Photochemical Formation of Heteromethylenecyclopropanes, 28[◇]

Photoextrusion of Molecular Nitrogen from Annulated 5-Alkylidene-4,5-dihydro-1*H*-tetrazoles: Annulated Iminoaziridines and the First Triplet Diazatrimethylenemethane☆

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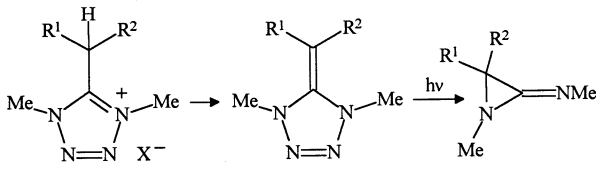
Deprotonation of the annulated tetrazolium salts **4**, **6**, **8**, **10**, and **12** with sodium or potassium hydride yields the alkylidenedihydrotetrazoles **5**, **7**, **9**, **11**, and **13**, respectively. While **5a** and **b** are unstable, even in solution at low temperatures, **7**, **9**, **11**, and **13** form yellow oils that are distilled under high vacuum. − Irradiation of solutions of **7**, **9**, and **11** in [D_8]toluene at −60°C yields, besides molecular nitrogen, annulated iminoaziridines that have an exocyclic CN double bond, i.e. **14**, **16**, and **18**, respectively. In addition, an equal amount of the isomer **19** with the endocyclic CN double bond is formed from **11**. On thermolysis, **14**, **16**, and **18** undergo [2 + 1] cycloreversion into methyl isocyanide and the cyclic imines **15**, **17**, and **20**, respectively. By contrast, **19** rearranges thermally to yield **18**. While the doubly bridged alkylidenedihydrotetrazole **13a** affords only unidentified decomposition products on photolysis, its methyl homologue **13b** is converted into the hexahydronaphthyridine **22** which is also formed on thermolysis. − Irradiation of **13b** in a 2-methyltetrahydrofuran or butyronitrile matrix at 77 K yields a triplet diradical showing a four-line EPR spectrum centred at 3362 G and a half-field transition (at 1669 G) with a hyperfine structure. The zero-field splitting parameters $|D/hc|$ = 0.031 cm^{-1} and $|E/hc|$ = 0.0014 cm^{-1} are obtained by simulation of the EPR spectrum. The signal-carrier is assigned the diazatrimethylenemethane structure **23** on the basis of the close similarity between its EPR spectrum and those of trimethylenemethane (**28**) and tris(*N*-methylimino)methane (**29**). − Structural features are discussed that are responsible for the observed differences between the photochemical pathways.

Deprotonation of 1,4,5-substituted tetrazolium salts **1** with sodium hydride yields the yellow 5-alkylidenedihydrotetrazoles **2**.[2][3][4] Irradiation of **2** with UV light results in a clean extrusion of molecular nitrogen and the quantitative, diastereoselective formation of (*E*)-iminoaziridines **3** which undergo (*E*) ⇌ (*Z*) equilibration at room temperature.[2][5][6] Iminoaziridines with unsaturated substituents, i.e. **3d**−**f**, can be observed only at temperatures below −40°C because subsequent reactions are initiated by intramolecular hydrogen shifts at higher temperatures.[6]

Recently, we have disclosed the synthesis of a number of annulated tetrazolium salts, viz. **4**, **6**, **8**, **10**, and **12**.[1] We now report on their deprotonation and the irradiation of the resulting annulated 5-alkylidenedihydrotetrazoles. This study was stimulated by the hope that the additional strain imposed by the second rings might render the formation of iminoaziridines difficult, if not impossible, and thus help to observe triplet diradicals generated by extrusion of nitrogen, e.g. in low-temperature matrices. This concept originates from the seminal work of Berson and coworkers[7][8] on bridged trimethylenemethane diradicals and has recently been extended to bridged oxyallyl diradicals.[9] It plays an important role in organic synthesis as demonstrated by many diyl trapping reactions.[10] We disclose here the detection by EPR spectroscopy of a novel nitrogen analogue of trimethylenemethane, i.e. the triplet diazatrimethylenemethane **23**. Furthermore, the results of this work broaden the basis for the definition of scope and limitation of the photochemical synthesis of iminoaziridines from 5-alkylidenedihydrotetrazoles.



1 **2** **3**

	R1	R2
1a – 3a	H	H
1b – 3b	H	*t*Bu
1c – 3c	H	Ph
1d – 3d	H	$CH=CH_2$

	R1	R2
1e – 3e	H	(*E*)-CH=CHMe
1f – 3f	H	(*E*)-CH=CH*t*Bu
1g – 3g	Me	Me
1h – 3h	Me	Ph

[◇] Part 27: Ref.[1].

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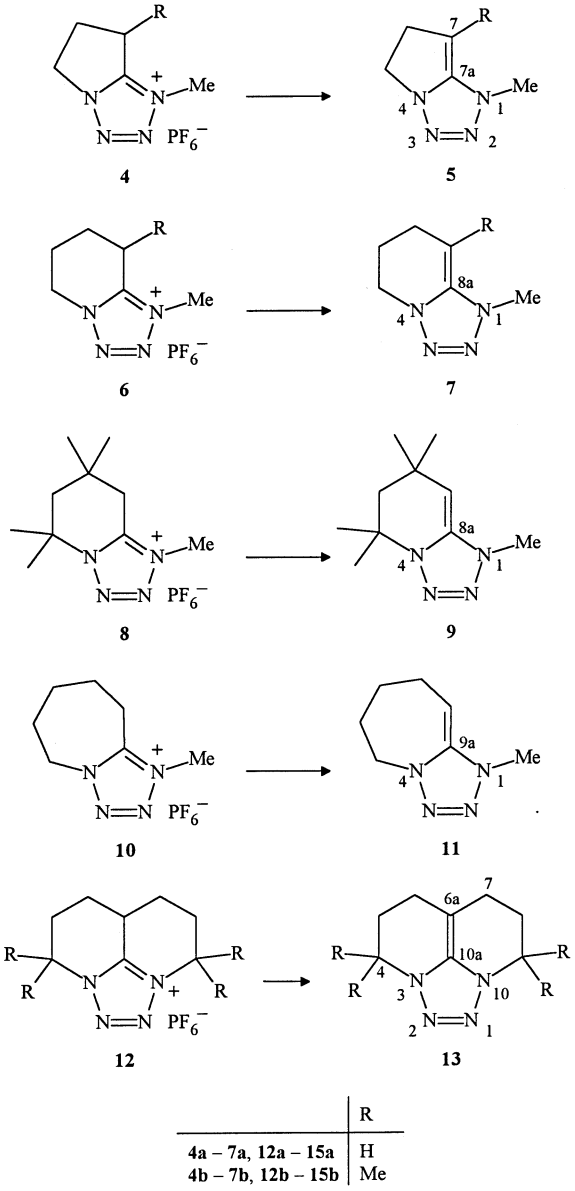
Annulated 5-Alkylidene-4,5-dihydro-1*H*-tetrazoles

Deprotonation of the annulated tetrazolium salts was performed with sodium or potassium hydride in ether solvents, sometimes in the presence of 18-crown-6 or the complex from 18-crown-6 and potassium cyanide,[11] handling of which is more convenient. The progress of the deprotonation reaction was indicated by the evolution of hydrogen and the development of a yellow colour which is characteristic for alkylidenedihydrotetrazoles.[2][3][4] A number of runs, performed with **6a**, served to optimise the experimental protocol. Deprotonation with sodium or potassium hydride in diethyl ether or *tert*-butyl methyl ether was very slow in the absence of 18-crown-6. Traces of the solvent inevitably appeared in the distilled alkylidenedihydrotetrazoles. Therefore, we preferred *tert*-butyl methyl ether as solvent, whose traces could be employed as standard in photolysis experiments that were monitored by NMR spectroscopy. On the other hand, tetrahydrofuran and 2-methyltetrahydrofuran as solvents allowed the very rapid and quantitative deprotonation of tetrazolium salts even with sodium hydride and in the absence of 18-crown-6, and were hence most convenient for the preparation of solutions of known concentration which were needed in spectroscopic studies.

