

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 ¹⁵N-NMR Spectra of Zwitterions and Spirocyclic Cycloadducts¹⁾

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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**; R¹ = 2,4,6-(NO₂)₃C₆H₂) and sulfonyl azides **2M–O** (R¹ = XSO₂; 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**; R¹ = 2,4,6-(*t*-Bu)₃C₆H₂). 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 ¹⁵N-NMR spectroscopy for the first time to characterize spirocyclic cycloadducts **10–14** and **17** (Table 6), and zwitterions **16** (Table 7).

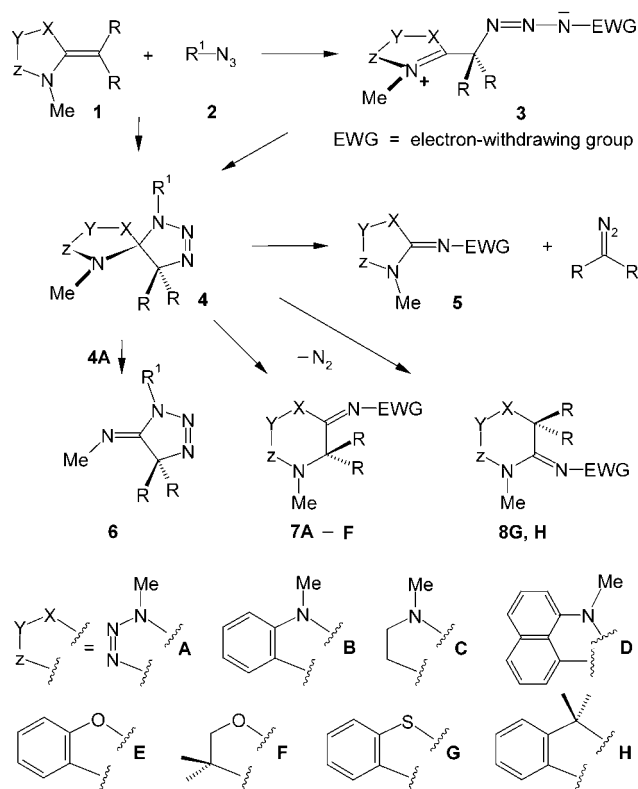
1. Introduction. – Huisgen's seminal and profound work on 1,3-dipolar cycloadditions has opened up a continent of concertedness which is bordered by two conceivable two-step pathways *via* zwitterionic intermediates which remained *terra incognita* for many years, however [1]. Almost 20 years ago, one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

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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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 N₂ from the dihydro-1*H*-triazole ring of **4** (R¹=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) ₂ C ₆ H ₃
2B	ⁱ BuCH ₂	2J	2,6-Me ₂ (4-NO ₂)C ₆ H ₂
2C	^t Bu	2K	4,6-Me ₂ (2-NO ₂)C ₆ H ₂
2D	Ph	2L	2,4,6-(NO ₂) ₃ C ₆ H ₂
2E	2,4,6- ⁱ Bu ₃ C ₆ H ₂	2M	MeSO ₂
2F	2,6-Me ₂ C ₆ H ₃	2N	4-MeC ₆ H ₄ SO ₂
2G	4-NO ₂ C ₆ H ₄	2O	Me ₂ NSO ₂
2H	2-NO ₂ C ₆ H 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 I*) 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 $\delta(\text{C}(\alpha))$ of **9A,B** [15] and **9C** [16] in *Table I*). Therefore, highly dipolar, ylide-like structures have been attributed to such ketene

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.

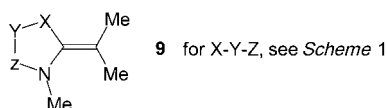


Table 1. *HOMO* Energies [eV], as Determined by Photoelectron Spectroscopy, and ^{13}C -NMR Chemical Shifts δ [ppm] of the Exocyclic C(α) Atom of Cyclic Ketene N,X-Acetals **9A–G** and Enamine **9H** [15]³⁾

	HOMO energy	$\delta(\text{C}(\alpha))$		HOMO energy	$\delta(\text{C}(\alpha))$
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	9H	6.84	102.1

