Cl$_2$): 18.2 (Me); 20.7 (Me); 123.8, 129.9 (CH); 135.6, 136.7, 136.8 144.1 (quart. C). Anal. calc. for $C_8H_8N_4O_2$ (192.17): C 50.00, H 4.20, N 29.16; found: C 50.02, H 4.29, N 30.03.

3.3. *Sulfonyl Azides.* For **2M**, see [9a]; for **2N**, see [37]; for **2O**, see [11].

4. *Small-Scale Experiments at Low Temperatures.* NMR Sample tubes were flushed with dry N$_2$, charged with a soln. of cyclic ketene N,X-acetal **1** in dry deuterated solvent (usually CD$_2$Cl$_2$), and cooled with EtOH/dry ice or liq. N$_2$. A soln. of azide **2** in the same solvent was placed cautiously on top of the cold mixture, which was kept in the cooling bath. Subsequently, the NMR sample tubes were allowed to attain the desired temp. inside the cavity of the NMR spectrometer. The solns. of **1** and **2** mixed during warm-up. Reactions were monitored by recording NMR spectra.

5. *1,3-Dipolar Cycloadducts* (**10** – **15**). For exper. details, yields, m.p. after recrystallization from the solvent given, and IR data, see *Tables 2* and *3*. ^{1}H-NMR: *Tables 4* and *8*. ^{13}C-NMR: *Tables 4* and *9*. Elemental analyses: *Table 10*. Experiments involving ketene N,X-acetals **1** were performed under dry N$_2$ or Ar.

5.1. *General Method A.* An excess (*ca.* 20%) of neat liquid azide **2A** – **D**,**F** or a soln. of a solid azide **2G**,**H** in the solvents listed in *Table 3* was added dropwise to a stirred soln. of purified, distilled **1** (for solvents, see *Tables 2* and *3*). Stirring was continued at the temp. listed followed by workup after the periods of time given in *Tables 2* and *3*. Workup involved either cooling of the mixtures at *ca.* – 30°, or distillation of the solvents *i. v.* The crude products were recrystallized from the solvents given in *Tables 2* and *3* or purified by sublimation under vacuum.

1,4,4,6,9-Pentamethyl-1,2,3,6,9-pentaazaspiro[4.4]non-2-ene (**12**). Methyl azide (**2A**; *ca.* 15 mmol) was distilled into a stirred soln. of **9C** (1.40 g, 10 mmol) in dry benzene (10 ml) kept at 0°. The mixture was cooled at 2° for 21 d. Distillation of the volatile material *i. v.* and sublimation of the oily residue at 50 – 60° bath temp./ 10^{-1} Torr yielded **12** (1.43 g, 78%). Colorless scales. M.p. 59 – 61°. ^{1}H-NMR (C_6D_6): 1.27 (*s*, 6 H); 2.15 (*s*, 6 H); 2.38 (2 H), 2.74 (2 H) (centres of *AA′BB′*); 2.82 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 22.1 (2 Me); 34.0 (Me); 36.8 (2 Me); 51.9 (2 CH$_2$); 78.6, 103.6 (quart. C).

4,4,6,9-Tetramethyl-1-phenyl-1,2,3,6,9-pentaazaspiro[4.4]non-2-ene (**15C**). The crude product (99%; m.p. 45 – 50°) was recrystallized from pentane to afford colorless crystals (56%). M.p. 56 – 57°. ^{1}H-NMR (CDCl$_3$): 1.28 (*s*, 6 H); 2.35 (*s*, 6 H); 3.02 (2 H), 3.24 (2 H) (centres of *AA′BB′*); 7.0 – 7.4 (*m*, 5 H). ^{13}C-NMR (CDCl$_3$): 22.5 (2 Me); 36.3 (2 Me); 51.4 (2 CH$_2$); 80.3, 103.7 (quart. C); 117.3, 123.0, 128.9 (CH); 142.4 (quart. C).

4,4,8,8,9-Pentamethyl-1-phenyl-6-oxa-1,2,3,9-tetraazaspiro[4.4]non-2-ene (**15F**). The crude product (89%; m.p. 70 – 76°) was recrystallized from pentane to afford colorless prisms (53%). M.p. 79 – 80°. ^{1}H-NMR (C_6D_6): 0.42 (*s*, 3 H); 0.68 (*s*, 3 H); 1.32 (*s*, 3 H); 1.42 (*s*, 3 H); 1.94 (*s*, 3 H); 3.25, 3.46 (*AB*, $^2J_{AB}$ = 7.7, 2 H); 6.9 – 7.7 (*m*,

Table 8. *^{1}H-NMR Chemical Shifts δ* [ppm] *of Cycloadducts* **10**, **11**, *and* **13**–**15**. The signals are *s* unless stated otherwise.

