The photochemical reactions of nitrogen-rich mesoionic 1,3-diphenyltetrazolium heterocycles and related compounds

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Photochemical reactions of azo and triazo derivatives of mesoionic 1,3-diphenyltetrazolium heterocycles and related compounds were studied. The reaction paths were found to depend markedly on the types of substrate, substituent and reaction solvent giving diverse products. Upon irradiation of the 1,1′3,3′-tetraphenylazoditetrazolium salt **1**, the addition of hydrogen and acetone to the N=N bond was observed in methanol and acetone, respectively, whereas the bond was cleaved in diethyl ketone to give the 5-aminotetrazolium salt **10**. The corresponding radical cation **11** also gave the reduction product in methanol. On the other hand, the 1,3-diphenyl-5-(phenylazo)tetrazolium salt **12** underwent nitrogen evolution giving the 1,3-diphenyltetrazolium salt **13** *via* the corresponding tetrazolium radical. Triazene derivatives **14** and **17** underwent an N–N bond cleavage to give tetrazolio-5-amide **4**. The mesoionic triazene compounds bearing a tosyl **18** or cyano group **19** gave products **20** and **23**. Triphenylphosphinotriazene **24** liberated nitrogen to give phosphinoimide **25** and its hydrolysis product **10**. Tetrazolylamide **26** lost a phenyldiazonium group from the 1,3-diphenyltetrazolium ring to give the guanidine derivative **27**.

Introduction

Mesoionic compounds have been employed as useful building blocks for the construction of polyheterocyclic compounds *via* various transformations, of which dipolar cycloaddition reactions have been extensively studied.[1] On the other hand, the photochemical reactions of mesoionic compounds have received relatively scarce attention. Photochemical processes provide attractive methodologies for the synthesis of compounds which are difficult to obtain by other methods. With a view to developing photochemical reactions of mesoionic compounds for new heterocycles, we recently reported the photoconversion of 5-azido-1,3-diaryltetrazolium salts, which leads, *via* novel nitrene intermediates, to different tricyclic mesoionic compounds depending on the aryl group at the 1-position.[2,3] Here, we describe the results on the photolysis of further types of 1,3-diaryltetrazolium derivatives; namely, azo and triazo mesoionic heterocycles and other nitrogen-rich mesoionic compounds.
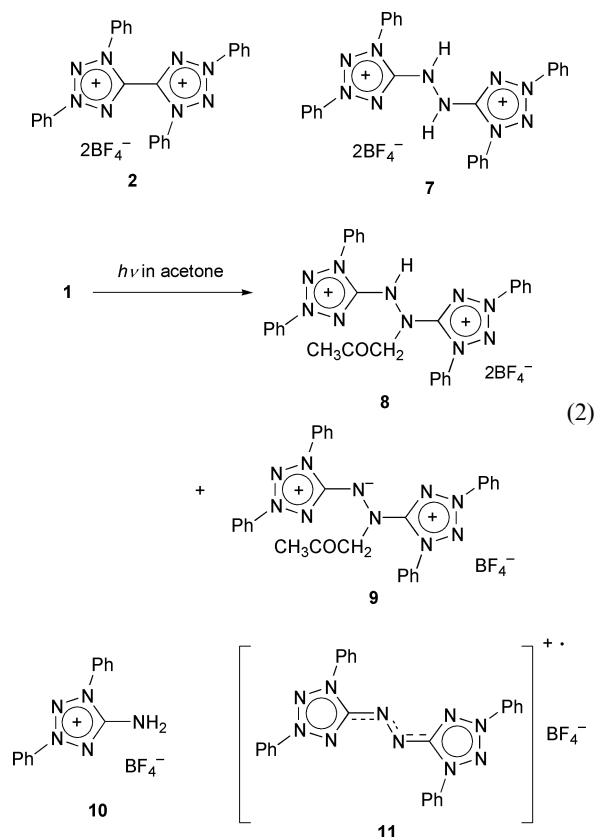
Results and discussion

Photochemical reaction of azo derivatives of 1,3-diphenyltetrazolium salts

1,1′,3,3′-Tetraphenylazoditetrazolium salt (1) and its radical cation 11. The photochemical reactions of azo compounds have been studied in detail.[4] The *cis–trans* isomerization of the N=N double bond and the formation of radical species with liberation of nitrogen are often observed processes. The latter is utilized for the synthesis of unusual organic molecules such as highly strained and sterically crowded compounds. If the photolysis of the 1,1′,3,3′-tetraphenylazoditetrazolium salt[5] **1** undergoes the latter type of reaction, the formation of the dicationic bis(tetrazolium) compound **2** is expected *via* recombination of the initially generated tetrazolium radical. Azo compound **1** was irradiated with a high-pressure mercury lamp in methanol or in dichloromethane (DCM). After treatment of the reaction mixture with base and column chromatographic purification, azinobis(tetrazolylene)[5] **3** was obtained as the major product [eqn. (1)]. Small amounts of amide[6] **4**,
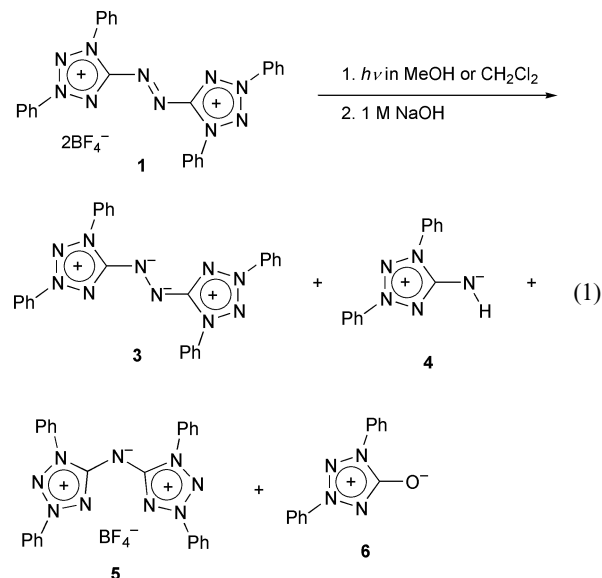
tripolar compound[6] **5** and olate[7] **6** were also isolated; however, the expected dicationic compound **2** was not found in the reaction mixture. The formation of **3** is rationalized by the deprotonation of the initially formed dication[5] **7** during the aqueous work-up procedure. When the same photolysis was carried out in acetone, compound **3** (or **7**) was not formed but the acetone adduct **8** and its conjugate base **9** were obtained in 52% combined yield [eqn. (2)]. The structure of **8** was unambiguously determined by X-ray crystallography.[8] The photoreduction of the N=N linkage of azo compounds has often been observed.[4] Also, the addition of ethers and alcohols to the N=N bond of photo-excited azo compounds is known.[9]