Attempts at the isolation of the products **5** of the trimethylenetetrazolium hexafluorophosphates **4** met with failure. Deprotonation of **4a** at room temperature yielded orange-coloured, very viscous, non-volatile decomposition products of **5a**. Experiments in [D_8]tetrahydrofuran solution at low temperatures showed the onset of deprotonation at a temperature of −50°C. Even at that temperature, slow decomposition occurred which only permitted characterisation of **5a** by NMR spectroscopy (Tables 2 and 3). Subsequent irradiation at −60°C ($\lambda \geq 320$ nm) afforded a complex mixture of unidentified products. Likewise, deprotonation of **4b** in [D_8]tetrahydrofuran commenced at −45°C. The resulting yellow solution of **5b**, which was pure according to proton and carbon-13 spectra (Tables 2 and 3), also furnished an unidentified mixture, however, on irradiation at −60°C ($\lambda \geq 320$ nm).

Unlike **5a** and **b**, which are extremely prone to decomposition, all other annulated alkylidenedihydrotetrazoles, viz. **7**, **9**, **11**, and **13**, could be prepared by deprotonation at 0°C (**13a**) or even room temperature and isolated by distillation under high vacuum as deeply yellow oils or as a low-melting solid (**13b**). Except **13a**, which decomposes at room temperature during one day, the distilled, neat alkylidenedihydrotetrazoles **7**, **9**, **11**, and **13b**, are reasonably stable at room temperature, as long as light, air, and moisture are excluded. During five days, only about 1% of **13b** lost molecular nitrogen to afford **22**.

Besides the long-wavelength absorption in the UV/Vis spectra (Figure 2), the most characteristic spectroscopic features of the annulated alkylidenedihydrotetrazoles are the high-field NMR signals of the methine groups (δ_H = 3−3.4, δ_C = 51−66) and the analogous quaternary vinylic carbon atoms (δ = 63−73) (Tables 2 and 3). These data resemble those of monocyclic alkylidenedihydrotetrazoles,[3][4] of course, and are indicative of highly polarised, electron-rich "double" bonds that characterise ylides.[12][13]



Photolysis in Solution

Dilute, degassed solutions of the annulated alkylidenedihydrotetrazoles, contained in sealed NMR sample tubes, were irradiated with the filtered ($\lambda \geq 305$ or 320 nm), focussed light of a high-pressure mercury lamp. In a number of experiments, low temperature (−60°C) was maintained during irradiation and recording of NMR spectra, and precluded thermal (*E*) ⇌ (*Z*) equilibration of the photolysis products of **7**, **9**, and **11**. Fading of the original yellow colour during irradiation indicated the disappearance of the alkylidenedihydrotetrazoles, which occurred slower at low temperature than at 20°C. The course of the photolyses was also monitored by NMR spectroscopy, which provided the clue to the structures of the photolysis products (Tables 4

and 5). In all cases except **7a**, the conversion and the yields, which were determined by a comparison with the internal standard *tert*-butyl methyl ether, were better than 95%, and no byproducts could be detected. Only **7a** formed substantial amounts of unidentified byproducts, and, therefore, the yield of **14a** dropped to 30−50%.

In most cases, mixtures of isomers were formed, the ratio of which changed slowly at room temperature. This process led eventually to a constant ratio and is doubtless the thermal (*E*) ⇌ (*Z*) equilibration, long-known from other iminoaziridines.[5][6][14][15][16][17] It allowed us to assign NMR signals to individual compounds. The iminoaziridine structures **14**, **16**, **18**, and **19** of the photoproducts were not only based on NMR evidence but also on the results of their thermal [2 + 1] cycloreversion into cyclic imines (**15**, **17**, **20**) and methyl isocyanide (see below). In addition, the IR spectrum of the photoproduct of **7a** showed a C=N absorption at a very high frequency (1795 cm^{-1}) which is characteristic for iminoaziridines.[14][15][16][17] The configuration was elucidated with the help of correlations that had been derived from the NMR spectra of monocyclic iminoaziridines. Accordingly, the methyl carbon atoms at the exocyclic nitrogen atom of (*E*) diastereomers resonate at lower field than those of (*Z*) diastereomers.[5][15][16][17] Furthermore, the extent of the long-range coupling between the proton at the aziridine ring and the protons of the *N*-methylimino group is larger for (*Z*) diastereomers than for (*E*) diastereomers ($^5J_{transoid} > {}^5J_{cisoid}$).[5][6][14][15][16][17]

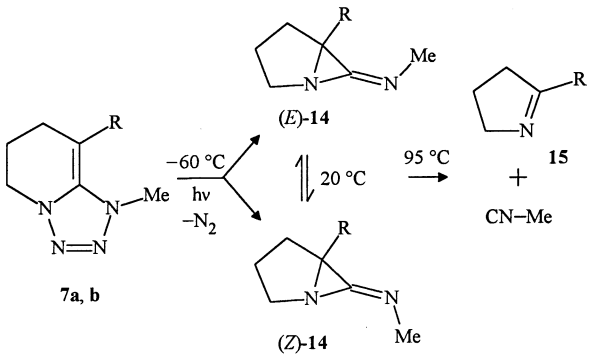
Experimental conditions and results of the irradiation experiments and the thermal (*E*) ⇌ (*Z*) equilibration of the annulated iminoaziridines **14**, **16**, and **18** are listed in Table 1.

Table 1. Conditions and results of irradiation experiments and the subsequent thermal *E* ⇌ *Z* equilibration of the photolysis products. The conversions and the yields were better than 95%

Cpd.	λ [nm]	Temp. [°C]	Time [h]	Prod.	*E* : *Z*	$(E:Z)_{eq.}$[a]		[b]
7a	≥ 320	−60	3.5	**14a**[c]	>99 : <1	46 : 54	(32 d, 20 °C)	T
	≥ 305	20	0.75	[d]	66 : 34	52 : 48 48 : 52	(37 d, 20 °C) (1 h, 60 °C)	B
7b	≥ 320	−60	4	**14b**	57 : 43	36 : 64 38 : 62	(7 d, 20 °C) (1 h, 80 °C)	T
9	≥ 320	−60	3	**16**	41 : 59	76 : 24	(7 d, 20 °C)	T
	≥ 320	20	0.67		38 : 62	77 : 23	(7 d, 20 °C)	A
	≥ 320	20	0.33		39 : 61	78 : 22	(10 d, 20 °C)	B
11	≥ 320	−60	3.5	**18** : **19** (47 : 53)	**18** 98 : 2			T
	≥ 305	20	3	(49 : 51)	85 : 15	66 : 34	(14 d, 20 °C)	B
13b	≥ 320	−60	1.25	**22**				T

[a] (*E*/*Z*) ratio after equilibration during the specified time at the given temperature. − [b] Solvent A: [D_8]tetrahydrofuran, B: [D_6]benzene, T: [D_8]toluene. − [c] The yield was only 30%. − [d] The yield was only 50%.

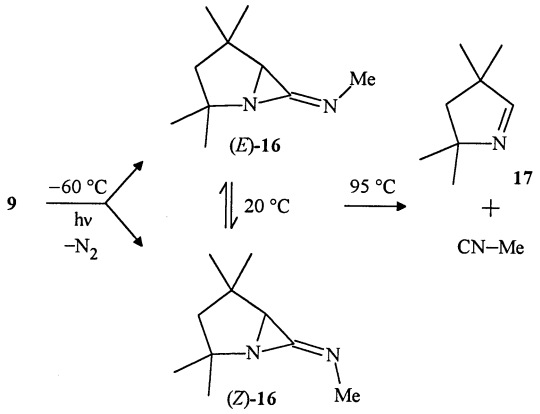
On photolysis at low temperatures, *monocyclic* alkylidenedihydrotetrazoles **2** yield (*E*) iminoaziridines (*E*)-**3** with high diastereoselectivity. Apparently, the geometry of the moiety $R^1R^2C{=}C{-}NMe$ of the precursors **2** is conserved.[5][6] In accord with these results, irradiation of **7a** in [D_8]toluene solution at −60°C afforded exclusively (*E*)-**14a**, while a mixture of (*E*)- and (*Z*)-**14a** (66 : 34) was obtained at 20°C, obviously by way of (*E*) ⇌ (*Z*) diastereomerisation of primarily formed (*E*)-**14a**, which eventually led to an equilibrium between almost equal amounts of both diastereomers. Replacement of the vinyl proton of **7a** with a methyl group, resulting in **7b**, changed the (*E*/*Z*) ratio obtained on photolysis. Besides (*E*)-**14b**, significant amounts of (*Z*)-**14b** arose even at −60°C [(*E*)-/(*Z*)-**14b** = 57:43]. In the equilibrium, (*Z*)-**14b** is slightly favoured over (*E*)-**14b**, probably because of steric repulsion between the two methyl groups in the (*E*) diastereomer. Thermal [2 + 1] cycloreversion of the annulated iminoaziridines **14** occurred smoothly at 95°C and gave 1:1 mixtures of methyl isocyanide and the dihydropyrroles **15** (**15a**, 67%; **15b**, 93%) of which **15a** was identified by a comparison of its NMR spectra (Tables 6 and 7) with those of the authentic compound.[18][19]