	R^1		R^2, R^3 = Me		R^4, R^5 = Me	Arom. H (*m*)	Solvent
10E	^{t}BuCH$_2$	0.94, 2.42	1.06		2.76		C_6D_6
10G	^{t}Bu	1.17	1.13		2.62		C_6D_6
11A	Me	2.41	1.14		2.34	6.20, 6.78[a])	C_6D_6
13A	Ph		1.04		2.51	6.7–7.2	C_6D_6
13F	2,6-Me$_2$C$_6$H$_3$	2.16	1.46		3.04	6.9–7.2	$CDCl_3$
13G	4-NO$_2$C$_6$H$_4$		1.43		2.95	6.92, 8.25[a])	$CDCl_3$
13J	2-NO$_2$C$_6$H$_4$		1.35		2.96	6.2–8.8	CD_3CN
13L	2,6-Me$_2$(4-NO$_2$)C$_6$H$_2$	2.15	1.50		3.21	7.88	CD_2Cl_2[b])
14A	Ph		1.13		2.28	6.2–7.1	C_6D_6
14J	2-NO$_2$C$_6$H$_4$		1.39		2.73		CD_2Cl_2
15D	Ph		0.91		2.46	6.1–7.8	C_6D_6
15E	Ph		1.12, 1.40	2.18		6.0–7.4	C_6D_6
15G	Ph		1.38, 1.49	2.47		6.2–7.3	$CDCl_3$
			R^2=Ph	R^3=Me			
10C	Me[c])	1.94	1.38		2.40, 2.71	7.0–7.5	C_6D_6
13C	Ph		1.43		1.87, 2.67	6.3–7.4	C_6D_6
			R^2=^{t}Bu	R^3=H			
10F	^{t}BuCH$_2$	0.88, 1.99[d]), 3.08[d])	1.09	3.37	2.57, 2.78		$CDCl_3$
11B	Me[c])	2.60	1.13	3.59	2.87, 2.89	6.2–6.8	$CDCl_3$
11F	^{t}BuCH$_2$	0.91, 2.25[e]), 3.16[e])	1.06	3.60	2.54, 2.59	6.26, 6.63[a])	$CDCl_3$
13B	Ph		1.10	3.56	2.40, 2.55	6.7–7.2	C_6D_6
13H	4-NO$_2$C$_6$H$_4$		1.03	3.47	2.23, 2.42	6.69, 7.78[a])	C_6D_6
14B	Ph		1.16	3.82	2.41, 2.88	6.2–7.2	$CDCl_3$
			R^2, R^3 = Me	R^4 = Ph	R^5 = Me		
10H	Me[c])	2.36	0.98,	1.12	2.62	6.7–7.3	C_6D_6
13D	Ph		1.04,	1.15	2.58	6.6–7.3	C_6D_6

[a]) Centers of an *AA'XX'* spectrum. [b]) The spectrum was recorded at − 50°. [c]) MeN signals may be exchanged. [d]) *d*, *J* = 13.4, 1 H. [e]) *d*, *J* = 13.6, 1 H.

5 H). ^{13}C-NMR (C_6D_6): 21.2, 21.9, 22.6, 25.7, 26.8 (Me); 57.8 (quart. C); 77.6 (CH$_2$); 78.4, 116.4 (quart. C); 124.0, 125.9, 128.8 (CH); 141.5 (quart. C).

*1,3,3',5'-Tetrahydro-1,3,3,5',5'-pentamethyl-3'-phenylspiro[2*H*-indole-2,4'-[4*H*-1,2,3]triazole]* (**15H**). The soln. of **2D** and **9H** in MeCN was kept at 20–25° for 20 d and subsequently at 60° for 10 d. The yellow oil (quant.) crystallized from pentane: **15H** (89%). Colorless plates. M.p. 93–94°. ^{1}H-NMR (C_6D_6): 1.16 (*s*, 3 H); 1.17 (*s*, 3 H); 1.27 (*s*, 3 H); 1.60 (*s*, 3 H); 2.26 (*s*, 3 H); 6.1–7.2 (*m*, 9 H). ^{13}C-NMR (C_6D_6): 20.2, 21.4, 22.4, 30.0, 32.3 (Me); 45.4, 80.6, 99.2 (quart. C); 106.7, 119.4, 120.2, 122.4, 124.5, 128.4, 128.7 (CH); 139.0, 143.1, 148.8 (quart. C).