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Table 1 Photolysis of radical cation **11**

2 2BF$_4^-$

7 2BF$_4^-$

1 $\xrightarrow{h\nu \text{ in acetone}}$

8 CH$_3$COCH$_2$ 2BF$_4^-$

(2)

+

9 CH$_3$COCH$_2$ BF$_4^-$

10 BF$_4^-$

11 BF$_4^-$ $^{+\cdot}$

	Conditions		products [yield (%)]		recovery of **11** (%)
Entry	Time/h	Solvent	3	6	
1	6	MeOH	54	10	5
2	6	Acetone	32	8	22
3	8	DCM	7	4	69
4	6	MeCN	0	0	100

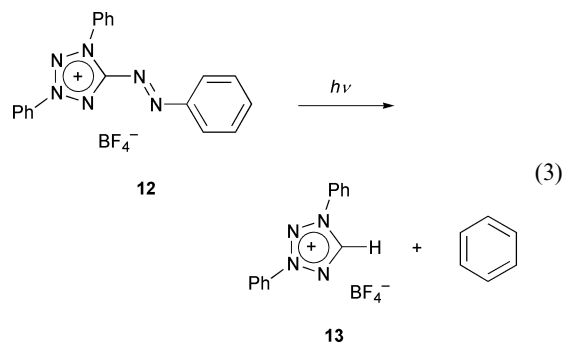**12** BF$_4^-$ $\xrightarrow{h\nu}$

13 BF$_4^-$ + (benzene)

(3)

In the case of **1**, these two processes occurred selectively depending on the solvent: hydrogen abstraction from the solvent took place in DCM and methanol, whereas the solvent acetone added to the N=N double bond. Interestingly, irradiation of **1** in diethyl ketone gave no addition product but the 5-aminotetrazolium salt[6] **10** was isolated in 33% yield. This is the sole case in this work where the central N=N bond of the azo compounds was cleaved in the photochemical reactions.

Next, the photolysis of radical cation[5] **11** was undertaken. If the product pattern of **11** is similar to that of **1**, the intermediacy of **11** is suggested for the photoreaction of **1**; that is, one-electron oxidation of **1** is involved during the photolysis of **1**. The results are summarized in Table 1. In methanol, azine **3** was obtained as the main product after a base treatment, as was the case of dication **1** (entry 1). Azine **3** was also produced even in acetone, and the acetone adducts **8** and **9** were not formed (entry 2). In DCM and acetonitrile, the photolysis was sluggish (entries 3 and 4). Thus, from both dication **1** and radical cation **11**, the conjugate acid **7** was formed. The reduction of **1** and **11** was hitherto realized *via* zinc reduction.[5] It is interesting that the reduction of **1** and **11** can also be carried out *via* the photochemical reaction. It should be pointed out that all the reactions of **1** and **11** examined here gave no products *via* tetrazolium radicals with an extrusion of nitrogen.

1,3-Diphenyl-5-(phenylazo)tetrazolium salt (12). Next, we undertook the photolysis of the 1,3-diphenyl-5-(phenylazo)-tetrazolium salt[6] **12**, which has a benzene ring and a 1,3-diphenyltetrazolium ring at each side of the azo group. With the irradiation of **12** in methanol, a gas evolution was observed and the 1,3-diphenyltetrazolium salt[10] **13** was obtained in 85% yield [eqn. (3)]. Direct gas chromatographic analysis of the photolysate revealed the formation of benzene in 57% yield. These results suggest that, in contrast to **1** and **11**, the azo compound **12** gave tetrazolium and phenyl radicals with liberation of nitrogen, which abstract hydrogen from the solvent methanol to give **13** and benzene, respectively. High yields (77–83%) of **13** were also obtained in acetonitrile and DCM.

It is interesting to compare the photochemical behaviour of azo compounds **1** and **12** whose reaction courses are thus found to be totally distinct. Liberation of nitrogen from photo-excited azo compounds occurs *via* the *cis*-configuration;[11] for compound **1** with two tetrazolium rings it is sterically more difficult to form the *cis*-configuration compared with **12**, hence **1** did not give the nitrogen-lost products.

Photochemical reaction of triazene derivatives of 1,3-diphenyl-tetrazolium salts

Although triazene is known as a photoactive compound, photochemical studies of it are considerably fewer than those of azo compounds.[12] From the structural similarity of triazene to an azo compound, similar photoreaction behaviour between these photo-labile compounds could be expected. However, two carbon radicals are formed by the photolytic denitrogenation of an azo compound, whereas triazene gives an aminyl radical. Here triazene derivatives **14**, **17**, **18**, **21** and **24** bearing one or two 1,3-diphenyltetrazolium rings have been investigated.

1,3-Bis(1,3-diphenyl-5-tetrazolio)triazenide (14) and 1-phenyl-3-(1,3-diphenyl-5-tetrazolio)triazenide (17). Irradiation of 1,3-bis(1,3-diphenyl-5-tetrazolio)triazenide[6] **14** in methanol, acetonitrile or acetone led to no reaction. However, in the presence of the sensitizer acetophenone the reaction proceeded and, after a base treatment, amide **4** (54%) and acetophenone hydrazone **15** (13%) were obtained [eqn. (4)]. The hydrazone

14 BF$_4^-$ $\xrightarrow[\text{2. 1 M NaOH}]{\text{1. } h\nu/\text{acetophenone}}$

4 +

15

(4)
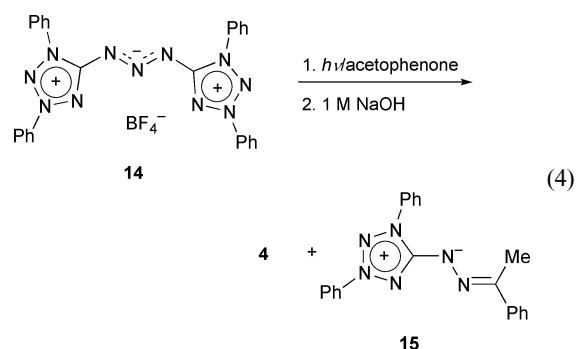
15 was identical to the authentic sample prepared by the acid-catalysed condensation of hydrazine **16** and acetophenone. The mechanism for the formation of **15** is not yet fully confirmed, but it is possible that hydrazine **16** was formed *in situ* by the