The two pairs of geminal methyl groups at the six-membered ring of **9** influenced the stereochemical result of the photolysis in a surprising way. Not only the *same* product ratio was formed at −60°C and 20°C, and in different solvents, but the (*Z*)-iminoaziridine (*Z*)-**16** predominated over its diastereomer [(*E*)-**16**/(*Z*)-**16** = 2:3]. Thermal equilibration changed this ratio into 3:1. Thermolysis of **16** occurred somewhat slower than that of **14**. Only after 27 h at 95°C, 89% of **16** had decomposed into methyl isocyanide and dihydropyrrol **17** (yield 86%).

While the nature of the thermolysis products left no doubt of the iminoaziridine structures **16**, the unexpected diastereomeric ratio obtained on photolysis of **9** stimulated the application of a third criterion for the assignment of configurations, viz. the asymmetric solvent-induced shift. The asymmetric solvation of the $C{=}NCH_3$ moiety of imines by [D_6]benzene molecules causes high-field shifts that are larger for protons *cis* to the imino methyl group than for *trans* protons.[20] Comparison of the proton spectra recorded for [D_8]tetrahydrofuran and [D_6]benzene solutions shows (Table 4) that the signal of the proton at the aziridine ring of the predominant photoproduct **16** experiences a high-field shift of only 0.06 ppm while that of the minor isomer is shifted to higher field by no less than 0.27 ppm.

This result confirms the assignment of configuration based on the extent of long-range proton-proton coupling and on chemical shifts in carbon-13 spectra.



Irradiation at low temperature of a [D_8]toluene solution of the alkylidenedihydrotetrazole **11**, annulated with a seven-membered ring, afforded two major products in similar amounts besides traces of a third product. The latter increased at the expense of one of the former when the experiment was performed at 20°C. This process continued after photolysis until a constant ratio was reached (2:1). Clearly, the photoproducts that interconvert at 20°C are (*E*)- and (*Z*)-**18**. The carbon-13 shift criterion (vide supra) allowed us to assign the (*E*) configuration to the predominating isomer. The structure **19** of the second major photoproduct is based on NMR evidence (Tables 4 and 5).

At 20°C, the ratio of the isomers [(*E*)-**18** + (*Z*)-**18**] / **19** remained almost unchanged during extended periods of time. As before, increase of the temperature up to 95°C eventually led to thermal decomposition into methyl isocyanide and tetrahydropyridine **20**, which was identified by comparison of its proton and carbon-13 spectra (Tables 5 and 6) with those of the authentic compound.[18][19] The thermolysis was monitored by proton spectroscopy. The resulting conversion vs. time diagramme (Figure 1) shows a simultaneous decrease of **18** and **19** and a deterioration of the material balance, which is indicative of the formation of unidentified decomposition products. No hint about the presence of the hypothetical [2 + 1] cycloreversion product of **19**, viz. **21**, could be derived from the proton and carbon-13 spectra, however. Interestingly, the yield of methyl isocyanide formed on thermolysis (61%) significantly exceeded the amount of **18** present at the beginning (44%). We rationalise this result in terms of the thermal isomerisation of **19** into **18** for which precedent exists in the series of monocyclic iminoaziridines[16] and in the equilibration of the analogous bicyclic alkenes.[21] This interpretation also explains the lack of **21**.

The photolysis of the doubly bridged alkylidenedihydrotetrazoles **13** appeared particularly intriguing because extremely strained closed-shell products such as **24** or **25**, or, at low temperatures, persistent diradicals like **23** might result from the photoextrusion of molecular nitrogen. Irradiation of a solution of **13a** in [D_8]toluene at −60°C yielded a mixture of unidentified compounds. Under the same conditions, the tetramethyl homologue **13b** furnished, by contrast, only a single photoproduct. This compound was also formed quantitatively by *thermal* denitrogenation of **13b**, which occurred slowly at 60, with a reasonable rate at 90°C. NMR and IR evidence left no doubt that photolysis and thermolysis had led to the hexahydronaphthyridine **22**. Apparently, **22** arises by a hydrogen shift from an elusive intermediate which is generated on photolysis of **13b**. Possible candidates for the intermediate(s) are **23**−**25**.

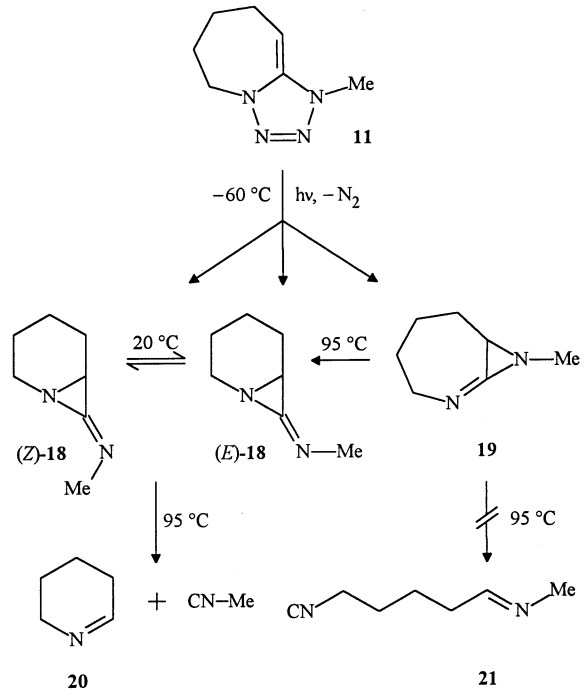
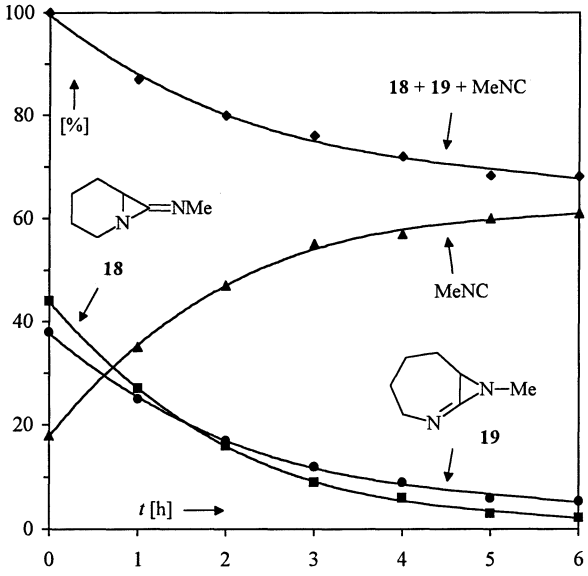
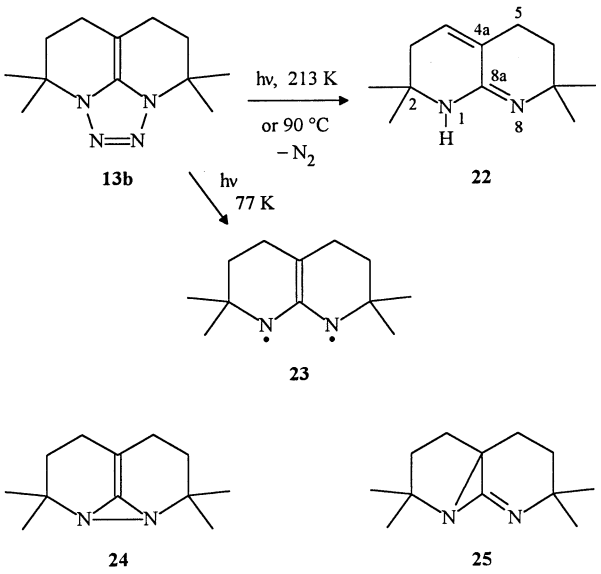