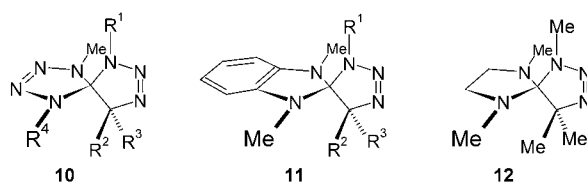
N,N-acetals [16–18]. On the other hand, ketene N,N-acetal **9D** with a six-membered ring is expected to be rather reluctant toward azides, at least according to the $\delta(\text{C})$ criterion. Besides ring size and heteroatoms of **1**, we varied the substituents of **1A** and **1B**.

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* ($\rightarrow$ **10D**) to avoid decomposition of the dipolarophile [17]. Isopropylidene dipolarophiles **9** = **1A** ($R = \text{Me}$) were preferred because their cycloadducts are stable toward base. By contrast, cycloadducts of 2,2-dimethylpropylidene dipolarophiles **1A** ($R, R = \text{H}, \text{tBu}$) are prone to base-mediated ring-opening elimination to yield 1*H*-1,2,3-triazol-5-amines [5][6a].

Disappearance 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.



	R ¹	R ²	R ³	R ⁴		R ¹	R ²	R ³	R ⁴
10A, 11A	Me	Me	Me	Me	10E	^t BuCH ₂	Me	Me	Me
10B, 11B	Me	^t Bu	H	Me	10F, 11F	^t BuCH ₂	^t Bu	H	Me
10C	Me	Ph	Me	Me	10G	^t Bu	Me	Me	Me
10D	Me	–CH ₂ –CH ₂ –	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*

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

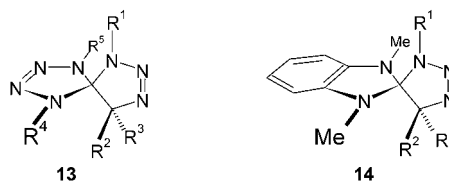
^{a)} *Method*: see text. The period of time given for *Method B* is the duration of the deprotonation step. ^{b)} Yields and m.p. after recrystallization.

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, ^tBu) with similar rates, *tert*-butyl azide (**2C**) reacted more slowly with **9A** and failed to add to **1A** (R, R = H, ^tBu), 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 ($\rightarrow$ **13–15**, Table 3). In accord with the estimated reactivities inferred from the data listed in Table 1, the isopropyl-



	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 ₂ C ₆ H ₃	Me	Me	Me	Me
13G	4-NO ₂ C ₆ H ₄	Me	Me	Me	Me
13H	4-NO ₂ C ₆ H ₄	^t Bu	H	Me	Me
13I	4-NO ₂ C ₆ H ₄	Me	Me	Et	Et
13J, 14J	2-NO ₂ C ₆ H ₄	Me	Me	Me	Me
13K	2-NO ₂ C ₆ H ₄	Me	Me	Et	Et
13L	2,6-Me ₂ (4-NO ₂)C ₆ H ₂	Me	Me	Me	Me

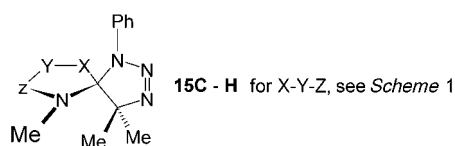


Table 3. *Methods and Reaction Conditions, Yields of 1,3-Dipolar Cycloadducts 13–15 of Aryl Azides to Cyclic Ketene N,X-Acetals 1, and Physical Data*

	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 → 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 → 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, ^tBu) 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 ^tBu 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**)

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

Cycloadduct	CH_3N	CH_3N	$\text{R}_2\text{C}(\text{R}_3)(=\text{C}(\alpha))$	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	CH_3N	CH_3N	$\text{R}_2\text{C}(\text{R}_3)(=\text{C}(\alpha))$	$\text{MeN}^+=\text{C}-\text{NMe}$		
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	$(\text{D}_6)\text{DMSO}$	[4a]
16E	3.99	37.7	61.4	152.0	$(\text{D}_6)\text{DMSO}$	^{a)}
	4.33	38.8				
16F	4.07	37.3	62.0	153.5	$(\text{D}_6)\text{DMSO}$	^{a)}
	4.32	38.3				
16G	3.89	37.9	56.1	155.5	CDCl_3 ^{e)}	[4a]
16H	3.61	37.5	62.2	153.6	$(\text{D}_6)\text{DMSO}$	^{a)}
	4.32	38.5				
16I ^{f)}	4.01	37.0	60.7	153.1	$(\text{D}_6)\text{DMSO}$	^{a)}
	4.21	38.6				