Table 2 Photolysis of (*E*)-**17**

		Conditions			
Entry	Time/h	Solvent	Additive	**4** [yield (%)]	Recovery of (*E*)-**17** (%)
1	6	MeOH	None	35	32
2	6	Acetone	None	15	65
3	1	MeOH	Acetophenone	26	33

Table 3 Photolysis of **18** and **21**

		Conditions		Products [yield (%)]					
Entry	Compound	Time/h	Solvent	**19**	**20**	**23**	**4**	**6**	Acetanilide
1	**18**	0.8	MeOH	5	1	—	53	0	0
2	**18**	0.7	MeCN	32	12	—	0	0	12
3	**21**	5	MeOH	0	—	21	6	43	0
4	**21**	3	MeCN	9	—	34	0	0	0

photo-cleavage of **14**, which subsequently reacted with aceto-phenone.


16

17
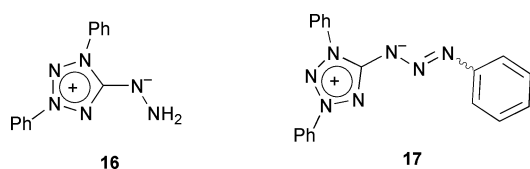
Next, triazenide **17** with tetrazolium and phenyl rings at each end of the triazo linkage was studied (Table 2). Triazenide **17**, which corresponds to the diazo compound **12**, was synthesized by the coupling of amide **4** and a benzenediazonium salt. Both the *E*- and *Z*-isomers could be isolated in pure forms; however, the latter isomerizes readily to the more stable *E*-form. The photolysis of (*E*)-**17** is sluggish and, even in the presence of acetophenone, **17** was not consumed completely. Nonetheless, moderate yields of amide **4** were obtained after 6 h in MeOH or acetone. In these reactions, neither the acetophenone adduct **15** nor acetophenone phenylhydrazone were formed.

1,3-Diphenyl-5-tetrazolio(3-tosyl)triazenide (18) and -5-tetra-zolio(3-cyano)triazenide (21). The photochemistry of triazen-ides **18** and **21** possessing a tosyl or cyano group was studied [eqn. (5)]. These compounds were prepared by the addition of


18 X=Ts
21 X=CN

(5)

19

20 X=Ts
23 X=CN

+ **4** + **6**
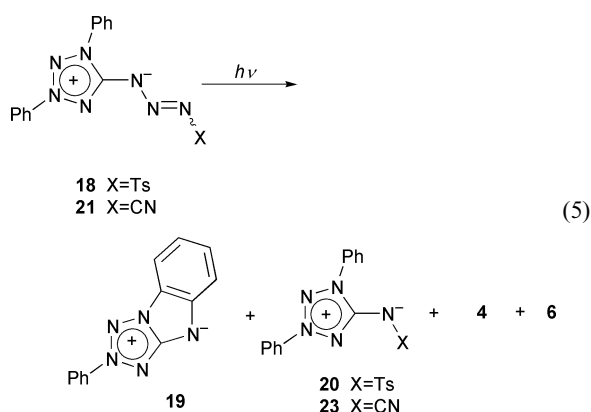
tosyl or cyanide anions to the 5-azido-1,3-diphenyltetrazolium salt (**22**).[6] The photolysis of **18** in methanol gave tetrazolium amide **4** in 53% yield together with small amounts of the tri-cyclic amide[6] **19** and tosylamide **20** (Table 3, entry 1). The reaction in acetonitrile (entry 2) gave higher yields of **19** and **20** than in methanol. A formation of a small amount of acetanilide was also observed. Amide **4** was not formed in this solvent. The photochemistry of cyanotriazenide **21** was

similarly studied. Olate **6** was the main product in methanol (entry 3). As triazenide **21** is stable in methanol in the dark, olate **6** is a photochemical product, though the precise mechanism of its formation is unknown. The tricyclic product **19** was not obtained; instead, cyanamide **23** was formed in a moderate yield. In acetonitrile (entry 4), the formation of **19** was observed and the yield of **23** increased compared with methanol. In turn, olate **6** and amide **4** were not formed. The formation of **19** strongly suggests the intermediacy of the azidotetrazolium compound **22**, whose photolysis is known to give a nitrene intermediate to furnish **19** and **4**.[2] The difference in the product pattern of these two triazenides **18** and **21** is considered to depend on the leaving nature of the substituents; tosyl anion dissociates more easily than cyanide anion giving azidotetrazolium **22** readily. Two mechanisms are possible for the formation of **20** and **23**: (a) intramolecular denitrogenation as is observed in the photolysis of **24** (*vide infra*) and (b) the nitrene intermediate generated from azido compound **22** couples with tosyl or cyanide anion.


22
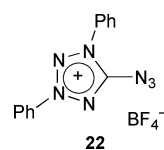
1,3-Diphenyl-5-(triphenylphosphinotriazeno)tetrazolium salt (24). The Staudinger reaction between an azido compound and triphenylphosphine has been extensively studied and triphenyl-phosphinotriazene is considered as the initial adduct of this reaction. Although this type of compound is generally unstable, some examples have hitherto been isolated and fully charac-terized.[13] We reported the synthesis of the 1,3-diphenyl-5-(tri-phenylphosphinotriazeno)tetrazolium salt **24** and its thermal decomposition was found to give triphenylphosphonoimine **25** in a high yield.[6] Now the photochemical reaction of **24** has been undertaken [eqn. (6)]. The photolysis was conducted in DCM

24

(6)

25

+ **10**
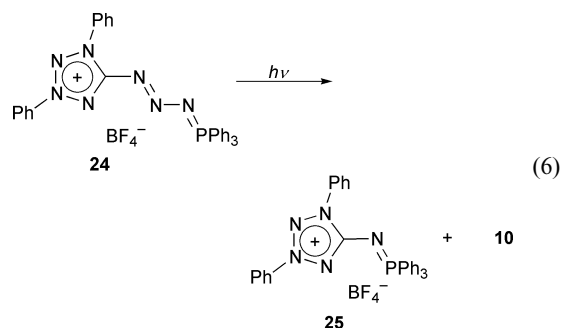
and acetonitrile. In each solvent, a gas evolution was observed. Interestingly, the aminotetrazolium salt **10** was obtained in 94% yield in DCM, whereas in acetonitrile iminophosphorane **25** was formed quantitatively. Triazene **24** is stable in DCM and acetonitrile in the dark. Also, **25** is not hydrolyzed to **10** in DCM in the dark. Therefore, **10** and **25** were produced selectively from the photochemical reaction of **24** depending on the solvent.