5.2. *General Method B.* A suspension of powdered 1*H*-tetrazolium trifluoromethanesulfonate or hexafluorophosphate [17] (→ **10C**,**H**, **13C**) or 1*H*-benzimidazolium tetrafluoroborate [15] (→ **11A**) (5.00 mmol) and NaH (0.36 g, 15 mmol) in dry Et$_2$O or THF (20 ml) was stirred in an 80-ml centrifuge tube equipped with a septum and connected to a supply of Ar, until the gas evolution had ceased. The solid material was removed with the help of a centrifuge. The supernatant soln. was transferred *via* syringe into a flask filled with Ar. The solid material was washed twice with the solvent (5 ml). Then **2A** (*ca.* 15 mmol) or **2D** (0.84 g, 7.0 mmol) was added to the combined solns. Stirring was continued, followed by distillation of the solvent *i. v.* and workup of the residue.

1,4,6,9-Tetramethyl-9-phenyl-1,2,3,4,6,7,8-heptaazaspiro[4.4]nona-2,7-diene (**10C**). The yellow-brown solid residue (1.16 g, 89%; m.p. 85–88°) was purified by FC (silica gel, petroleum ether (30–50°)/AcOEt 9 : 1): pale yellow crystals.

Table 9. *^{13}C-NMR Chemical Shifts* δ [ppm] *of Cycloadducts* **10**, **11**, *and* **13**–**15**

	R¹		R², R³ = Me		R²*C*(R³)	R⁴, R⁵ = Me	Spiro-C	Arom. CH	quart. arom. C	Solvent
10E	^{t}BuCH$_2$	29.0, 33.2[b], 58.4	21.0		74.2	34.9	105.3			*B*
10G	^{t}Bu	29.6, 54.7[b]	22.1		77.8	35.1	103.1			*B*
11A	Me[c]	32.14	21.8		79.2	32.14	108.5	103.7, 104.7,	139.0	*B*
		32.98	22.3		78.6	33.19	110.0	118.9, 119.8	139.9	*M*
13A	Ph		21.6		79.7	34.3	101.5	115.9, 123.6, 129.0	141.0	*B*
13F	2,6-*Me*$_2$C$_6$H$_3$	20.3	21.4		76.6	34.9	101.4	125.9, 129.0	128.1, 135.9	*C*
13G	4-NO$_2$C$_6$H$_4$		21.7		80.6	34.6	101.2	115.1, 125.8	143.3, 145.2	*C*
13J	2-NO$_2$C$_6$H$_4$		21.1		79.3	35.1	103.2	119.5, 126.1, 126.7, 132.9	134.6, 142.2	*A*
14A	Ph		22.1		83.3	31.9	106.3	104.2, 115.5, 119.4, 123.2, 129.8	138.3, 141.1	*B*
14J	2-NO$_2$C$_6$H$_4$		21.4		82.5	32.3	107.3			*D*
15D	Ph		23.0		89.9	34.5	94.3	103.0, 115.7, 117.2, 123.7, 127.6, 129.6	112.5, 134.3, 139.6, 141.3	*C*
15E	Ph		20.7, 21.7		83.1	30.5	116.5	104.8, 107.5, 117.2, 119.1, 122.5, 124.1, 129.5	138.2, 139.9, 146.5	*B*
15G	Ph		18.2, 25.1		83.0	31.4	101.9	106.2, 117.3, 119.0, 121.0 124.0, 126.0, 129.1	121.2, 139.6, 145.4	*C*
			R² = ^{t}Bu	R³ = H						
10F	^{t}BuCH$_2$[d]	28.4, 33.0[b], 58.9	27.6	31.9	77.7	31.6, 34.8	104.4			*C*
11B	Me[c]	28.5	27.9	31.7	81.5	32.2, 32.4	108.4	102.8, 103.2, 118.0, 118.8	137.37, 137.44	*C*
11F	^{t}BuCH$_2$[d]	28.2, 32.6[b], 56.0	27.8	31.4	80.4	28.8, 31.0	110.0	102.1, 102.4, 117.5, 118.5	137.0, 137.1	*C*
13B	Ph		27.6	32.8	81.9	31.5, 33.9	101.1	115.8, 123.8, 129.9	141.2	*B*
13H	4-NO$_2$C$_6$H$_4$		27.4	32.8	82.0	31.3, 33.6	101.0	114.7, 125.8	143.6, 145.4	*B*
14B	Ph		27.7	32.3	84.1	28.5, 31.7	107.0	103.6, 103.7, 115.6, 118.4, 119.2, 123.3, 129.4	136.5, 137.6, 140.4	*C*
			R²–R³ = (CH$_2$)$_2$							
10D	Me[c]	33.3	11.6		56.3	31.1	99.4			*B*
			R² = Ph	R³ = Me						
10C	Me[c]	33.5	23.2		79.2	32.8, 35.2	104.1	126.1, 127.6, 128.2	138.9	*C*
13C	Ph		22.9		82.8	32.5, 34.9	101.9	115.6, 123.8, 126.1, 127.9, 128.3, 129.6	138.2, 139.8	*C*
			R², R³ = Me			R⁴ = Ph, R⁵ = Me				
10H	Me[c]	34.8	20.7, 23.9		80.0	31.9	101.1	117.3, 123.3 129.6	141.2	*B*
13D	Ph		21.5, 23.4		82.8	34.4	98.5	115.5, 118.0, 123.9, 124.0, 129.4, 129.9	139.9, 140.7	*B*
						R⁴, R⁵ = Et				
13E	Ph		22.1		79.0	13.6, 42.2[e]	100.2	115.8, 123.5, 129.4	140.0	*C*
13I	4-NO$_2$C$_6$H$_4$		22.1		78.8	13.8, 42.5[e]	101.3	115.7, 125.8	143.4, 145.7	*C*
13K	2-NO$_2$C$_6$H$_4$		21.0		78.3	13.7, 42.3[e]	102.3	118.6, 124.6, 125.8, 133.0	132.6, 142.2	*C*