^{a)} This work. ^{b)} At -50° . ^{c)} At -30° . ^{d)} At -75° . ^{e)} The ^1H -NMR spectrum was recorded in CD_3CN . ^{f)} The ^1H -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 ^1H -NMR spectroscopy. Although a ^{13}C -NMR spectrum was not recorded due to the fleeting existence of the intermediate, its ^1H -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** ($\text{R} = \text{Me}$) 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 ^1H -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, ^tBu).

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-NO ₂ C ₆ H ₄	1A R, R = H, ^t Bu	2H R ¹ = 2-NO ₂ C ₆ H ₄
2G R ¹ = 4-NO ₂ C ₆ H ₄	1A R = Me	2I R ¹ = 2,4-(NO ₂) ₂ C ₆ H ₃
2H R ¹ = 2-NO ₂ C ₆ H ₄	1A R = Me	2I R ¹ = 2,4-(NO ₂) ₂ C ₆ H ₃
2J R ¹ = 2,6-Me ₂ (4-NO ₂)C ₆ H ₂	1A R = Me	2K R ¹ = 4,6-Me ₂ (2-NO ₂)C ₆ H ₂

^{a)} Zwitterions could not be detected by NMR spectroscopy at low temperatures.

¹⁵N-NMR Spectra. ¹⁵N-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 ¹⁵N-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 ¹⁵N-NMR spectra recorded for the cycloadducts **4** not only served for their characterization but also offer welcome additions to the ¹⁵N-NMR data base of 1*H*-1,2,3-triazoles and 1*H*-tetrazoles. ¹⁵N-NMR Spectra for zwitterions of type **3** are reported here for the first time.

The assignment of the ¹⁵N-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

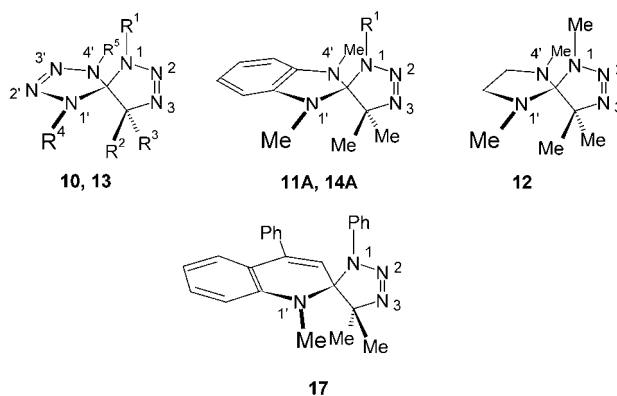


Table 6. ^{15}N -NMR Chemical Shifts δ [ppm] of 1,3-Dipolar Cycloadducts of Azides to Cyclic Ketene *N,N*-Acetals. Arbitrary numbering.

	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)} $\delta(\text{NO}_2)$ 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 , ^1H -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 $\delta(\text{H})$ 2.93 to *Me*–N(1). The assignment of the H-signals was

completed by homonuclear NOE difference spectroscopy (strong NOE (13%) for ${}^t\text{Bu}/\text{H}-\text{C}(4)$, weak NOE (1%) for ${}^t\text{Bu}/\text{Me}-\text{N}(1')$). The completely assigned ${}^1\text{H}$ -NMR spectrum allowed us to assign the $\delta(\text{N})$ of N(3), N(2'), and N(3'). Negative NOEs cause diminished ${}^{15}\text{N}$ -NMR signals, especially for saturated N-atoms during broadband decoupling. This effect was employed to distinguish N(1') and N(4') by selective ${}^1\text{H}$ -decoupling experiments. Irradiation of the frequencies of $\text{Me}-\text{N}(1')$ or ${}^t\text{Bu}-\text{C}(4)$ decreased the N(1') signal, while irradiation of $\text{Me}-\text{N}(4')$ or $\text{H}-\text{C}(4)$ weakened the N(4') signal.