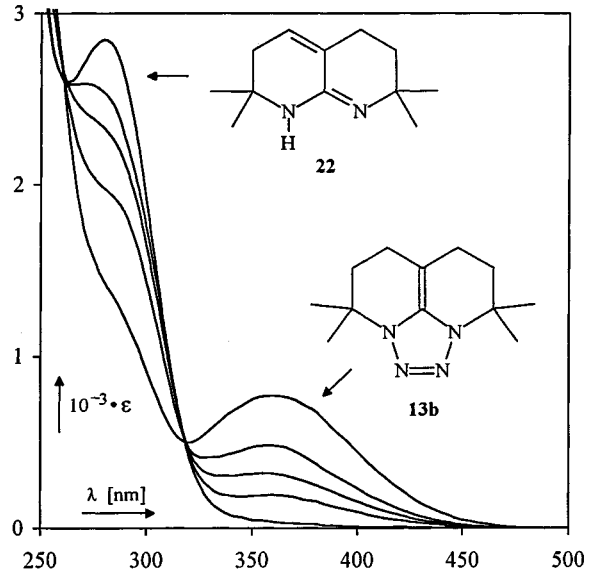
Figure 1. Conversion vs. time diagram for the thermolysis of a mixture of **18** and **19** in [D_8]toluene solution at 95°C





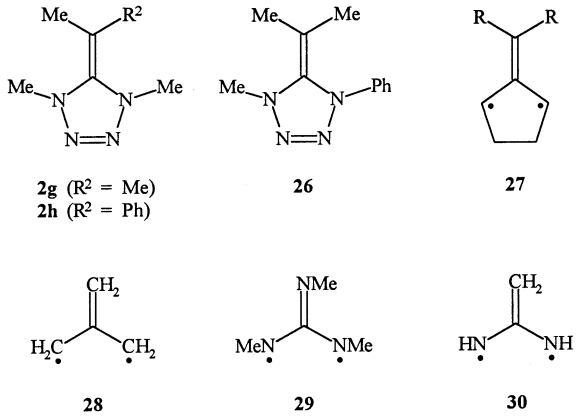
With the view of observing labile intermediates, the course of photolysis of **13b** was monitored by UV/Vis spectroscopy (Figure 2). Two isosbestic points at 260 and 320 nm, observed in irradiation experiments performed at room temperature, were indicative of the absence of detectable intermediates on the way to the hexahydronaphthyridine **22**, however.

Figure 2. UV/Vis spectrum of **13b** (tetrahydrofuran solution), UV/Vis spectra recorded after irradiation of a $1.00 \cdot 10^{-2}$ M solution of **13b** in tetrahydrofuran for 30, 60, and 90 min with a 100-W daylight lamp, and UV spectrum of **22** obtained by irradiation of a $1.00 \cdot 10^{-2}$ M solution of **13b** in tetrahydrofuran with a high-pressure mercury lamp (5 min, $\lambda \geq 320$ nm)



EPR Detection of a Matrix-Isolated Diazatrimethylenemethane Diradical

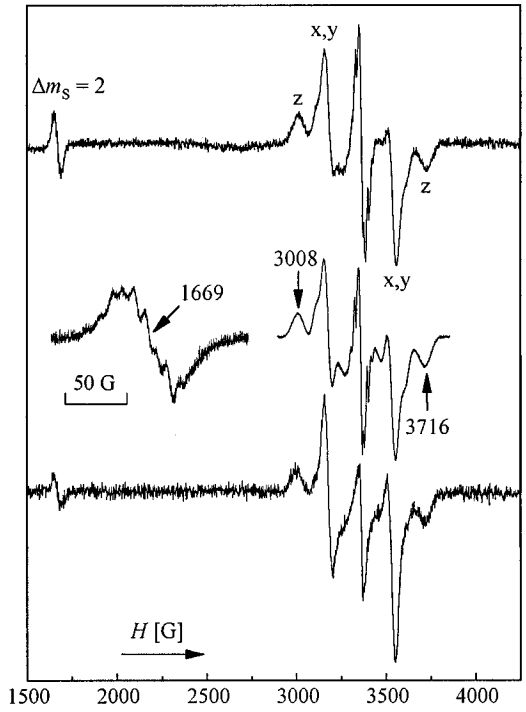
Photoextrusion of molecular nitrogen from iminodihydrotetrazoles in low-temperature matrices gives rise to the formation of triplet tris(imino)methanes, e.g. **29**, the first



and, so far, only nitrogen analogues of trimethylenemethane (**28**).[22] Therefore, the smooth photolysis of alkylidenedihydrotetrazoles stimulated the hope to generate triplet *diaza*trimethylenemethanes, which might be detected by EPR spectroscopy at low temperatures. Irradiation with an argon ion laser of the monocyclic alkylidenedihydrotetrazoles **2g**, **h**, and **26**, and the annulated alkylidenedihydrotetrazoles **5b**, **7b**, **9**, and **13a** in 2-methyltetrahydrofuran matrices at 77 K for a few minutes followed by recording the EPR spectra at that temperature produced only signals of monoradicals, however. By contrast, photolysis of **13b** under the same conditions furnished a centrosymmetric four-line spectrum, centred at 3362 ± 10 G, which closely resembled the EPR spectra of tris(*N*-methylimino)methane (**29**)[22] and trimethylenemethane (**28**)[23] (Figure 3, lower trace). The spectrum persisted for hours at 77 K. The half-field transition ($\Delta m_S = 2$) which is a criterion of triplets is observed at 1669 G. It exhibits a hyperfine structure of at least 12 equidistant lines separated by 8.5 ± 1 G. The absorption near the centre of the four-line high-field spectrum stems from monoradicals generated during the irradiation.

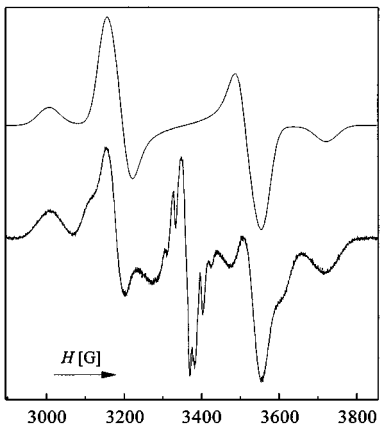
At the first glance, the apparent four-line spectrum can be assigned to the z and x,y signals of randomly oriented triplet molecules having an axis of threefold or higher symmetry, i.e. $E/hc \approx 0$ cm^{-1}.[24] Close scrutiny of EPR spectra, recorded with a much higher signal-to-noise ratio, uncovered a shoulder of both apparent x,y lines, however (Figure 3, middle spectrum). A very similar EPR spectrum appeared in a butyronitrile matrix (Figure 3, upper trace). The intensity of this shoulder indicated that it could not be the result of a poor resolution of otherwise separated x and y lines. This was unequivocally demonstrated by calculation of the EPR spectrum with extensive variation of the zero-field splitting parameters D' and E'. Eventually, the best agreement between the experimental and the calculated spectrum (Figure 4) was obtained with the zero-field splitting parameters $D' = 335$ G ($|D/hc| = 0.031$ cm^{-1}) and $E' = 15$ G ($|E/hc| = 0.0014$ cm^{-1}) which differed slightly from those that could be directly read-off from the EPR spectrum, viz. $|D/hc| = 0.033$ cm^{-1} and $|E/hc| \approx 0$. None of the numerous calculated EPR spectra reproduced the shoulder of the virtually collapsed x and y lines. Therefore, we conclude that it belongs to an additional, minor para-

Figure 3. First derivatives of the EPR absorption obtained after irradiation of the alkylidenedihydrotetrazole **13b** in 2-methyltetrahydrofuran matrices at 77 K (spectra below and middle) and in a butyronitrile matrix at 77 K (above). The insert in the middle shows the expanded signal of the half-field transition ($\Delta m_S = 2$)



magnetic species. The simulation of the EPR spectrum was also indispensable for the determination of the E' value (15 G) because it was significantly smaller than half of the estimated linewidth (40 G) of the x and y lines. Otherwise, the collapsing of the x and y lines would have misled into the wrong assumption of a triplet molecule having an axis of threefold symmetry.