1,3-Diphenyl-5-tetrazolio(1-phenyltetrazol-5-yl)amide (26).

The photolysis of tetrazole derivatives is known to give a variety of products depending on the substitution pattern and the nature of substituents.[14] Various substituted tetrazoles as well as the parent tetrazole have been studied so far.[15] Here, the photochemical reaction of the 1,5-disubstituted tetrazole **26**[6] has been examined. Tetrazole **26** was photochemically inert in the absence of a sensitizer. However, irradiation with acetophenone gave the product **27** in 45% yield [eqn. (7)]. The
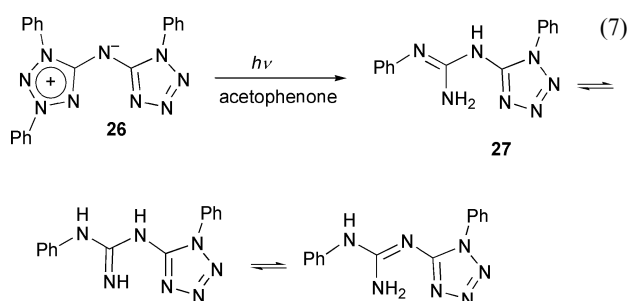
analytical and spectroscopic data show that **27** is a guanidine derivative; the 1,3-diphenyltetrazolium ring of **26** was cleaved at the N^1–N^2 and N^3–N^4 bonds, losing a phenyldiazonium group, to give **27**. In this reaction no products from the cleavage of the 1-phenyltetrazole ring were observed. It is interesting to note that the zinc-reduction of some 5-substituted 1,3-diphenyl-tetrazolium compounds also gives guanidine derivatives.[5]

In summary, the photochemical reactions of various 1,3-diphenyltetrazolium ring-bearing mesoionic compounds have been studied. The azo compounds **1** and **12** showed completely different photolytic behaviour. The results of the other nitrogen-rich mesoionic heterocycles can be classified into three categories: (i) exocyclic N–N bond cleavage (compounds **14**, **17** and **24**), (ii) formation of the 5-azidotetrazolium salt **22** and subsequent decomposition to the nitrene intermediate (compounds **18** and **21**) and (iii) cleavage of the 1,3-diphenyl-tetrazolium ring (compound **26**). Thus, it turned out that the photochemical behaviour of the nitrogen-rich mesoionic 1,3-diphenyltetrazolium heterocycles is strongly influenced by the types of compound, substituent and reaction solvent, giving diverse photolysis products.

Experimental

General

Melting points were determined with a hot-stage apparatus and are uncorrected. Infrared spectra were taken for potassium bromide discs with a JASCO A-102 instrument. ^{1}H and ^{13}C NMR spectra were run with a Varian Gemini 200 (200 MHz and 50 MHz, respectively) and referenced using either the residual non-deuterated solvent or tetramethylsilane. *J*-Values are given in Hz. Electronic spectra were measured on a Hitachi U-3500 spectrophotometer. Mass spectra were measured with a Hitachi M-2000S spectrometer (EI, 70 eV). Elemental analyses were performed at Elemental Analysis Centre of Kyoto University. Column chromatography was carried out on silica gel or on 3-aminopropylsilane-modified silica gel (Fuji Silysia Chemical, Chromatorex NH-DM 1020, 100–200 mesh).

For photochemical reactions, a Riko Kagaku Sangyo UVL-100HA–100P apparatus was used. Photolyses were carried out under an argon atmosphere using a 100 W high pressure mercury lamp with a Pyrex filter. The tetrazolium substrates used in this work were prepared according to the published procedures.

1. Photochemical reaction of 1

In methanol. A solution of 1,1′,3,3′-tetraphenylazoditetra-zolium tetrafluoroborate[5] **1** (0.10 g, 0.15 mmol) in methanol (120 ml) was irradiated. The solution turned from yellow to dark brown. After 4 h, the solvent was evaporated and the residue was resolved in DCM. Aqueous sodium hydroxide (1 M) was added and the organic layer was separated. After being dried (Na$_2$SO$_4$), the solvent was removed and the residue was chromatographed on NH-DM 1020 (DCM) to give a crude solid of **3**[5] (42 mg), amide **4**[6] (2 mg, 3%) and **5**[6] (5 mg, 6%). Recrystallization (DCM–Et$_2$O) of the crude solid of **3** gave pure **3** (24 mg, 34%) and olate **6**[7] (13 mg, 18%).

In DCM. A solution of **1** (0.10 g, 0.15 mmol) in DCM (120 ml) was similarly photolyzed. The reaction mixture turned colourless. After 6 h, the mixture was treated as above to furnish crude crystals of **3** (51 mg), **4** (4 mg, 6%) and **5** (2 mg, 2%). Recrystallization (DCM–Et$_2$O) of the crude crystals of **3** gave pure **3** (44 mg, 62%) and olate **6** (3 mg, 4%).

In acetone. A solution of **1** (0.20 g, 0.30 mmol) in acetone (220 ml) was similarly photolyzed. The reaction mixture turned to yellowish brown. After 6 h, the solvent was removed and the residue was recrystallized from ethanol to give compound **8** (71 mg, 34%). The mother liquor was chromatographed on silica gel (DCM–acetone = 10 : 1) to give compound **9** (33 mg, 18%). The conjugate acid **8** gave the corresponding base **9** upon treatment with saturated aqueous NaHCO$_3$. The base **9**, in turn, gave back **8** upon protonation with aqueous HBF$_4$ (42%). The structure of **8** was unambiguously determined by X-ray crystallography.[7]

In diethyl ketone. A solution of **1** (0.10 g, 0.15 mmol) in diethyl ketone (120 ml) was similarly photolyzed. A gas evolution was observed. After 3 h, the solvent was removed and the residue was chromatographed on silica gel (DCM–acetone = 4 : 1) to give 5-aminotetrazolium tetrafluoroborate[6] **10** (32 mg, 33%).