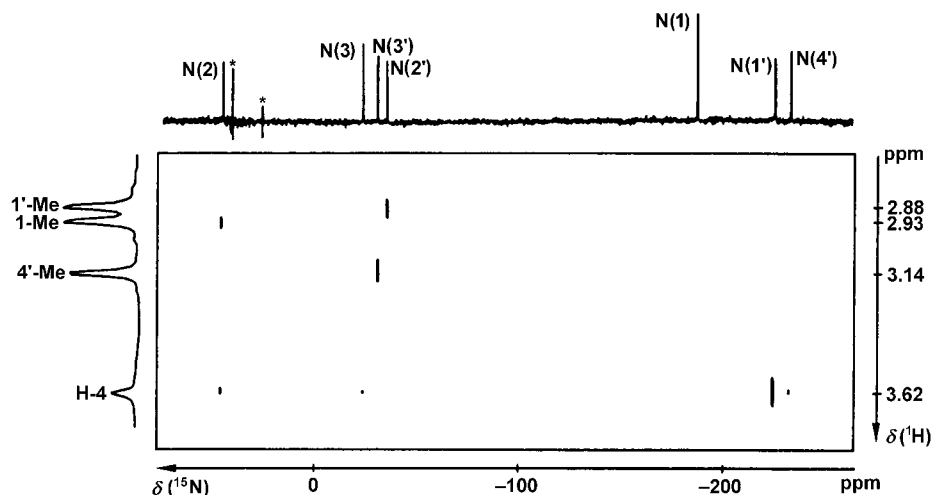


Figure. ${}^{15}\text{N}, {}^1\text{H}$ -Heteronuclear COSY plot of the spirocyclic dihydro-1H-1,2,3-triazole **10B**. The asterisk * indicates noise artifacts which were specific to the spectrometer employed. H-4, 4'-Me, etc., are short forms of $\text{H}-\text{C}(4)$, $\text{Me}-\text{N}(4')$, etc.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

The influence of different substituents on the ${}^{15}\text{N}$ -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** $\rightarrow$ **10E,G**; **10B** $\rightarrow$ **10F**) or a phenyl group (**10A** $\rightarrow$ **13A**; **10B** $\rightarrow$ **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 ${}^t\text{Bu}$ group and a H-atom (**10A** $\rightarrow$ **10B**; **10E** $\rightarrow$ **10F**; **13A** $\rightarrow$ **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 ${}^{15}\text{N}$ -NMR spectroscopy. We report here ${}^{15}\text{N}$ -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 ${}^{15}\text{N}$ -NMR chemical shifts, which differ significantly from those of **10** and **13**, with those of the 1H-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 ${}^{15}\text{N}$ -NMR signals of N(1') and N(4') as well as of N(2') and

N(3'), and of the ^1H - and ^{13}C -NMR signals for the two *MeN* 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.

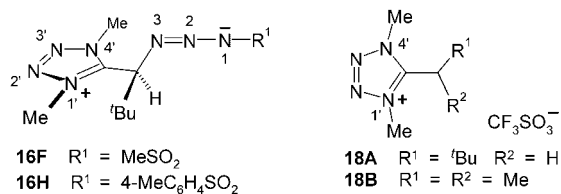


Table 7. ^{15}N -NMR Chemical Shifts δ [ppm] of Zwitterions **16F,H** and Tetrazolium Salts **18A,B**. Arbitrary numbering.

	N(1)/N(3)	N(2)	N(1')/N(4')	N(2')/N(3')	Solvent	Temp. [°]
16F	– 54.25 – 76.8	+ 90.9	– 149.4 – 152.2	– 14.8 – 15.75	(D_6)DMSO	19
16H	– 49.9 – 75.4	+ 92.3	– 149.75 – 153.1	– 14.6 – 16.1	(D_6)DMSO	19
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 the border was indicated by intermediate zwitterions that were observed by means of NMR spectroscopy at low temperatures.