Figure 4. Experimental and calculated (with the parameters given in the text) high-field part of the EPR spectrum obtained after irradiation of the alkylidenedihydrotetrazole **13b** in a 2-methyltetrahydrofuran matrix at 77 K



The assignment of the diazatrimethylenemethane structure **23** to the species responsible for the predominant EPR spectrum is based on the close resemblance of the spectrum to those of tris(*N*-methylimino)methane (**29**) ($|D/hc| = 0.033 \pm 0.001$ cm^{-1})[22] and trimethylenemethane (**28**) ($|D/hc| = 0.025$ cm^{-1}),[23][25] and the structure of the precursor **13b**. In terms of a dipole approximation,[24] the separation 2 D' between the low-field and high-field z lines corresponds to an average separation r of the unpaired electrons of 3.5 Å (Eq. 1),[26] in reasonable agreement with the proposed structure **23** and the value found for **29**.[22]

$$D' = D/g\mu_B = 3g\mu_B/2r^3 = 1.39 \cdot 10^4\ ^{g}/r^3\ [G] \quad (r \text{ in Å}) \qquad (1)$$

Perturbations of the D_{3h} structure of **28**, such as the five-membered ring of Berson's bridged trimethylenemethanes, give rise to measurable E values, e.g. $|E/hc| = 0.0055$ cm^{-1} for **27**, R = H, 0.0034 cm^{-1} for **27**, R = CH_3.[8][24b] Likewise, the disturbation in **23** of the threefold axial symmetry lifts the degeneracy of the sublevels, which is observed for **28** and **29**, thus yielding an E parameter of similar size.

Discussion

Not unexpected, strain plays the predominant role for the stability of annulated alkylidenedihydrotetrazoles and for the results of their photolysis as well. Both alkylidenedihydrotetrazoles with the shortest bridge, viz. **5a** and **b**, are highly unstable and give rise to the formation of complex mixtures of products. All other annulated alkylidenedihydrotetrazoles are readily obtained by deprotonation of tetrazolium salts and form distillable yellow oils which show moderate persistence at room temperature under inert conditions.

On photoextrusion of nitrogen from **7a**, **b**, and **9**, ring contraction occurs exclusively which leads to annulated iminoaziridines having an exocyclic CN double bond, i.e. **14a**, **b**, and **16**, respectively. No trace of their hypothetical isomers with an endocyclic CN double bond at the bridgehead of a bicyclo[4.1.0] system could be detected, even at temperatures as low as −60°C. By contrast, approximately equal amounts of both types of iminoaziridines, i.e. **18** and **19**, are formed on photolysis of **11**, whose seven-membered ring is obviously large enough to accommodate a CN double bond at the bridgehead. Clearly, the direction of cyclisation of the aziridine rings reflects the relative stabilities of the corresponding carbocyclic systems.[21][27] We note in passing, that some other heteroanalogues of 6-methylenebicyclo[3.1.0]hexane[28] and 7-methylenebicyclo[4.1.0]heptane[29] are already known.

An interpretation of the (*E*/*Z*) diastereoselectivity in the formation of the exocyclic imines **14**, **16**, and **18** is less straightforward. On photolysis at low temperatures, the monocyclic alkylidenedihydrotetrazoles **2** form (*E*)-iminoaziridines with high diastereoselectivity under kinetic control as evidenced by the subsequent (*E*/*Z*) equilibration at elevated temperatures.[2][3][4] This behaviour is also shown by **7a** [→ (*E*)-**14a**] and **11** [→ (*E*)-**18a**] but not by **7b** (→ **14b**) and **9** (→ **16**), which produce mixtures of (*E*) and (*Z*) diastereomers. The compositions of these mixtures differ significantly from those at equilibrium and even don't depend on the temperature of the photolysis experiments in case of **9** (Table 1). Apparently, (*E*) diastereoselectivity, that

is preservation of the geometric arrangement of the C=C−N−Me moiety of the alkylidenedihydrotetrazole, is observed only, if these are not encumbered by a methyl group at the CC double bond or geminal methyl groups at the trimethylene bridge. Otherwise, intermediates are formed that undergo (*E*) → (*Z*) diastereomerisation before closing the aziridine ring.

Thermal [2 + 1] cycloreversion of the photochemically formed annulated iminoaziridines into cyclic imines and methyl isocyanide served as a convenient method to confirm the structure. Compound **19** with the endocyclic CN double bond does not follow this path, which would lead to the acyclic ω-iminoisocyanide **21**, but rearranges to the isomer **18** which decomposes in the usual way. Perhaps, **19** cannot undergo cheletropic one-step cleavage because it is locked in the (*E*) configuration which is less favourable for a non-linear cheletropic pathway than the (*Z*) configuration.[30]

The most intriguing aspect of the present work is the identification of the triplet diazatrimethylenemethane **23** by EPR spectroscopy. Non-Kekulé molecules derived conceptually by heteroatom-for-carbon substitution in trimethylenemethane (**28**) are rare species. While *singlet* molecules of this type have been and still are invoked as intermediates on innumerable occasions, a few heterotrimethylenemethanes have been studied by high-level calculations more recently, viz. oxyallyl,[9a][9b][9c][31] thioxyallyl,[32] and diazatrimethylenemethane.[16] Accordingly, the unsubstituted oxyallyl shows a slight preference for a triplet ground state (by 1−2 kcal mol^{-1}) while a pair of methyl groups already suffices to confer a singlet ground state on this diradical.[31] All three planar diastereomers [(*E,E*), (*E,Z*), and (*Z,Z*)] of the parent diazatrimethylenemethane (**30**) are calculated on the CCSD(T)/UHF level to possess triplet ground states.[16] While we have not yet probed the preference of the diradical **23** for a triplet or singlet ground state with the help of Curie′s law, the computational results support the assumption of a triplet ground state for **23** which is suggested by the persistence of its EPR signal in low-temperature matrices. The failure to observe triplet EPR signals in irradiated low-temperature matrices of the other alkylidenedihydrotetrazoles investigated in this way reveals the structural features that favour formation of triplet diazatrimethylenemethanes: (i) Cyclisation of intermediates in the photolysis of alkylidenedihydrotetrazoles must be prohibited by strain, (ii) the comparison of **13a** with **13b** shows that kinetic stabilisation by methyl groups at the bridges is necessary to avoid reactions that furnish monoradicals or EPR-silent products. These structural requirements are much more stringent than in the case of tris(imino)methanes, the only other triplet heterotrimethylenemethanes that have been identified experimentally as yet.[22]

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Experimental Section

Conditions and results of irradiation and (*E*) ⇌ (*Z*) equilibration experiments: Table 1. − ^{1}H NMR: Tables 2, 4, 6. − ^{13}C NMR: Tables 3, 5, 7. − ^{1}H NMR: Bruker AC 200, AC 250 and DMX 600 (**14a**, **18**−**20**). The assignments are based on ^{1}H,^{1}H COSY spectra (**14a**, **18**−**20**, **22**), decoupling experiments (**15b**), or NOE experiments (**9**, **17**, **22**). Ranges of chemical shifts refer to multiplets, single figures denote the chemical shifts of singlets unless specified otherwise. − ^{13}C NMR: Bruker AC 200, AC 250, and DMX 600 (**14a**, **18**−**20**). The signals were assigned on the basis of DEPT, ^{13}C,^{1}H COSY (**7**, **9**, **11**, **13b**−**15b**, **16**, **17**, **22**) and ^{1}H,^{13}C COSY (DMX 600; **14a**, **18**−**20**) spectra. − IR: Perkin-Elmer 1420. − UV/Vis: Hitachi U 3200; $1.00 \cdot 10^{-2}$ M solutions in 1-mm quartz cells. − EPR: Bruker ESP 300, klystron frequency 9.4 GHz. A total of 12−36 spectra was accumulated with the help of the Bruker 1620 data system. The EPR spectrum of Figure 3 (middle) and Figure 4 was recorded with a sweep width of 960 G and 2048 data points. Calculation of the EPR spectra was performed with the Bruker programme WIN EPR SimFonia, version 1.25 (1996). The best agreement between experimental and calculated spectrum was obtained with the zero-field splitting parameters given in the text, the following Hamilton parameters of the electrons $g(x) = g(y) = 2.006$, $g(z) = 2.003$, a linewidth of the *x* and *y* direction of 40 G and the *z* direction of 55 G.

tert-Butyl methyl ether was distilled from KH and kept under Ar. [D_8]Tetrahydrofuran, [D_6]benzene, and [D_8]toluene were dried with NaH. 2-Methyltetrahydrofuran (99%, Acros Organics) was distilled from NaH, carefully degassed and saturated with Ar. Butyronitrile (≥ 99%) was purchased from Fluka, carefully degassed and saturated with Ar. The annulated tetrazolium salts **4**, **6**, **8**, **10**, and **12a** were prepared as described.[1]

All experiments with alkylidenedihydrotetrazoles were carried out under purified Ar (99.998%) with strict exclusion of air and moisture in rigorously dried glassware. The deprotonation of tetrazolium salts was carried out with exclusion of daylight. Solutions of alkylidenedihydrotetrazoles in sealed tubes were stored in the dark at 77 K.