Acetone adduct (conjugate acid) (8). Colourless crystals; mp 173–175 °C (from EtOH) (Found: C, 49.19; H, 3.72; N, 19.67. Calc. for C$_{29}$H$_{26}$B$_2$F$_8$N$_{10}$O (704.2): C, 49.46; H, 3.72; N, 19.89%); ν_{max}/cm^{-1} 3400, 1730, 1620, 1600, 1574, 1488, 1460, 1340, 1296, 1080, 760 and 680; δ_H (200 MHz; CD$_3$CN) 2.23 (3H, s, Me), 4.95 (2H, br s, CH$_2$), 7.12–7.17 (2H, m, Ph), 7.61–7.87 (14H, m, Ph) and 8.17–8.25 (4H, m, Ph); δ_C (50 MHz; CD$_3$CN) 26.5 (Me), 61.5 (CH$_2$), 121.5 (C-o), 121.6 (C-o), 125.3 (C-o), 126.7 (C-o), 131.1 (C-m), 131.1 (C-m), 133.5 (C-p), 134.3 (C-p), 130.1 (C-i), 132.6 (C-i), 135.3 (C-i), 135.4 (C-i), 157.5 (C$^+$), 158.1 (C$^+$) and 200.3 (C=O).

Acetone adduct (conjugate base) (9). Orange crystals; mp 155–157 °C (from EtOH) (Found: C, 55.48; H, 4.08; N, 22.49. Calc. for C$_{29}$H$_{25}$BF$_4$N$_{10}$O·0.5H$_2$O (625.4): C, 55.70; H, 4.19; N, 22.37%); ν_{max}/cm^{-1} 1730, 1600, 1572, 1486, 1460, 1292, 1260, 1080, 800, 760 and 680; λ_{max} (MeCN)/nm 226 (log ε 4.44), 269 (4.67) and 380 (3.77); δ_H (200 MHz; CD$_3$CN) 2.28 (3H, s, Me), 4.78 (2H, s, CH$_2$), 7.36–7.46 (8H, m, Ph), 7.60–7.63 (2H, m, Ph), 7.73–7.80 (6H, m, Ph) and 8.14–8.20 (4H, m, Ph); δ_C (50 MHz; CD$_3$CN) 27.1 (Me), 61.1 (CH$_2$), 120.9 (C-o), 121.3 (C-o), 121.9 (C-o), 126.5 (C-o), 129.5 (C-m), 129.7 (C-m), 130.6 (C-m), 130.9 (C-m), 131.8 (C-p), 132.8 (C-p), 133.7 (C-p), 134.4

(C-*i*), 135.6 (C-*i*), 136.2 (C-*i*), 157.8 (C$^+$), 162.7 (C$^+$) and 201.4 (C=O).

Photochemical reaction of 1,1′,3,3′-tetraphenylazinoditetrazolylene radical cation[5] (11)

In methanol. A solution of **11** (0.10 g, 0.18 mmol) in methanol (80 ml) was photolyzed for 6 h. The reaction mixture turned from greenish brown to pale orange. The solvent was removed, and the residue was partitioned between DCM and aqueous sodium hydroxide (1 M). The organic layer was separated, dried (Na$_2$SO$_4$) and concentrated. The residue was chromatographed (SiO$_2$–DCM) to give **3** (46 mg, 54%), **6** (9 mg, 10%) and **11** (5 mg, 5%).

In acetone. A solution of **11** (0.10 g, 0.18 mmol) in acetone (80 ml) was irradiated for 6 h. An alkaline treatment and column chromatography (DCM) gave **3** (27 mg, 32%), **6** (7 mg, 8%) and **11** (22 mg, 22%).

Photochemical reaction of 1,3-diphenyl-5-(phenylazo)tetrazolium tetrafluoroborate[6] (12)

A solution of **12** (0.10 g, 0.24 mmol) in methanol (100 ml) was irradiated. After 15 min, a gas evolution started. The irradiation was continued for 1 h. The reaction mixture was analysed by GLC (DB-5 column, 0.25 mm × 30 m, 50 °C; toluene as the internal standard t_r 4.97 min) to reveal that benzene was formed in 57% yield (t_r 3.23 min). The solvent was evaporated and the residue was recrystallized (MeCN–diethyl ether) to give **13**[10] (63 mg, 85%). The reactions in acetonitrile, acetone and DCM were similarly carried out. The yields of **13** were 77, 83 and 27%, respectively.

Photochemical reaction of 1,3-bis(1,3-diphenyl-5-tetrazolio)triazenide tetrafluoroborate[6] (14)

A solution of **14** (0.10 g, 0.17 mmol) in MeOH (100 ml) containing acetophenone (5 ml) was irradiated for 1.5 h. The colour turned from pale yellow to intense yellow. The solvent was removed and the residual oil was washed with hexane and dissolved in DCM. Aqueous sodium hydroxide (1 M) was added and the organic layer was separated. The solvent was removed and the residue was column chromatographed on NH–DM 1020 (DCM–hexane = 3 : 2) to give **15** (8 mg, 13%) and **4** (22 mg, 54%).

Acetophenone (1,3-diphenyl-5-tetrazolio)hydrazone (15). Red crystals; mp 178–179 °C (from DCM–hexane) (Found: C, 71.07; H, 5.25; N, 23.85. Calc. for C$_{21}$H$_{18}$N$_6$ (354.4): C, 71.17; H, 5.12; N, 23.71%); ν_{max}/cm^{-1} 1618, 1576, 1550, 1492, 1468, 1376, 1328, 1296, 1166, 1078, 1038, 978, 762, 702, 698 and 692; λ_{max} (MeCN)/nm 244 (log ε 4.27), 285 (4.35), 339 (4.45) and 452 (3.56); δ_H (200 MHz; CDCl$_3$) 2.53 (3H, s, Me), 7.30–7.61 (9H, m, Ph), 7.92 (2H, br d, J = 6.9 Hz, Ph) and 8.25–8.40 (4H, m, Ph); δ_C (50 MHz; CDCl$_3$) 14.5 (Me), 120.4 (C-*o*), 120.9 (C-*p*), 126.2 (C-*o*), 127.7 (C-*o*), 127.8 (C-*p*), 127.9 (C-*m*), 129.1 (C-*m*), 129.5 (C-*m*), 131.3 (C-*p*), 135.3 (C-*i*), 136.1 (C-*i*), 140.1 (C-*i*), 155.1 (C$^+$) and 161.1 (C=N); *m/z* 354 (M$^+$, 90%), 353 (82), 249 (11), 224 (10), 223 (63), 221 (6), 194 (5), 167 (10), 103 (89) and 77 (Ph, 100).