We express our gratitude to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*, Frankfurt am Main, for financial support of our work. *D. R.* is indebted to the *Fonds der Chemischen Industrie* for a doctoral stipend. We thank Professor Dr. *H. Günther* and his co-workers, especially Dr. *W. P. Frankmölle*, for stimulating and helpful discussions while a great part of the ^{15}N -NMR measurements were performed at the University of Siegen.

Experimental Part

1. *General.* FC=Flash chromatography. Instrumentation: see [4b][9a][27]. UV Spectra: λ_{max} (log ϵ) in nm. IR Spectra: in cm^{-1} . NMR Spectra: δ in ppm, J in Hz; $\delta(\text{C})$ assignments supported by DEPT spectra. ^{15}N , ^1H -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 (^1H) as 2048 $\times$ 128 complex files in F_1 with 512 transients accumulated per t_1

increment; mixing time optimized to $^2J(\text{N,H})$ and $^3J(\text{N,H})$ 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 (^1H).

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 **9H**, 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). ^1H -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_2O (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_2O (35 ml) at –5°. The mixture was stirred at 0° for 1 h. A soln. of NaN_3 (38 mmol) in H_2O (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). ^1H -NMR (CD_2Cl_2): 2.47 (s, 6 H); 7.91 (s, 2 H). ^{13}C -NMR (CD_2Cl_2): 18.5 (2 Me); 124.2 (CH); 133.6, 143.3, 144.9 (quart. C). Anal. calc. for $\text{C}_8\text{H}_8\text{N}_4\text{O}_2$ (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). ^1H -NMR (CD_2Cl_2): 2.35 (s, 3 H); 2.38 (s, 3 H); 7.21 (1 H); 7.59 (1 H). ^{13}C -NMR (CD_2Cl_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 $\text{C}_8\text{H}_8\text{N}_4\text{O}_2$ (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_2Cl_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. ^1H -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°. ^1H -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°. ^1H -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°. ^1H -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. ^1H -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 (<i>m</i>)	Solvent
10E	^t BuCH ₂	0.94, 2.42	1.06	2.76		C ₆ D ₆
10G	^t Bu	1.17	1.13	2.62		C ₆ D ₆
11A	Me	2.41	1.14	2.34	6.20, 6.78 ^a)	C ₆ D ₆
13A	Ph		1.04	2.51	6.7–7.2	C ₆ D 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 ₃ CN
13L	2,6-Me ₂ (4-NO ₂)C ₆ H ₂	2.15	1.50	3.21	7.88	CD ₂ Cl ₂ ^b)
14A	Ph		1.13	2.28	6.2–7.1	C ₆ D ₆
14J	2-NO ₂ C ₆ H ₄		1.39	2.73		CD ₂ Cl ₂
15D	Ph		0.91	2.46	6.1–7.8	C ₆ D ₆
15E	Ph		1.12, 1.40	2.18	6.0–7.4	C ₆ D 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 ₆ D ₆
13C	Ph		1.43	1.87, 2.67	6.3–7.4	C ₆ D 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	CDCl ₃
11F	^t BuCH ₂	0.91, 2.25 ^c), 3.16 ^c)	1.06	3.60	2.54, 2.59	6.26, 6.63 ^a)
13B	Ph		1.10	3.56	2.40, 2.55	6.7–7.2
13H	4-NO ₂ C ₆ H ₄		1.03	3.47	2.23, 2.42	6.69, 7.78 ^a)
14B	Ph		1.16	3.82	2.41, 2.88	6.2–7.2
			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
13D	Ph		1.04,	1.15	2.58	6.6–7.3

^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.

^a) Centers of an $AA'XX'$ spectrum. ^b) The spectrum was recorded at -50° . ^c) MeN signals may be exchanged.

^d) $d, J = 13.4, 1 \text{ H}$. ^e) $d, J = 13.6, 1 \text{ H}$.