[a] *A* = CD$_3$CN, *B* = C$_6$D$_6$, *C* = CDCl$_3$, *D* = CD$_2$Cl$_2$, *M* = CD$_3$OD. [b] The signals of ^{t}Bu groups are listed in the order Me$_3$C. [c] MeN Signals may be exchanged. [d] ^{t}Bu Signals may be exchanged. [e] The signals of Et groups are listed in the order MeCH$_2$.

Table 10. *Molecular Formulae and Masses and Elemental Analyses for Cycloadducts* **10**–**15**

	Molecular formula	Molecular mass		C	H	N
10C	$C_{12}H_{17}N_7$	259.3	calc.	55.58	6.61	37.81
			found	55.82	6.88	37.78
10D	$C_7H_{13}N_7$	195.2	calc.	43.07	6.71	50.22
			found	43.34	6.67	50.19
10E	$C_{11}H_{23}N_7$	253.4	calc.	52.12	9.15	38.70
			found	52.44	9.34	38.40
10F	$C_{13}H_{27}N_7$	281.4	calc.	55.49	9.67	34.84
			found	55.11	9.87	35.16
10G	$C_{10}H_{21}N_7$	239.3	calc.	50.19	8.84	40.97
			found	50.49	9.06	41.22
10H	$C_{12}H_{17}N_7$	259.3	calc.	55.58	6.61	37.81
			found	55.28	6.67	37.66
11A	$C_{13}H_{19}N_5$	245.3	calc.	63.65	7.81	28.55
			found	63.70	7.87	28.44
11B	$C_{15}H_{23}N_5$	273.4	calc.	65.90	8.48	25.62
			found	65.82	8.78	25.72
11F	$C_{19}H_{31}N_5$	329.5	calc.	69.26	9.48	21.26
			found	69.37	9.74	21.14
12	$C_9H_{19}N_5$	197.3	calc.	54.79	9.71	35.50
			found	55.12	9.99	35.04
13A	$C_{12}H_{17}N_7$	259.3	calc.	55.58	6.61	37.81
			found	55.35	6.58	38.03
13B	$C_{14}H_{21}N_7$	287.4	calc.	58,52	7.37	34.12
			found	58.12	7.64	34.39
13C	$C_{17}H_{19}N_7$	321.4	calc.	63.53	5.96	30.51
			found	63.30	5.91	30.18
13D	$C_{17}H_{19}N_7$	321.4	calc.	63.53	5.96	30.51
			found	63.42	5.99	30.23
13E	$C_{14}H_{21}N_7$	287.4	calc	58.52	7.37	34.12
			found	58.50	7.02	34.47
13G	$C_{12}H_{16}N_8O_2$	304.3	calc.	47.36	5.30	36.82
			found	47.48	5.52	36.99
13H	$C_{14}H_{20}N_8O_2$	332.4	calc.	50.59	6.07	33.71
			found	50.23	5.71	33.39
13I	$C_{14}H_{20}N_8O_2$	332.4	calc.	50.59	6.07	33.71
			found	50.58	6.19	33.92
13J	$C_{12}H_{16}N_8O_2$	304.3	calc.	47.36	5.30	36.82
			found	47.04	5.18	36.95
13K	$C_{14}H_{20}N_8O_2$	332.4	calc.	50.59	6.07	33.71
			found	50.86	5.92	34.01
14A	$C_{18}H_{21}N_5$	307.4	calc.	70.33	6.89	22.78
			found	70.46	7.01	22.59
14B	$C_{20}H_{25}N_5$	335.5	calc.	71.61	7.51	20.88
			found	71.62	7.71	20.73
14J	$C_{18}H_{20}N_6O_2$	352.4	calc.	61.35	5.72	23.85
			found	61.34	5.81	24.25
15C	$C_{14}H_{21}N_5$	259.4	calc.	64.84	8.16	27.00
			found	64.57	8.06	27.29
15D	$C_{22}H_{23}N_5$	357.5	calc.	73.92	6.49	19.59
			found	73.67	6.54	19.67
15E	$C_{17}H_{18}N_4O$	294.4	calc.	69.37	6.16	19.03
			found	69.17	6.08	18.79
15F	$C_{15}H_{22}N_4O$	274.4	calc.	65.67	8.08	20.42
			found	65.99	8.37	20.67
15H	$C_{20}H_{24}N_4$	320.4	calc.	74.97	7.55	17.48
			found	74.84	7.60	17.52
15G	$C_{17}H_{18}N_4S$	310.4	exact mass calc.		310.12523	
			found		310.12604	