Compound **15** was alternatively prepared from 1,3-diphenyltetrazolium-5-hydrazide (**16**) and acetone. A mixture of **16** (0.10 g, 0.40 mmol), acetophenone (47 μl, 0.40 mmol) and acetic acid (5 drops) in DCM was heated overnight under reflux. The solvent was removed and the residue was chromatographed on NH–DM 1020 (DCM–hexane = 1 : 1). Further purification by reprecipitation (DCM–hexane) gave **15** (0.10 g, 71%).

Synthesis of 1,3-diphenyltetrazolium-5-hydrazide (16).
A mixture of 5-chloro-1,3-diphenyltetrazolium tetrafluoroborate

(0.35 g, 1.0 mmol) and benzoylhydrazine (0.14 g, 1.0 mmol) in dry acetonitrile (10 ml) was stirred at room temperature for 24 h. Aqueous sodium hydroxide (1 M, 10 ml) was added and the product was extracted with DCM. The extracts were dried (Na$_2$SO$_4$) and the solvent was removed. The residue (0.33 g) was purified by recrystallization from ethanol and preparative TLC (alumina–DCM) to yield 1,3-diphenyltetrazolium-5-benzoylhydrazide (42 mg, 12%); dark red crystals; mp 176–177 °C (decomp.) (from EtOH) (Found: C, 67.14; H, 4.62; N, 23.58. Calc. for C$_{20}$H$_{16}$N$_6$O (356.4) C, 67.40; H, 4.52; N, 23.58%); ν_{max}/cm^{-1} 3430, 3050, 2850, 2330, 1648, 1606, 1568, 1550, 1490, 1468, 1380, 1328, 1312, 1290, 1230, 1184, 1172, 1112, 1070, 1026, 976, 924, 814, 792, 752, 702, 688 and 678; λ_{max} (MeCN)/nm 278 (log ε 4.44) and 434 (3.58); δ_H (200 MHz; CDCl$_3$) 7.36–7.65 (9H, m, Ph), 7.88 (2H, m, Ph), 8.15 (2H, m, Ph), 8.32 (2H, m, Ph) and 8.55 (1H, br s, NH); δ_C (50 MHz; CDCl$_3$) 120.2 (C-*o*), 120.3 (C-*o*), 126.9 (C-*o*), 128.0 (C-*p*), 128.5 (C-*m*), 129.6 (C-*m*), 129.8 (C-*m*), 130.8 (C-*p*), 131.7 (C-*p*), 134.7 (C-*i*), 135.0 (C-*i*), 135.8 (C-*i*), 157.3 (C$^+$) and 162.8 (C=O); *m/z* 356 (M$^+$, 10%), 328 (30), 250 (46), 237 (18), 223 (8), 207 (6), 195 (6), 182 (12), 169 (53), 145 (35), 118 (16), 105 (66), 91 (11) and 77 (100).

A solution of 1,3-diphenyltetrazolium-5-benzoylhydrazide (1.3 g, 3.6 mmol) in hydrochloric acid (20%, 120 ml) was heated at reflux for 30 min. The reaction mixture was cooled and kept overnight at 5 °C. The resulting solid (benzoic acid) was filtered off and the filtrate was made alkali with aqueous sodium hydroxide (10 M, 120 ml). A dark red solid precipitated which was filtered, washed with water and dried (0.76 g, 84%). Recrystallization from DCM–hexane gave a pure sample of **16**; dark red crystals; mp 107 °C (decomp.) (from DCM–hexane) (Found: C, 62.34; H, 4.76; N, 32.66. Calc. for C$_{13}$H$_{12}$N$_6$ (252.3): C, 61.89; H, 4.79; N, 33.31%); ν_{max}/cm^{-1} 3475, 3090, 2340, 1700, 1668, 1600, 1580, 1494, 1470, 1384, 1336, 1290, 1220, 1196, 1184, 1164, 1120, 1104, 1074, 1040, 1028, 974, 914, 812, 750 and 684; λ_{max} (MeCN)/nm 276 (log ε 4.38) and 486 (3.45); δ_H (200 MHz; CDCl$_3$) 7.27–7.64 (6H, m, Ph) and 8.09–8.24 (4H, m, Ph); δ_C (50 MHz; CDCl$_3$) 119.8 (C-*o*), 120.4 (C-*o*), 127.2 (C-*p*), 129.5 (C-*m*), 129.8 (C-*m*), 131.4 (C-*p*), 135.6 (C-*i*), 136.5 (C-*i*) and 156.3 (C$^+$); *m/z* 252 (M$^+$, 56%), 237 (9), 130 (5), 119 (6), 104 (24) and 77 (100).

Synthesis of 1-phenyl-3-(1,3-diphenyl-5-tetrazolio)triazenide (17).
To a solution of **4** (0.40 g, 1.7 mmol) in MeCN was added a solution of benzenediazonium tetrafluoroborate (0.32 g, 1.7 mmol) in MeCN (20 ml) at 0 °C. The mixture was stirred at 0 °C for 4 h. Aqueous sodium hydroxide (1 M, 40 ml) was added and the solvent (MeCN) was removed. The product was extracted with DCM, dried (Na$_2$SO$_4$) and concentrated. The residue (0.51 g) was chromatographed on NH–DM 1020 (DCM–hexane = 1 : 1) to give (*E*)-**17** (0.24 g, 41%) and (*Z*)-**17** (66 mg, 11%) together with recovered **4** (62 mg, 16%). In solution the *Z*-isomer isomerizes gradually to the *E*-form.

(*E*)-17. R_f 0.77 (NH–DM 1020–DCM); orange crystals; mp 204–206 °C (from DCM–hexane) (Found: C, 66.75; H, 4.28; N, 28.43. Calc. for C$_{19}$H$_{15}$N$_7$ (341.4): C, 66.85; H, 4.43; N, 28.72%); ν_{max}/cm^{-1} 1590, 1544, 1484, 1450, 1420, 1396, 1354, 1336, 1300, 1256, 1124, 984, 768 and 686; λ_{max} (MeCN)/nm 226 (log ε 4.22), 238 (4.26), 276 (4.13), 342 (sh, 4.45) and 370 (4.24); δ_H (200 MHz; CDCl$_3$) 7.22–7.76 (11H, m, Ph) and 8.20–8.31 (4H, m, Ph); δ_C (50 MHz; CDCl$_3$) 120.6 (C-*o*), 122.0 (C-*o*), 122.9 (C-*p*), 127.2 (C-*o*), 128.7 (C-*m*), 129.5 (C-*m*), 129.6 (C-*m*), 129.9 (C-*p*), 132.2 (C-*p*), 134.0 (C-*i*), 135.8 (C-*i*), 151.3 (C-*i*) and 165.0 (C$^+$): *m/z* 341 (M$^+$, 37%), 313 (15), 285 (6), 237 (13), 105 (92) and 77 (100).