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[2H-indole-2,4'-[4H-1,2,3]triazole] (**15H**). The soln. of **2D** and **9H** in MeCN was kept at $20-25^\circ$ for 20 d and subsequently at 60° for 10 d. The yellow oil (quant.) crystallized from pentane: **15H** (89%). Colorless plates. M.p. $93-94^\circ$. ^1H -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 1H-tetrazolium trifluoromethanesulfonate or hexafluorophosphate [17] ($\rightarrow$ **10C.H**, **13C**) or 1H-benzimidazolium tetrafluoroborate [15] ($\rightarrow$ **11A**) (5.00 mmol) and NaH (0.36 g, 15 mmol) in dry Et_2O 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. $85-88^\circ$) was purified by FC (silica gel, petroleum ether ($30-50^\circ$)/AcOEt 9:1): pale yellow crystals.

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

R ¹	R ² , R ³ = Me	R ² C(R ³)	R ⁴ , R ⁵ = 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		<i>B</i>
10G ^t Bu	29.6, 54.7 ^b)	22.1	77.8	35.1	103.1		<i>B</i>
11A Me ^c)	32.14	21.8	79.2	32.14	108.5	103.7, 104.7,	<i>B</i>
	32.98	22.3	78.6	33.19	110.0	118.9, 119.8	<i>M</i>
13A Ph		21.6	79.7	34.3	101.5	115.9, 123.6, 129.0	<i>B</i>
13F 2,6-Me ₂ C ₆ H ₃	20.3	21.4	76.6	34.9	101.4	125.9, 129.0	<i>C</i>
13G 4-NO ₂ C ₆ H ₄		21.7	80.6	34.6	101.2	115.1, 125.8	<i>C</i>
13J 2-NO ₂ C ₆ H ₄		21.1	79.3	35.1	103.2	119.5, 126.1,	<i>A</i>
						126.7, 132.9	
14A Ph		22.1	83.3	31.9	106.3	104.2, 115.5, 119.4,	<i>B</i>
						123.2, 129.8	
14J 2-NO ₂ C ₆ H ₄		21.4	82.5	32.3	107.3		<i>D</i>
15D Ph		23.0	89.9	34.5	94.3	103.0, 115.7, 117.2,	<i>C</i>
						123.7, 127.6, 129.6	
15E Ph		20.7, 21.7	83.1	30.5	116.5	104.8, 107.5, 117.2,	<i>B</i>
						119.1, 122.5,	
						124.1, 129.5	
15G Ph		18.2, 25.1	83.0	31.4	101.9	106.2, 117.3, 119.0,	<i>C</i>
						121.0 124.0,	
						126.0, 129.1	
		R ² = ^t Bu R ³ = 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	<i>C</i>
11B Me ^c)	28.5	27.9	31.7	81.5	32.2, 32.4	108.4	<i>C</i>
						102.8, 103.2,	
						118.0, 118.8	
11F ^t BuCH ₂ ^d)	28.2, 32.6 ^b), 56.0	27.8	31.4	80.4	28.8, 31.0	110.0	<i>C</i>
						102.1, 102.4,	
						117.5, 118.5	
13B Ph		27.6	32.8	81.9	31.5, 33.9	101.1	<i>B</i>
13H 4-NO ₂ C ₆ H ₄		27.4	32.8	82.0	31.3, 33.6	101.0	<i>B</i>
14B Ph		27.7	32.3	84.1	28.5, 31.7	107.0	<i>C</i>
						103.6, 103.7,	
						115.6, 118.4,	
						119.2, 123.3, 129.4	
		R ² –R ³ = (CH ₂) ₂					
10D Me ^c)	33.3	11.6		56.3	31.1	99.4	<i>B</i>
		R ² = Ph R ³ = Me					
10C Me ^c)	33.5	23.2		79.2	32.8, 35.2	104.1	<i>C</i>
13C Ph		22.9		82.8	32.5, 34.9	101.9	<i>C</i>
						115.6, 123.8,	
						126.1, 127.9,	
						128.3, 129.6	
		R ² , R ³ = Me					
10H Me ^c)	34.8	20.7, 23.9		80.0	31.9	101.1	<i>B</i>
13D Ph		21.5, 23.4		82.8	34.4	98.5	<i>B</i>
						117.3, 123.3 129.6	
						115.5, 118.0, 123.9,	
						124.0, 129.4, 129.9	
		R ⁴ , R ⁵ = Et					
13E Ph		22.1		79.0	13.6, 42.2 ^c)	100.2	<i>C</i>
13I 4-NO ₂ C ₆ H ₄		22.1		78.8	13.8, 42.5 ^c)	101.3	<i>C</i>
13K 2-NO ₂ C ₆ H ₄		21.0		78.3	13.7, 42.3 ^c)	102.3	<i>C</i>
						118.6, 124.6,	
						125.8, 133.0	