1,6,9,9-Tetramethyl-4-phenyl-1,2,3,4,6,7,8-heptaazaspiro[4.4]nona-2,7-diene (**10H**). FC (silica gel, petroleum ether/AcOEt 9 : 1) of the remaining yellow oil (1.24 g) yielded colorless crystals (0.82 g, 63%). M.p. 80–81°.

*1,3,3′,5′-Tetrahydro-1,3,3′,5′5′-pentamethylspiro[2*H*-benzimidazole-2,4′-[4*H*-1,2,3]triazole]* (**11A**). Recrystallization of the remaining colorless powder (0.795 g, 65%; m.p. 63–68°) from Et_2O/pentane 1 : 4 at –20° yielded colorless prisms (0.735 g, 60%). M.p. 71–72°.

1,4,9-Trimethyl-6,9-diphenyl-1,2,3,4,6,7,8-heptaazaspiro[4.4]nona-2,7-diene (**13C**). Recrystallization of the yellow crystals (1.38 g, 86%; m.p. 113–115°) from hexane at –30° gave colorless crystals (1.34 g, 82%). M.p. 128–129°.

5.3. *General Method C.* Methyl azid **2A** (*ca.* 15 mmol) or an aryl azide **2D**,**G**,**H** (6 mmol) was added to a stirred suspension of powdered 1*H*-tetrazolium trifluoromethanesulfonate ([17] → **10D**; **21** → **13E**,**I**,**K**) (5.00 mmol) and NaH (0.36 g, 15 mmol) in dry solvent (30 ml). Stirring was continued until the gas evolution had ceased. The excess of NaH was cautiously destroyed by the addition of H_2O (30 ml) at 0°. The mixture was neutralized with 2M HCl. The aq. layer was extracted with CH_2Cl_2 (3 × 30 ml), the combined org. layer washed with sat. aq. NaCl soln., dried (Na_2SO_4), and evaporated, and the residue purified.

5,8,9-Trimethyl-5,6,7,8,9,10,11-heptaazadispiro[2.0.4.3]undeca-6,10-diene (**10D**). The semisolid yellow residue (0.77 g, 79%) was recrystallized from hexane at –25° to afford a colorless powder which sublimed at 50–60° (bath temp.)/10^{-2} Torr: **10D** (0.30 g, 31%). Colorless crystals. M.p. 103–104°. ^{1}H-NMR (250 MHz, 0.153 Hz/pt., C_6D_6): 0.72 ($\delta_X = \delta_{X'}$, 2 H), 1.34 ($\delta_A = \delta_{A'}$, 2 H) ($AA'XX'$, $^3J_{AA'} = 10.6$, $^3J_{XX'} = 10.2$, $^2J_{AX} = {}^2J_{A'X'} = -4.5$, $^3J_{AX'} = {}^3J_{A'X} = 7.8$); 2.49 (*s*, 6 H); 2.56 (*s*, 3 H).

1,4-Diethyl-9,9-dimethyl-6-phenyl-1,2,3,4,6,7,8-heptaazaspiro[4.4]nona-2,7-diene (**13E**). Recrystallization of the pale yellow crystals (0.82 g, 57%; m.p. 75–82°) from pentane gave **13E** (0.45 g, 31%). Colorless crystals. M.p. 87°. ^{1}H-NMR ($CDCl_3$): 1.37 (*s*, 6 H); 1.39 (*t*, 6 H); 2.91 (*m*, 4 H); 6.80–7.37 (*m*, 5 H).

1,4,-Diethyl-9,9-dimethyl-6-(4-nitrophenyl)-1,2,3,4,6,7,8-heptaazaspiro[4.4]nona-2,7-diene (**13I**). Recrystallization of the pale yellow crystals (1.41 g, 85%) from hexane gave **13I** (1.03 g, 62%). Colorless crystals. M.p. 124° (dec.). ^{1}H-NMR ((D_8)toluene): 1.38 (*s*, 6 H); 1.37 (*t*, 6 H), 2.89 (center of *AB* part, 4 H) (2 ABX_3, $^2J_{AB} = 13.1$, $^3J_{AX} = 6.9$, $^3J_{BX} = 7.5$); 7.79 (center of $AA'BB'$, 4 H).