4,4,9,9-Tetramethyl-5,6,6a,7,8,9-hexahydro-4H-1,2,3,10-tetraazaacenaphthylenium Hexafluorophosphate (**12b**): A solution of 5-[4-chloro-1-(3-chloro-3-methylbutyl)-4-methylpentyl]-1*H*-1,2,3,4-tetrazole (46 g, 0.21 mol)[1] in $CHCl_3$ (90 ml) was placed into 3 thick-walled glass tubes (30 × 4 cm). Dry HCl was introduced for 5 h into the cooled (0−5°C) solutions. The glass tubes were sealed with a flame and heated for 15 h at 110°C. Distillation of the solvent from the combined mixtures afforded a viscous, brown oil (81 g) which was dissolved in ethanol (100 ml). A solution of NH_4PF_6 (53 g, 0.33 mol) in water (0.1 l) was added dropwise to the stirred solution. After 1 d, the precipitate was collected by filtration to afford a colourless solid (75 g, 89%), m.p. 216−222°C. Recrystallisation from ethanol/acetonitrile (2:1) yielded colourless crystals (52 g, 68%), m.p. 230−233°C (dec.) [ref.[1]: 50% (in two steps), m.p. 232°C (dec.)].

1-Methyl-5,6-dihydro-1H-pyrrolo[1,2-d][1,2,3,4]tetrazole (**5a**): A suspension of **4a** (54 mg, 0.2 mmol), KH (28 mg, 0.4 mmol) and 18-crown-6 (3 mg, 10 μmol) in [D_8]tetrahydrofuran (0.6 ml) was magnetically stirred at −78°C in an NMR sample tube attached to a bubble counter. The temperature was gradually raised until a yellow colour indicated the formation of an alkylidenedihydrotetrazole (−50°C). The suspension was stirred for 1 h while the colour changed to brown. After removal of the magnetic stirring-bar, the suspension was degassed by several freeze-thaw cycles (−196 → −60°C/10^{-2} Torr), and the NMR sample tube was sealed with a

flame. The solid material was allowed to settle during 1 h at −60°C before NMR spectra were taken at −40°C.

1,7-Dimethyl-5,6-dihydro-1H-pyrrolo[1,2-d][1,2,3,4]tetrazole (**5b**): As described in the preceding experiment from **4b** (85 mg, 0.3 mmol), KH (28 mg, 0.4 mmol), and 18-crown-6 (3 mg, 10 μmol) in [D_8]tetrahydrofuran (0.6 ml). The suspension was stirred at −45°C for 3 h until the evolution of H_2 had subsided and the colour had changed to yellow.

Table 2. Chemical shifts (δ values) and coupling constants [Hz] (absolute values, *in italics*) in proton spectra of annulated alkylidenedihydrotetrazoles. The shift ranges include multiplets which stem from a pair of geminal protons unless specified otherwise

Cpd.	MeN–C(N)=CH—$(CH_2)_n$–					n	[a]
5a[b]	3.28	3.43 (t, *2.1*)	2.90 (td, *8.3*, *2.0*)	3.73 (t, *2.1*)		2	A
7a	2.64	2.95 (t, *3.6*)	2.07 (td, *5.8*, *3.6*)	1.30 (quin, *5.9*)	3.31 (t, *5.8*)	3	T
11	2.81	3.08 (t, *4.5*)	2.09 – 2.12	1.33 – 1.42 (4H)	3.41 – 3.45	4	T
	MeN–C(N)=CH—CMe_2—CH_2—CMe_2–						
9	2.80	2.99	1.11	1.48	1.31		T
	MeN–C(N)=CMe—$(CH_2)_n$–						
5b[b]	3.35	1.68	2.73 (t, *8.2*)	3.61 (t, *8.2*)		2	A
7b	3.07	1.62	1.87 (t, *6.2*)	1.47 (quin, *6.0*)	3.37 (t, *5.8*)	3	T
	N–C(N)=C—CH_2—CH_2—CR_2–					R	
13a		1.76 – 1.83	1.50 – 1.62	3.23 – 3.29		H	T
13b		1.88 – 1.96	1.49 – 1.56	1.19		Me	T

[a] Solvent A: [D_8]tetrahydrofuran, T: [D_8]toluene. − [b] The spectrum was recorded at −40°C.

Synthesis of the Alkylidenedihydrotetrazoles **7**, **9**, **11**, *and* **13**. − *General Procedure:* A suspension of tetrazolium salt, KH, and 18-crown-6·KCN in *tert*-butyl methyl ether (7 ml) was magnetically stirred overnight in a small tube (12 ml) closed with a rubber septum. The solid material was allowed to settle with the help of a centrifuge. The clear, yellow solution was transferred via syringe into a 25-ml flask attached to the high-vacuum distillation apparatus described previously[4] which had been filled with Ar. The remaining grey solid was washed with *tert*-butyl methyl ether (2 × 1.5 ml). Distillation of the solvent in vacuo (−50 → 20°C/10^{-2} Torr) afforded viscous, deeply yellow oils which were distilled at 20−40°C bath temp./10^{-5} Torr upon the cold finger (−196°C).

1-Methyl-1,5,6,7-tetrahydro[1,2,3,4]-tetrazolo[1,5-a]pyridine (**7a**): From **6a** (0.28 g, 1 mmol), KH (0.2 g, 5 mmol), and 18-crown-6·KCN (16 mg, 50 μmol). The suspension was stirred for 15 h.

1,8-Dimethyl-1,5,6,7-tetrahydro[1,2,3,4]tetrazolo[1,5a]pyridine (**7b**): From **6b** (0.15 g, 0.5 mmol), KH (0.1 g, 2.5 mmol), and 18-crown-6·KCN (16 mg, 50 μmol). The suspension was stirred for 17.5 h.

1,5,5,7,7-Pentamethyl-1,5,6,7-tetrahydro[1,2,3,4]tetrazolo-[1,5-a]pyridine (**9**): From **8** (0.68 g, 0.2 mmol), KH (40 mg, 1 mmol), and 18-crown-6·KCN (2 mg, 5 μmol). The suspension was stirred for 17.5 h. − UV/Vis (acetonitrile): λ_{max} = 349 nm, λ_{min} = 311 nm.

Table 3. Chemical shifts (δ values) in carbon-13 spectra of annulated alkylidenedihydrotetrazoles. Chemical shifts that are printed *in italics* and may be exchanged

Cpd.	MeN—C(N)=CH—$(CH_2)_n$–							n	[a]
5a[b]	35.2	151.3	59.7	35.2	51.8			2	A
7a	31.5	138.6	51.4	*21.36*	*21.06*	44.3		3	T
11	32.3	141.9	59.8	27.0	*28.0*	*29.7*	50.6	4	T
	MeN—C(N)=CH—$C(Me_2)$—CH_2—$C(Me_2)$–								
9	31.84	137.8	66.0	31.39	(34.0)	51.3	55.5 (27.7)		T
	MeN—C(N)=C(Me)—$(CH_2)_n$–								
5b[b]	34.5	144.5	72.6	(10.8)	39.6	50.7		2	A
7b	35.5	134.0	62.9	(15.3)	29.2	22.0	44.5	3	T
	N—C(N)=C—CH_2—CH_2—$C(R_2)$–							R	
13a		138.0	69.9	23.3	24.3	44.9		H	T
13b		135.8	67.9	22.8	37.4	54.9	(25.1)	Me	T

[a] Solvent A: [D_8]tetrahydrofuran, T: [D_8]toluene. − [b] The spectrum was recorded at −40°C.