^a) *A* = CD₃CN, *B* = C₆D₆, *C* = CDCl₃, *D* = CD₂Cl₂, *M* = CD₃OD. ^b) The signals of ^tBu groups are listed in the order Me₃C. ^c) MeN Signals may be exchanged. ^d) ^tBu Signals may be exchanged. ^e) The signals of Et groups are listed in the order MeCH₂.

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 ₇ H 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 ₉ H 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 ₈ O ₂	304.3	calc.	47.36	5.30	36.82
			found	47.48	5.52	36.99
13H	C ₁₄ H ₂₀ N ₈ O ₂	332.4	calc.	50.59	6.07	33.71
			found	50.23	5.71	33.39
13I	C ₁₄ H ₂₀ N ₈ O ₂	332.4	calc.	50.59	6.07	33.71
			found	50.58	6.19	33.92
13J	C ₁₂ H ₁₆ N ₈ O ₂	304.3	calc.	47.36	5.30	36.82
			found	47.04	5.18	36.95
13K	C ₁₄ H ₂₀ N ₈ O 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 ₆ O 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 ₄ O	294.4	calc.	69.37	6.16	19.03
			found	69.17	6.08	18.79
15F	C ₁₅ H ₂₂ N ₄ O	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 ₄ S	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[2H-benzimidazole-2,4'-[4H-1,2,3]triazole] (11A). Recrystallization of the remaining colorless powder (0.795 g, 65%; m.p. 63–68°) from Et₂O/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 azide **2A** (ca. 15 mmol) or an aryl azide **2D,G,H** (6 mmol) was added to a stirred suspension of powdered 1H-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 H₂O (30 ml) at 0°. The mixture was neutralized with 2M HCl. The aq. layer was extracted with CH₂Cl₂ (3 × 30 ml), the combined org. layer washed with sat. aq. NaCl soln., dried (Na₂SO₄), 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°. ¹H-NMR (250 MHz, 0.153 Hz/pt., C₆D₆): 0.72 (δ_X = δ_{X'}, 2 H), 1.34 (δ_A = δ_{A'}, 2 H) (AA'XX', ³J_{AA'} = 10.6, ³J_{XX'} = 10.2, ²J_{AX} = ²J_{AX'} = –4.5, ³J_{AX} = ³J_{AX'} = 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°. ¹H-NMR (CDCl₃): 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.). ¹H-NMR ((D₈)toluene): 1.38 (s, 6 H); 1.37 (t, 6 H); 2.89 (center of AB part, 4 H) (2 ABX₃, 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°. ¹H-NMR ((D₈)toluene): 1.40 (s, 6 H); 1.43 (t, 6 H); 3.03 (center of AB part, 4 H) (2 ABX₃, 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-1H-tetrazolium Inner Salt (16A)**. ¹H-NMR (200 MHz, CD₂Cl₂, –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). ¹³C-NMR (50 MHz, CD₂Cl₂, –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-1H-tetrazolium Inner Salt (16B). ¹H-NMR (200 MHz, CD₂Cl₂, –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-1H-tetrazolium Inner Salt (16C). ¹H-NMR (200 MHz, CD₂Cl₂, –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]-1H-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/Et₂O: **16D** (90%). Red crystals. M.p. 125–126°. UV/VIS (MeCN): 442 (log ε 4.376). IR (KBr): 1605, 1625 (C=C), 1315, 1525 (NO₂). ¹H- and ¹³C-NMR: see [4a]. Anal. calc. for C₁₂H₁₄N₁₀O₆ (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-1H-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, ^tBu; 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 (NO₂). ¹H-NMR ((D₆)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). ¹³C-NMR ((D₆)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 C₁₄H₁₈N₁₀O₆ (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-1H-tetrazolium Inner Salt (**16F**). At -20° , **2M** (5.1 mmol) was added dropwise to a stirred soln. of **1A** (R, R = H, '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. $93-97^{\circ}$) was recrystallized from $^i\text{PrOH}$: **16E** (77%). Colorless crystals. M.p. $111-112^{\circ}$. UV (MeCN): 236 (3.822). IR (KBr): 1145, 1290 (SO_2). $^1\text{H-NMR}$ ((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). $^{13}\text{C-NMR}$ ((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 $\text{C}_9\text{H}_{19}\text{N}_7\text{O}_2\text{S}$: C 37.36, H 6.62, N 33.88; found: C 37.31, H 6.61, N 34.11.