1,4-Diethyl-9,9-dimethyl-6-(2-nitrophenyl)-1,2,3,4,6,7,8-heptaazaspiro[4.4]nona-2,7-diene (**13K**). Recrystallization of the light brown crystals (1.40 g, 84%; m.p. 84°) from hexane gave **13K** (0.73 g, 44;%). Colorless crystals M.p. 98–99°). ^{1}H-NMR ((D_8)toluene): 1.40 (*s*, 6 H); 1.43 (*t*, 6 H), 3.03 (center of *AB* part, 4 H) (2 ABX_3, $^2J_{AB} = 13.2$, $^3J_{AX} = 7.2$, $^3J_{BX} = 7.3$); 6.2–7.8 (*m*, 4 H).

6. *Zwitterions* (**16**). 6.1. *5-{2,2-Dimethyl-1-[3-(2-nitrophenyl)triaz-1-enyl]propyl}-1,4-dimethyl-1*H*-tetrazolium Inner Salt* (**16A**). ^{1}H-NMR (200 MHz, CD_2Cl_2, –30°): 1.16 (*s*, 9 H); 3.96 (*s*, 3 H); 4.21 (*s*, 3 H); 4.64 (*s*, 1 H); 6.7–8.0 (*m*, 4 H). ^{13}C-NMR (50 MHz, CD_2Cl_2, –30°): 26.9 (3 Me); 37.4 (Me); 38.4 (Me and quart. C); 61.7 (CH); 118.5, 123.5, 124.8, 132.3 (CH); 139.1, 147.1, 151.8 (quart. C).

6.2. *5-{1-[3-(2,4-Dinitrophenyl)triaz-1-enyl]-1-methylethyl}-1,4-dimethyl-1*H*-tetrazolium Inner Salt* (**16B**). ^{1}H-NMR (200 MHz, CD_2Cl_2, –30°): 1.69 (*s*, 6 H); 3.80 (*s*, 6 H); 7.44 (br. *d*, *J* = 9.5, 1 H); 8.13 (*dd*, *J* = 9.5, 2.7, 1 H); 8.51 (*d*, *J* = 2.7, 1 H).

6.3. *5-{1-[3-(2,4-Dimethyl-6-nitrophenyl)triaz-1-enyl]-1-methylethyl}-1,4-dimethyl-1*H*-tetrazolium Inner Salt* (**16C**). ^{1}H-NMR (200 MHz, CD_2Cl_2, –75°): 1.49 (*s*, 3 H); 1.62 (s, 6 H); 2.15 (*s*, 3 H); 3.97 (*s*, 6 H); 6.91 (1 H); 7.02 (1 H).

6.4. *1,4-Dimethyl-5-{1-methyl-1-[3-(2,4,6-trinitrophenyl)triaz-1-enyl]ethyl}-1*H*-tetrazolium Inner Salt* (**16D**). A soln. of **2L** (5.1 mmol) in dry toluene (5 ml) was added dropwise to a stirred soln. of **9A** (5.0 mmol) in dry toluene (2 ml) under Ar at 0°. Stirring was continued for 1 h at 20°. The orange-red powder (1.95 g, 99%; m.p. 110° (dec.)) was recrystallized from acetone/Et_2O: **16D** (90%). Red crystals. M.p. 125–126°). UV/VIS (MeCN): 442 (log *ε* 4.376). IR (KBr): 1605, 1625 (C=C), 1315, 1525 (NO_2). ^{1}H- and ^{13}C-NMR: see [4a]. Anal. calc. for $C_{12}H_{14}N_{10}O_6$ (394.3): C 36.55, H 3.58, N 35.52; found: C 36.90, H 3.59, N 35.92.

6.5. *5-{2,2-Dimethyl-1-[3-(2,4,6-trinitrophenyl)triaz-1-enyl]propyl}-1,4-dimethyl-1*H*-tetrazolium Inner Salt* (**16E**). A soln. of **2L** (5.1 mmol) in dry toluene (5 ml) was added dropwise to a stirred soln. of **1A** (R, R = H, ^{t}Bu; 5.0 mmol) in dry toluene (2 ml) under Ar at 0°. Stirring was continued for 1 h at 20° followed by rapid workup to afford a black powder (1.58 g; m.p. 94° (dec.)). FC (silica gel, petroleum ether (30–70°)/AcOEt 2 : 8) afforded **16E** (37%). Red crystals. M.p. 115°. UV/VIS (MeCN): 421 (4.438). IR (KBr): 1605, 1625 (C=C), 1320, 1530 (NO_2). ^{1}H-NMR ((D_6)DMSO): 1.16 (*s*, 9 H); 3.99 (*s*, 3 H); 4.33 (*s*, 3 H); 5.02 (*s*, 1 H); 8.51 (*s*, 2 H). ^{13}C-NMR ((D_6)DMSO): 26.4 (3 Me); 37.7 (Me); 38.2 (quart. C); 38.8 (Me); 61.4 (CH); 122.5 (2 CH); 133.8, 140.1, 145.3, 152.0 (quart. C). Anal. calc. for $C_{14}H_{18}N_{10}O_6$ (422.4): C 39.81, H 4.30, N 33.16; found: C 39.87, H 4.45, N 33.44.