(*Z*)-17. R_f 0.53 (NH–DM 1020–DCM); yellow crystals; mp 140–142 °C (from DCM–hexane) (Found: C, 66.83; H, 4.49; N, 28.43. Calc. for C$_{19}$H$_{15}$N$_7$ (341.4): C, 66.85; H, 4.43; N, 28.72%); ν_{max}/cm^{-1} 1594, 1548, 1484, 1424, 1330, 1288, 1256,

1080, 1020, 984, 760 and 684; λ_{max} (MeCN)/nm 204 (log ε 4.91), 224 (4.35), 238 (4.34), 299 (4.60) and 393 (4.01); m/z 341 (M$^+$, 1%), 313 (9), 237 (20), 194 (8), 104 (23), 77 (100) and 51(17); during the attempted NMR measurements, this compound isomerized to the E-isomer.

Photolysis of (E)-17

Without acetophenone. A solution of (E)-**17** (0.10 g, 0.29 mmol) in MeOH (100 ml) was irradiated. A gas evolution was observed. After 6 h, the solvent was evaporated and the residue (70 mg) was chromatographed on NH–DM 1020 (DCM) to give **4** (24 mg, 35%) together with unchanged (E)-**17** (32 mg, 32%). The same reaction in acetone gave **4** (10 mg, 15%) and unchanged (E)-**17** (65 mg, 65%).

With acetophenone. A solution of (E)-**17** (0.10 g, 0.29 mmol) in methanol (100 ml) was irradiated in the presence of acetophenone (5 ml). A gas evolution was observed. After 1 h, the solvent was evaporated and the residue was chromatographed on NH–DM 1020 (DCM–hexane = 1 : 1) to give **4** (18 mg, 26%) together with (E)-**17** (33 mg, 33%).

Photochemical reaction of 1,3-diphenyl-5-tetrazolio(3-tosyl)-triazenide[6] (18)

In methanol. A solution of **18** (0.10 g, 0.24 mmol) in methanol (100 ml) was photolyzed. A gas evolution was observed. After 45 min, the solvent was evaporated and the residue (80 mg) was chromatographed on NH–DM 1020 (DCM) and then reprecipitated from (DCM–hexane) to give **19**[2] (3 mg, 5%), **20** (1 mg, 1%), **4** (30 mg, 53%).

In acetonitrile. In a similar manner, **18** (0.10 g, 0.24 mmol) in acetonitrile (100 ml) was irradiated for 40 min to give **19** (18 mg, 32%), **20** (11 mg, 12%) and acetanilide (8 mg, 12%).

1,3-Diphenyl-5-tetrazolio(tosyl)amide (20). Colourless crystals, mp 242 °C (from EtOH) (Found: C, 61.10; H, 4.26; N, 17.96. Calc. for C$_{20}$H$_{17}$N$_5$O$_2$S (391.5): C, 61.37; H, 4.38; N, 17.89%); ν_{max}/cm^{-1} 1596, 1556, 1490, 1468, 1454, 1326, 1282, 1150, 1082, 930 and 760; λ_{max} (MeCN)/nm 218 (log ε 4.38), 249 (4.45) and 337 (3.91); δ_H (200 MHz; CDCl$_3$) 2.39 (3H, s, Me), 7.27 (2H, d, J 8.2, Ar-H), 7.54–7.65 (6H, m, Ph) and 8.04–8.15 (6H, m, Ph and Ar-H); δ_C (50 MHz; [^{2}H$_6$]DMSO) 21.0 (Me), 120.6 (C-o), 122.7 (C-Ar), 124.2 (C-o), 127.2 (C-Ar), 128.9 (C-m), 129.6 (C-m), 130.4 (C-p), 132.3 (C-p), 132.8 (C-i), 135.4 (C-i), 140.1 (C-Ar), 141.5 (C-Ar) and 156.0 (C$^+$); m/z 391 (M$^+$, 100%), 327 (70), 284 (10), 195 (18), 167 (7), 139 (80), 104 (99) and 77 (Ph, 98).

Alternative synthesis of 20. Tosyl chloride (80 mg, 0.42 mmol) was added to a solution of **4** (0.10 g, 0.042 mmol) in MeCN (2 ml). The yellow colour of **4** faded and colourless crystals deposited. After 1 h, the solvent was removed and the residue was dissolved in DCM, washed with aqueous sodium hydroxide (0.5 M) and dried. The solvent was evaporated and the residue was recrystallized from ethanol to give **20** (0.13 g, 81%).

Photolysis of 1,3-diphenyl-5-tetrazolio(3-cyano)triazenide[6] (21)

In methanol. A solution of **21** (0.10 g, 0.34 mmol) in MeOH (100 ml) was irradiated. A gas evolution was observed. After 5 h, the solvent was evaporated and the residue (78 mg) was chromatographed on NH–DM 1020 (DCM–hexane = 2 : 1) to give **6** (35 mg, 43%), **23** (19 mg, 21%) and **4** (5 mg, 6%).

In acetonitrile. A solution of **21** (0.10 g, 0.34 mmol) in MeCN (100 ml) was irradiated. A gas evolution was observed. After 3 h, the solvent was evaporated and the residue (97 mg) was chromatographed on NH–DM 1020 (DCM) to give **19** (7 mg, 9%) and **23** (30 mg, 34%).

1,3-Diphenyl-5-tetrazoliocyanamide (23). Pale yellow crystals, mp 211–212 °C (from EtOH) (Found: C, 64.39; H, 3.93; N, 32.02. Calc. for C$_{14}$H$_{10}$N$_6$ (262.3): C, 64.11; H, 3.84; N, 32.05%); ν_{max}/cm^{-1} 2175, 1616, 1582, 1492, 1372, 1346 and 758; λ_{max} (MeCN)/nm 251 (log ε 4.38), 271 (sh, 4.14) and 352 (3.77); δ_H (200 MHz; CDCl$_3$) 7.54–7.69 (6H, m, Ph), 8.03–8.08 (2H, m, Ph) and 8.19–8.24 (2H, m, Ph); δ_C (50 MHz; CDCl$_3$) 117.1 (CN), 120.3 (C-o), 122.2 (C-o), 129.7 (C-m), 130.1 (C-m), 130.1 (C-p), 132.6 (C-p), 133.0 (C-i), 135.4 (C-i) and 161.2 (C$^+$); m/z 262 (M$^+$, 100%), 130 (31), 105 (44) and 77 (Ph, 100).