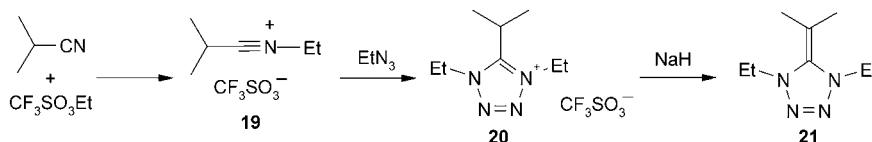
6.7. 1,4-Dimethyl-5-[1-methyl-1-[3-[(4-methylphenyl)sulfonyl]triaz-1-enyl]ethyl]-1H-tetrazolium Inner Salt (**16G**). Compound **9A** (35 mg, 0.25 mmol) was placed under dry Ar into an NMR sample tube and cooled to -78° . A soln. of **2N** (52 mg, 0.26 mmol) in dry (D_8)toluene (0.7 ml), which was cooled 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° . ^1H - and ^{13}C -NMR: see [4a].

6.8. 5-[2,2-Dimethyl-1-[3-[(4-methylphenyl)sulfonyl]triaz-1-enyl]propyl]-1,4-dimethyl-1H-tetrazolium Inner Salt (**16H**). At 0° , **2N** (5.1 mmol) was added dropwise to a stirred soln. of **1A** (R, R = H, '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). ^1H - and ^{13}C -NMR (CDCl_3): see [4a]. $^1\text{H-NMR}$ ((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). $^{13}\text{C-NMR}$ ((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 $\text{C}_{15}\text{H}_{23}\text{N}_7\text{O}_2\text{S}$ (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-1H-tetrazolium Inner Salt (**16I**). At 0° , **2O** (5.1 mmol) was added dropwise to a stirred soln. of **1A** (R, R = H, '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 $^i\text{PrOH}$ gave **16I**. Colorless crystals. M.p. $144-145^{\circ}$. UV (MeCN): 242 nm (3.753). IR (KBr): 1110, 1310 (SO_2). $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ ((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 $\text{C}_{10}\text{H}_{22}\text{N}_8\text{O}_2\text{S}$ (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-1H-tetrazole Derivatives (Scheme 2). 7.1. N-(2-Methylpropylidene)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 $^1\text{H-NMR}$ 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)1H-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. $54-57^{\circ}$). Recrystallization from $^i\text{PrOH}$ yielded **20** (39.9 g, 85%). Colorless scales. M.p. $72-73^{\circ}$. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz): 13.7 (2 Me); 18.4

(2 Me); 24.3 (CH); 46.9 (2 CH₂); 155.8 (quart. C). Anal. calc. for C₉H₁₇F₃N₄O₃S (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)-1H-tetrazole (21)*. A suspension of **20** (10.0 g, 31.4 mmol) and NaH (1.64 g, 68 mmol) in dry Et₂O (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. ¹H-NMR (CDCl₃, 200 MHz): 1.14 (t, *J* = 7.0, 6 H); 1.72 (s, 6 H); 3.85 (q, *J* = 7.0, 4 H). ¹³C-NMR (CDCl₃, 50 MHz): 13.4 (2 Me); 19.8 (2 Me); 45.1 (2 CH₂); 67.1 (quart. C); 133.9 (quart. C).

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Received March 2, 2005