6.6. *5-{2,2-Dimethyl-1-[3-(methylsulfonyl)triaz-1-enyl]propyl}-1,4-dimethyl-1*H*-tetrazolium Inner Salt* (**16F**). At – 20°, **2M** (5.1 mmol) was added dropwise to a stirred soln. of **1A** (R, R = H, ^{t}Bu; 5.0 mmol) in dry toluene (2 ml) under Ar. Stirring was continued for 1 h at – 20° followed by distillation of the solvent *i. v.* The colorless powder (1.42 g, 98%; m.p. 93 – 97°) was recrystallized from ^{i}PrOH: **16E** (77%). Colorless crystals. M.p. 111 – 112°. UV (MeCN): 236 (3.822). IR (KBr): 1145, 1290 (SO_2). ^{1}H-NMR ((D_6)DMSO): 1.23 (*s*, 9 H); 2.90 (*s*, 3 H); 4.07 (*s*, 3 H); 4.32 (*s*, 3 H); 4.60 (*s*, 1 H). ^{13}C-NMR ((D_6)DMSO): 27.1 (3 Me); 37.0 (quart. C); 37.3, 38.3, 39.0 (Me); 62.0 (CH); 153.5 (quart. C). Anal. calc. for $C_9H_{19}N_7O_2S$: C 37.36, H 6.62, N 33.88; found: C 37.31, H 6.61, N 34.11.

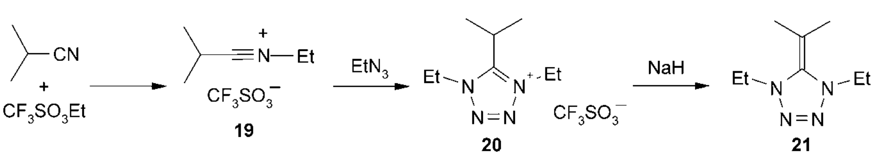
6.7. *1,4-Dimethyl-5-{1-methyl-1-{3-[(4-methylphenyl)sulfonyl]triaz-1-enyl}ethyl}-1*H*-tetrazolium Inner Salt* (**16G**). Compound **9A** (35 mg, 0.25 mmol) was placed under dry Ar into an NMR sample tube and cooled to – 78°. A soln. of **2N** (52 mg , 0.26 mmol) in dry (D_8)toluene (0.7 ml), which was cooled to – 30°, was added, and the mixture was kept at – 30° for 2 h. The solid product was rapidly isolated at 0° by centrifugation. The supernatant liquid was decanted followed by the addition of dry (D_8)toluene (0.5 ml, – 30°), isolation of the colorless product as before, and separation of the supernatant liquid. The colorless crystals were dissolved in $CDCl_3$, cooled to – 30°, followed by recording of the NMR spectra at – 30°. ^{1}H- and ^{13}C-NMR: see [4a].

6.8. *5-{2,2-Dimethyl-1-{3-[(4-methylphenyl)sulfonyl]triaz-1-enyl}propyl}-1,4-dimethyl-1*H*-tetrazolium Inner Salt* (**16H**). At 0°, **2N** (5.1 mmol) was added dropwise to a stirred soln. of **1A** (R, R = H, ^{t}Bu; 5.0 mmol) in dry toluene (2 ml) under Ar. Stirring was continued for 1 h at 20° followed by filtration of the precipitate: **16H** (quant.). Colorless powder. M.p. 137°. UV (MeCN): 256 nm (4.101). IR (KBr): 1550 (C=C), 1150, 1300 (SO_2). ^{1}H- and ^{13}C-NMR ($CDCl_3$): see [4a]. ^{1}H-NMR ((D_6)DMSO): 1.15 (*s*, 9 H); 2.36 (*s*, 3 H); 3.61 (*s*, 3 H); 4.32 (*s*, 3 H); 4.58 (*s*, 1 H); 7.14 (2 H); 7.48 (2 H). ^{13}C-NMR ((D_6)DMSO): 21.2 (Me); 27.0 (3 Me); 36.8 (quart. C); 37.5 (Me); 38.5 (Me); 62.2, 126.7, 128.7 (CH); 139.6, 141.4, 153.6 (quart. C). Anal. calc. for $C_{15}H_{23}N_7O_2S$ (365.2): C 49.30, H 6.34, N 26.83; found: C 48.92, H 6.40, N 27.09.