1-Methyl-5,6,7,8-tetrahydro-1H-[1,2,3,4]tetrazolo[1,5-a]-azepine(**11**): From **10** (0.3 g, 1 mmol), KH (0.2 g, 5 mmol), and 18-crown-6·KCN (16 mg, 50 μmol). The suspension was stirred for 18 h.

5,6,8,9-Tetrahydro-4 H,7H-1,2,3,10-tetraazaacenaphthylene (**13a**): From **12a** (62 mg, 0.2 mmol), KH (70 mg, 1 mmol), and 18-crown-6 (3 mg, 10 μmol). The suspension was stirred at 0°C for 23 h.

4,4,9,9-Tetramethyl-5,6,8,9-tetrahydro-4 H,7H-1,2,3,10-tetraaza-acenaphthylene (**13b**): a) According to the General Procedure from **12b** (73 mg, 0.2 mmol), KH (70 mg, 1 mmol), and 18-crown-6 (3 mg, 10 μmol). The suspension was stirred for 17 h.

b) Preparative experiment: A suspension of **12b** (0.73 g, 2 mmol), KH (0.4 g, 10 mmol) and 18-crown-6 (5 mg, 0.02 mmol) in *tert*-butyl methyl ether (7 ml) was stirred for 19 h in a small tube (12 ml) closed with a rubber septum. The solid material was allowed to settle with the help of a centrifuge. The clear, yellow solution was transferred via syringe into a 25-ml flask attached to the high-vacuum distillation apparatus.[4] Distillation of the solvent afforded a yellow solid (m.p. ca. 30°C) which was sublimed at 30−40°C bath temp./10^{-5} Torr upon the cold finger (−40°C). The product may contain some **22** (IR) formed by decomposition of **13b**. − UV/Vis (tetrahydrofuran, Figure 2): λ_{max} [nm] (ε) = 359 (780), λ_{min} [nm] (ε) = 320 (500). − IR ([D_8]tetrahydrofuran): $\tilde{\nu}$ = 1717 cm^{-1} (C=C).

Solutions of Alkylidenedihydrotetrazoles. − a) *For NMR Spectroscopy:* The deuterated solvent (0.6 ml, Table 1), which had been degassed by several freeze-thaw cycles (−196°C/10^{-5} Torr), was condensed upon the yellow solid on the cold finger of the high-vacuum distillation apparatus[4] (see General Procedure). After warming, the yellow solution dropped into the NMR sample tube

Table 4. Chemical shifts (δ values) and coupling constants [Hz] (absolute values, *in italics*) in proton spectra of annulated iminoaziridines. The shift ranges include multiplets which stem from a single proton unless specified otherwise. The chemical shifts of the geminal methyl groups of **16** (printed *in italics*) may be exchanged

Cpd.[a]	MeN=C(N)—CH—$(CH_2)_n$–				
(*E*)-**14a**	3.07 (d, *0.3*)	2.70 (br. d, *6.0*)	1.38 – 1.45 1.58 – 1.61	1.13 – 1.21 (2 H)	2.66 – 2.71 3.21 – 3.27
(*Z*)-**14a**	3.16 (d, *0.7*)	2.81 (br. d, *5.9*)	1.38 – 1.45 1.73 – 1.76	1.07 – 1.11 1.13 – 1.21	2.59 – 2.64 3.03 – 3.08
(*E*)-**18**	3.14	2.81 (dd, *6.2, 2.0*)	1.25 – 1.31 1.38 – 1.45	0.89 – 0.94 (2 H) 1.01 – 1.06 1.07 – 1.10	3.07 – 3.11 (2 H)
(*Z*)-**18**	3.22	2.78 (dd, *6.8, 2.5*)		[b]	
	MeN=C(N)—CH—CMe_2—CH_2—CMe_2–				
(*E*)-**16**	3.18 (d, *0.3*)	2.61	*0.856* *1.031*	1.26, 1.32 (AB, *13.2*)	*1.295* *1.446*
	3.138 (d, *0.4*)	2.88	*1.125* *1.297*	1.46, 1.63 (AB, *13.1*)	*1.335* *1.344*
(*Z*)-**16**	3.28 (d, *0.7*)	2.62	*1.026* *1.071*	[b]	*1.143* *1.281*
	3.138 (d, *0.8*)	2.68	*1.124* *1.285*	1.44, 1.71 (AB, *13.2*)	*1.346* *1.365*
	MeN=C(N)—CMe—CH_2—CH_2—CH_2–				
(*E*)-**14b**	3.11	1.28	1.29 – 1.43 1.71 – 1.81	1.21 – 1.42 (2 H)	2.77 – 2.89 3.13 – 3.27
(*Z*)-**14b**	3.16	1.29	1.29 – 1.43 1.81 – 1.91	1.21 – 1.42 (2 H)	2.70 – 2.84 2.94 – 3.15
	–CH_2N=C(NMe)—CH—CH_2—CH_2—CH_2–				
19[c]	3.16 – 3.18 3.73 – 3.76	2.88 (dd, *8.3, 6.6*)	0.59 – 0.65 1.38 – 1.45	0.97 – 1.10 (2 H) 1.38 – 1.45	1.48 – 1.54

[a] **14a**, **16** (First lines), **18**, **19**: solvent [D_6]benzene; **14b**: solvent [D_8]toluene; **16** (second lines): solvent [D_8]tetrahydrofuran. – [b] The chemical shifts could not be determined because the signals were hidden under those of the major isomers. – [c] δ = 2.34 (NMe).

Table 5. Chemical shifts (δ values) in carbon-13 spectra of annulated iminoaziridines. The chemical shifts of the geminal methyl groups of **16** (printed *in italics*) may be exchanged

Cpd.[a]	MeN=C(N)—CH—$(CH_2)_n$–							n
(*E*)-**14a**	41.1	156.93	42.9	27.94	23.29	54.8		3
(*Z*)-**14a**	38.7	156.43	43.9	28.04	23.73	53.5		3
(*E*)-**18**	40.4	154.76	36.82	20.88	18.58	22.11	46.8	4
(*Z*)-**18**	38.0	154.16	36.53	20.77	18.47	22.53	44.9	4
	MeN=C(N)—CH—$C(Me_2)$—CH_2—$C(Me_2)$–							
(*E*)-**16**	42.0	156.2	53.84	44.43	*27.27* *28.64*	53.21	69.72	*29.06* *30.41*
	42.0	156.66	54.36	45.31	*27.31* *29.03*	53.80	70.14	*29.48* *30.60*
(*Z*)-**16**	40.7	155.8	53.46	43.46	*27.89* *29.23*	54.16	70.47	*29.87* *30.18*
	40.5	156.14	53.78	44.19	*28.09* *29.63*	54.77	71.13	*30.13* *30.38*
	MeN=C(N)—C(Me)—CH_2—CH_2—CH_2–							
(*E*)-**14b**	41.1	161.10	51.06	(18.93)	34.14	25.41	55.1	
(*Z*)-**14b**	38.4	160.37	51.52	(18.81)	34.14	25.99	53.8	
	–CH_2N=C(NMe)—CH—CH_2—CH_2—CH_2– NMe							
19	53.7	160.3	44.2	23.3	27.0	30.0	34.7	

[a] **14a**, **16** (First lines), **18**, **19**: solvent [D_6]benzene; **14b**: solvent [D_8]toluene; **16** (second lines): solvent [D_8]tetrahydrofuran.

which was finally sealed with a flame after cooling at −196°C and evacuating at 10^{-5} Torr.

b) *For EPR Spectroscopy:* A suspension of powdered tetrazolium salt, e.g. **4b**, **6b**, **8**, or **12** (0.2 mmol), and NaH (24 mg, 1 mmol) in 2-methyltetrahydrofuran, saturated with Ar, (1.5 ml) was magnetically stirred for 1 h or 5 min (**4b**) in a small tube (12 ml) closed with a rubber septum. The solid material was allowed to settle with the help of a centrifuge. The clear, yellow solution was transferred via syringe into a quartz EPR sample tube. − Likewise, a solution of **13b** in butyronitrile was obtained from **12b** (0.22 g, 0.6 mmol) and NaH (12 mg, 0.5 mmol) in butyronitrile (4 ml) saturated with Ar.

c) *For UV/Vis Spectroscopy:* A suspension of powdered **12b** (183 mg, 0.500 mmol) and NaH (60 mg, 2.5 mmol) in tetrahydrofuran (50 ml) was magnetically stirred for 1 h in a 50-ml volumetric flask. The solid material was allowed to settle during 30 min. The clear, yellow solution was transferred via syringe into a 1-mm quartz UV cell.

d) *For IR Spectroscopy:* A suspension of **12b** (73 mg, 0.2 mmol) and NaH (24 mg, 1 mmol) in [D_8]tetrahydrofuran (2.5 ml) was magnetically stirred for 5 min in a small tube (12 ml) closed with a rubber septum. The solid material was allowed to settle with the help of a centrifuge. The clear, yellow solution was transferred via syringe into a 0.5-mm NaCl IR cell.