Photochemical reaction of 1,3-diphenyl-5-(triphenylphosphino-triazeno)tetrazolium tetrafluoroborate[6] (24)

In methanol. A solution of **24** (0.10 g, 0.16 mmol) in MeOH (100 ml) was irradiated. A gas evolution was observed. After 1 h, the solvent was evaporated and the residue was reprecipitated to give a mixture (68 mg) of **25**[6] and **10**. The yields were estimated by ^{1}H NMR spectroscopy to be 57% for **25** and 29% for **10**.

In acetonitrile. A solution of **24** (0.10 g, 0.16 mmol) in acetonitrile (100 ml) was irradiated. A gas evolution was observed. After 45 min, the solvent was evaporated to give **25** (97 mg, 100%).

Photochemical reaction of 1,3-diphenyl-5-tetrazolio(1-phenyl-tetrazolyl-5)amide[6] (26)

A solution of **26** (0.10 g, 0.26 mmol) in MeOH (100 ml) was irradiated in the presence of acetophenone (5 ml). After 4 h, the solvent was removed and the residue was washed with hexane. The residual oil was subjected to column chromatography on NH–DM 1020 (DCM) to give the guanidine derivative **27** (33 mg, 45%) and **26** (13 mg, recovery 13%).

Guanidine derivative (27). Colourless crystals; mp 237–238 °C (from DCM–hexane) (Found: C, 60.13; H, 4.65. Calc. for C$_{14}$H$_{13}$N$_7$ (291.3): C, 60.20; H, 4.69%); ν_{max}/cm^{-1} 3350, 1638, 1594, 1570, 1530, 1490, 1450, 1406, 728 and 680; δ_H (200 MHz; CD$_3$CN) 6.90–7.17 (2H, m, Ph and NH), 7.27–7.57 (8H, m, Ph and NH), 7.71 (1H, br s, NH) and 7.85–7.92 (2H, m, Ph); δ_C (50 MHz; CD$_3$CN) 123.4, 123.5, 124.4, 125.2, 125.3, 129.1, 129.8 and 129.9 (two quaternary carbons were not observed); m/z 279 (M$^+$, 70%), 251 (74), 235 (11), 159 (10), 147 (10), 146 (100), 144 (10), 133 (34), 129 (23), 120 (17), 119 (69), 118 (17), 94 (14), 93 (50), 92 (19), 91 (23), 78 (11) and 77 (89); HRMS found: m/z 279.1241 (M$^+$). Calc. for C$_{14}$H$_{13}$N$_7$: 279.1231.

References

1 K. T. Potts, *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley-Interscience, New York, 1984; For a recent example: A. Padwa, T. M. Heidelbaugh and J. T. Kuethe, *J. Org. Chem.*, 2000, **65**, 2368.

2 S. Araki, H. Hattori, N. Shimizu, K. Ogawa, H. Yamamura and M. Kawai, *J. Heterocycl. Chem.*, 1999, **36**, 863.

3 S. Araki, H. Hattori, H. Yamamura and M. Kawai, *J. Heterocycl. Chem.*, 2000, **37**, 1129.

4 J. Griffiths, *Chem. Soc. Rev.*, 1972, **1**, 481; P. S. Engel and C. Steel, *Acc. Chem. Res.*, 1973, **6**, 275; P. S. Engel, *Chem. Rev.*, 1980, **80**, 99; W. Adam and O. De Lucchi, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 762; W. Adam, S. Grabowski and R. M. Wilson, *Acc. Chem. Res.*, 1990, **23**, 165.

5 S. Araki, K. Yamamoto, T. Inoue, K. Fujimoto, H. Yamamura, M. Kawai, Y. Butsugan, J. Zhou, E. Eichhorn, A. Rieker and M. Huber, *J. Chem. Soc., Perkin Trans. 2*, 1999, 985.

6 S. Araki, K. Yamamoto, M. Yagi, T. Inoue, H. Fukagawa, H. Hattori, H. Yamamura, M. Kawai and Y. Butsugan, *Eur. J. Org. Chem.*, 1998, 121.

7 R. N. Hanley, W. D. Ollis and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 2*, 1979, 736.

8 Full details of the X-ray crystallography will be reported separately.

9 G. O. Schenck and H. Formanek, *Angew. Chem.*, 1958, **70**, 505; R. C. Cookson, I. D. R. Stevens and C. T. Watts, *J. Chem. Soc., Chem. Commun*, 1965, 259.
10 S. Araki, Y. Wanibe, F. Uno, A. Morikawa, K. Yamamoto and Y. Butsugan, *Chem. Ber.*, 1993, **126**, 1149.
11 P. S. Engel and D. J. Bishop, *J. Am. Chem. Soc.*, 1975, **97**, 6754; see also,; P. S. Engel, D. J. Bishop and M. A. Page, *J. Am. Chem. Soc.*, 1978, **100**, 7009.
12 For an example of photochemical reaction of triazenes: see, H. Balli, T. Eichenberger, B. Hellrung and P. Scheibli, *Helv. Chim. Acta*, 1985, **68**, 1394.
13 H. Bock and M. Schnöller, *Chem. Ber.*, 1969, **102**, 38; J. E. Leffler and R. D. Temple, *J. Am. Chem. Soc.*, 1967, **89**, 5235, and references cited therein.
14 S. T. Reid, *Adv. Heterocycl. Chem.*, 1970, **11**, 1; R. M. Moriarty and J. M. Kliegman, *J. Am. Chem. Soc.*, 1967, **89**, 5959.
15 (*a*) Parent tetrazole: G. Maier, J. Eckwert, A. Bothur, H. P. Reisenauer and C. Schmidt, *Liebigs Ann. Chem.*, 1996, 1041; (*b*) disubstituted tetrazoles: P. D. Hobbs and P. D. Magnus, *J. Chem. Soc., Perkin Trans. 1*, 1973, 469; A. Padwa, S. Nahn and E. Sato, *J. Org. Chem.*, 1978, **43**, 1664; (*c*) trisubstituted tetrazoles: H. Quast and L. Bieber, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 428; H. Quast, A. Fuss and W. Nüdling, *Eur. J. Org. Chem.*, 1998, 317.