6.9. *5-{2,2-Dimethyl-1-{3-[(dimethylamino)sulfonyl]triaz-1-enyl}propyl}-1,4-dimethyl-1*H*-tetrazolium Inner Salt* (**16I**). At 0°, **2O** (5.1 mmol) was added dropwise to a stirred soln. of **1A** (R, R = H, ^{t}Bu; 5.0 mmol) in dry toluene (2 ml) under Ar. Stirring was continued for 1 h at 20° followed by filtration of the precipitate to afford colorless crystals (1.37 g, 86%). Recrystallization from ^{i}PrOH gave **16I**. Colorless crystals. M.p. 144 – 145°. UV (MeCN): 242 nm (3.753). IR (KBr): 1110, 1310 (SO_2). ^{1}H-NMR ($CDCl_3$): 1.12 (*s*, 9 H); 2.66 (*s*, 6 H); 4.01 (*s*, 3 H); 4.21 (*s*, 3 H); 4.53 (*s*, 1 H). ^{13}C-NMR ((D_6)DMSO): 26.6 (3 Me); 36.8 (quart. C); 37.0 (Me); 38.3 (2 Me); 38.6 (Me); 60.7 (CH); 153.1 (quart. C). Anal. calc. for $C_{10}H_{22}N_8O_2S$ (318.4): C 37.72, H 6.96, N 35.19; found: C 37.70, H 7.26, N 35.43.

7. *1,4-Diethyl-1*H*-tetrazole Derivatives* (*Scheme 2*). 7.1. *N-(2-Methylpropylidyne)ethanaminium Trifluoromethanesulfonate* (**19**). According to [5][17], a mixture of 2-methylpropanenitrile (10.4 g, 0.15 mol) and ethyl trifluoromethanesulfonate (26.7 g, 0.15 mol) was kept in a closed flask for 14 d at r.t., while the conversion was monitored by ^{1}H-NMR spectroscopy, to afford a viscous oil.

Scheme 2



7.2. *Ethyl Azide* (**Caution!** *Ethyl azide tends to violent explosions* [38]). Diethyl sulfate (126 ml, 0.85 mol) and a sol. of potassium hydroxide hydrate (31.9 g, 0.43 mol) in H_2O (70 ml) were added dropwise and simultaneously to a stirred soln. of NaN_3 (16.2 g, 0.25 mol) in H_2O (70 ml), kept at 80°, while the product was removed by a stream of N_2 passing through the mixture. The gaseous mixture was dried by allowing it to pass through a 50 × 3 cm column filled with KOH pellets and heated at 70°. EtN_3 was condensed in an efficient cooler (– 40°) and directly introduced into the flask containing **19**.

7.3. *1,4-Diethyl-5-(1-methylethyl)1*H*-tetrazolium Trifluoromethanesulfonate* (**20**). EtN_3 (10.7 g, 0.15 mol) was added dropwise with stirring to **19** (36.4 g, 0.15 mol) kept at 0°. Stirring was continued for 2 h, followed by cooling at – 10° for 3 d. Filtration gave pale yellow crystals (45.9 g; m.p. 54 – 57°). Recrystallization from ^{i}PrOH yielded **20** (39.9 g, 85%). Colorless scales. M.p. 72 – 73°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.57 (*d*, *J* = 7.2, 6 H); 1.70 (*t*, *J* = 7.2, 6 H); 3.79 (*sept.*, *J* = 7.2, 1 H); 4.64 (*q*, *J* = 7.2, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 13.7 (2 Me); 18.4

(2 Me); 24.3 (CH); 46.9 (2 CH_2); 155.8 (quart. C). Anal. calc. for $C_9H_{17}F_3N_4O_3S$ (318.3): C 33.96, H 5.38, N 17.60; found: C 33.87, H 5.33, N 17.84.

7.4. *1,4-Diethyl-4,5-dihydro-5-(2-methylethylidene)-1*H*-tetrazole* (**21**). A suspension of **20** (10.0 g, 31.4 mmol) and NaH (1.64 g, 68 mmol) in dry Et_2O (100 ml) was stirred until the gas evolution had ceased (17 h). Distillation of the solvent *i. v.* and of the yellow oily residue at 40–50° (bath temp.)/10^{-3} Torr in a short-path distillation apparatus (condenser at $-20°$) afforded **21** (3.11 g, 59%). Yellow oil which was kept at low temp. under dry Ar. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.14 (*t*, $J = 7.0$, 6 H); 1.72 (*s*, 6 H); 3.85 (*q*, $J = 7.0$, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 13.4 (2 Me); 19.8 (2 Me); 45.1 (2 CH_2); 67.1 (quart. C); 133.9 (quart. C).

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