Irradiation Experiments: a) Solutions of the alkylidenedihydrotetrazoles **5**, **7**, **9**, **11**, and **13** in sealed, degassed NMR sample tubes were placed in a 1-cm quartz UV cell filled with methanol. The UV cell was held in the middle of a copper block which was connected to a low-temperature thermostat. The copper block was placed in a quartz dewar equipped with suprasil quartz windows and flushed with dry N_2. A 500-W high-pressure mercury lamp (Osram HBO 500 W/2) was employed which was focussed by quartz optics. The light passed through a 10-cm water filter and a 5-mm cut-off filter (WG 305 or 320 from Schott, Mainz). The conversion was monitored with the help of proton spectra recorded at the temperature that was maintained during the irradiation (integration of singlets of starting material, products, and the internal standard, i.e. *tert*-butyl methyl ether). Results: Tables 1, 4, and 5.

b) Solutions of the alkylidenedihydrotetrazoles **2g**, **h**, **5b**, **7b**, **9**, **13**, and **26** in quartz EPR sample tubes were placed in a quartz dewar filled with liquid N_2. The solid glasses were irradiated for 2 min with the light of an argon ion laser (Coherent Innova 100, λ = 333, 351, 364 nm, 1.5−2.0 W output, quartz optics). The EPR sample tubes were placed into the precooled cavity (77 K) of the

Table 6. Chemical shifts (δ values) and coupling constants [Hz] (absolute values, *in italics*) in proton spectra of cyclic imines

Cpd.	– N = CH — $(CH_2)_n$ –				n	[a]
15a	7.27 (mc)	1.93 (tm, *8.1*)	1.29 (mc)	3.68 (mc)	3	B[b]
20	7.65 (mc)	1.62 (mc)	1.22–1.29 (4 H)	3.49 (mc)	4	B[b]
	– N = CH — CMe_2 — CH_2 — CMe_2 –					
17	6.77	0.88	1.06	1.25		T
	– N = CMe — CH_2 — CH_2 — CH_2 –					
15b	1.7 (tt[c])	1.98 (tm, *8.2*)	1.49 (mc)	3.69 (mc)		T

[a] Solvent B: [D_6]benzene, T: [D_8]toluene. – [b] Spectra recorded for [D]trichloromethane solutions: ref.[18] (80 MHz), ref.[19] (270 MHz). – [c] $^4J_{2\text{-Me}/3\text{-H}} = 0.7$ Hz, $^5J_{2\text{-Me}/5\text{-H}} = 1.8$ Hz.

Table 7. Chemical shifts (δ values) in carbon-13 spectra of cyclic imines

Cpd.	– N = CH — $(CH_2)_n$ –						n	[a]
15a	165.3	36.6	20.7	61.5			3	B
	167.4	36.7	20.3	60.7				C[b]
20	161.3	28.7	19.1	22.7	49.5		4	B
	163.6	28.5	18.5	22.0	48.1			C[b]
	– N = CH — $C(Me_2)$ — CH_2 — $C(Me_2)$ –							
17	169.4	50.70	(27.2)	50.58	72.3	(31.3)		T
	– N = C(Me) — CH_2 — CH_2 — CH_2 –							
15b	172.3	(19.3)	38.5	23.3	61.5			T

[a] Solvent B: [D_6]benzene, C: [D]trichloromethane, T: [D_8]toluene. – [b] 20-MHz spectrum: ref.[18].

EPR spectrometer and EPR spectra were taken immediately. Evolution of gas was observed on warming the EPR sample tubes to 20°C. Results with **13b**: Figure 3.

c) A $1.00 \cdot 10^{-2}$ M solution of **13b** in tetrahydrofuran contained in a 1-mm quartz UV cell was irradiated with a 100-W daylight lamp, placed at a distance of 5 cm. UV/Vis spectra were recorded after time intervals of 30, 60, and 90 min. Results: Figure 2.

2,2,7,7-Tetramethyl-1,2,3,5,6,7-hexahydro[1,8]naphthyridine (**22**): a) By irradiation of a solution of **13b** in [D_8]toluene at −60°C: Table 1.

b) **22** was obtained quantitatively, when a solution of **13b** in [D_8]toluene was heated for 3 h at 60°C and for 1 h at 90°C (^{1}H NMR).

c) Preparative experiment: A stirred, orange-coloured solution of **12b** (2 mmol) in *tert*-butyl methyl ether (7 ml) prepared as described above was heated under reflux for 3 d. The pale orange-coloured suspension was transferred via syringe into a 25-ml flask attached to the high-vacuum distillation apparatus.[4] Distillation of the solvent afforded a viscous oil which was distilled at 30–40°C bath temp./10^{-5} Torr upon the cold finger (−40°C) to yield a colourless oil. – ^{1}H NMR ([D_8]toluene): δ = 0.90 (br. s, 2-Me_2), 1.25 (br. s, 7-Me_2), 1.48 (dd, 6-H_2, $^3J_{6\text{-H}/5\text{-H}} = 6.2$, 7.2 Hz), 1.87 (dt, 3-$H_2$, $^3J_{3\text{-H}/4\text{-H}} = 4.3$, $^5J_{3\text{-H}/5\text{-H}} = 2.2$ Hz), 2.25 (ddtd, 5-H_2, $^4J_{5\text{-H}/4\text{-H}} = 2.0$ Hz), 3.89 (br. s, NH), 5.41 (tt, 4-H). – ^{13}C NMR ([D_8]toluene, −60°C): δ = 25.0 (CH_2-6), 26.8 (2-Me_2), 28.6 (7-Me_2), 35.3 (CH_2-5), 37.9 (CH_2-3), 49.1, 50.1 (C-2, C-7), 123.9 (C-4a), 127.1 (CH-4), 152.2 (C-8a). – UV/Vis (tetrahydrofuran, Figure 2): λ_{max} [nm] (ε) = 281 (2850), λ_{min} [nm] (ε) = 260 (2610). – IR (neat liquid): $\tilde{\nu}$ = 1605, 1666 (C=C, C=N), 3350 (NH) cm^{-1}.

Thermal Equilibration of Annulated Iminoaziridines. Colourless solutions of the annulated iminoaziridines, obtained by irradiation of **7a**, **b**, **9**, or **11**, were kept at 20°C in the dark for several days. The equilibration was monitored with the help of proton spectroscopy (integration of NMe singlets). Results: Table 1.

Thermolysis of Annulated Iminoaziridines. The NMR sample tubes containing solutions of **14a**, **14b**, **16**, **18**, and **19**, prepared in the preceding experiments were completely immersed in an oil bath and heated at constant temperatures [**14a**: 1 h at 60, 75, and 90, 6 h at 95°C, 95% conversion, yield of (**15a** + CN−Me) = 67%; **14b**: 1 h at 80, 6 h at 95°C, 96% conversion, yield of (**15b** + CN−Me) = 93%; **16**: 1 h at 80, 27 h at 95°C, 89% conversion, yield of (**17** + CN−Me) = 86%; mixture of **18** and **19** (44:56): 1 h at 55, 65, 75, and 85, 7 h at 95°C (Figure 1)]. The conversions were monitored with the help of proton spectra recorded at 20°C (integration of singlets and the 1:1:1 triplet of methyl isocyanide, internal standard *tert*-butyl methyl ether). The products were identified on the basis of their proton (Table 6) and carbon-13 spectra (Table 7).

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