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Iminodiaziridines by Regio- and Stereoselective Cyclization of Diastereomeric Singlet Triazatrimethylenemethane Diradicals Generated Through Photolysis of 5-Imino-4,5-dihydro-1*H*-tetrazoles†

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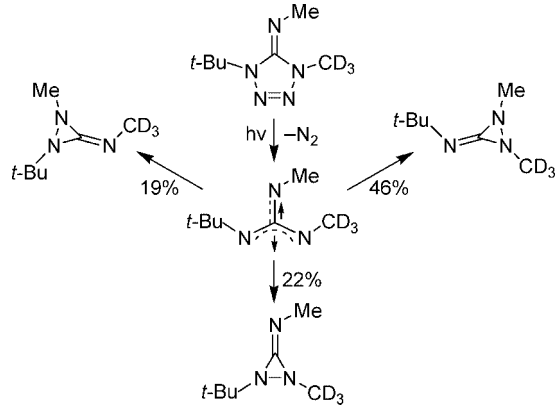
Received December 19, 2007



1,4-Dialkyl-5-(*N*-alkylimino)-4,5-dihydro-1*H*-tetrazoles were prepared in high yields by deprotonation with sodium hydride of 1,4-dialkyl-5-(*N*-alkylamino)tetrazolium salts that were adorned with two or three different alkyl groups, including methyl, trideuteriomethyl, and *tert*-butyl groups. Direct irradiation ($\lambda >$ 255 nm) at −60 °C yielded molecular nitrogen and mixtures of 1,2-dialkyl-3-(*N*-alkylimino)diaziridines (83–87%) along with carbodiimides (13–17%) arising by 1,3-dipolar cycloreversion. The missing 1,3-dipoles, alkyl azides, did not survive photolysis. Each member of a pair of isotopomers and of a pair of isomers, and an iminodihydrotetrazole, whose three nitrogens were tagged, yielded a characteristic mixture of three isomeric iminodiaziridines that allowed the mode of formation to be deduced. The results are interpreted in terms of photodenitrogenation of the iminodihydrotetrazoles to furnish diastereomeric singlet triazatrimethylenemethane diradicals that retain the inherited configurations before ring closure to iminodiaziridines, presumably in two steps via mono-orthogonal diradicals.

Introduction

Photoextrusion of molecular nitrogen from five-membered heterocyclic azo compounds with unconjugated exocyclic double bonds affords three-membered rings (Scheme 1, top).[1–10] In addition, certain dihydrotetrazole derivatives yield small amounts of alkyl azides and isocyanates[8b,9] or carbodiimides[9] by photochemical 1,3-dipolar cycloreversion.[11] Besides these photoproducts, triplet diradicals were detected by EPR spectroscopy in organic matrixes at low temperatures, viz., trimethylenemethanes (TMMs), including Dowd's famous parent system[12] and Berson's bridged TMMs,[13] a diazaTMM,[7e] and triazaTMMs.[14]

The results of direct irradiation of cyclic azo compounds of the general type in Scheme 1 may be interpreted in terms of spin-conservative cleavage into molecular nitrogen and singlet TMM-type diradicals. These undergo intersystem crossing to ground-state triplet diradicals or cyclize to three-membered rings,[13b] unless certain structural features provide alternative reaction channels.[15] In principle, this photocleavage may proceed in a concerted way or in steps.[16] The latter mechanism would lead to diazenyl allyl diradicals, which might lose molecular nitrogen to yield singlet TMM-type diradicals, cyclize again to

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† This paper is dedicated to Professor Dieter Seebach on the occasion of his 70th birthday.

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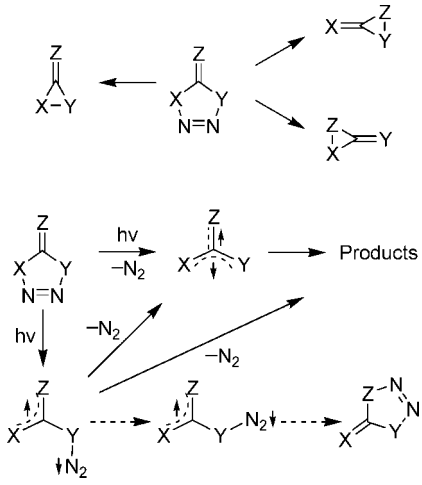
10.1021/jo702697f CCC: $40.75
Published on Web 04/17/2008

turn-around isomers, or close a three-membered ring by radical substitution of the diazenyl group (Scheme 1, bottom). However, convincing evidence for stepwise cleavage exists only for Berson's bicyclic TMM precursor, 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-3-ene, and only on thermal but not on photochemical excitation.[17,18]

SCHEME 1. Products (Top) and Possible Mechanisms (Bottom) of the Photolysis of Five-Membered Heterocyclic Azo Compounds with Unconjugated Exocyclic Double Bonds



Long-standing, continued interest in singlet diradicals[19] prompts us to report on the regio- and stereoselectivity of iminodiaziridine formation during irradiation of iminodihydrotetrazoles **1**. We irradiated a number of iminodihydrotetrazoles whose nitrogens were labeled by substituents, including methyl, trideuteriomethyl, and *tert*-butyl groups, and determined the structures of their products formed at low temperatures. The results are consistent with intermediate diastereomeric singlet triazaTMM diradicals whose geometries resemble those of the precursors **1** and are reluctant to undergo change of configuration.

Results

Deuterium labeling has been used to study the formation of methylenecyclopropanes by photolysis[1i,1k,1m,1n] and thermolysis[20] of 4-alkylidenedihydropyrazoles. We employed the same method to investigate the pathways of product formation on photolysis of 5-imino-4,5-dihydro-1*H*-tetrazoles **1**. These were prepared from 1,4-dialkyl-5-(*N*-alkylamino)tetrazolium salts which were synthesized on various, in principle known routes (Scheme 2). Because alkylation of 5-aminotetrazoles[21] affords mixtures of isomers,[22] the synthesis of each salt was optimized. Detailed experimental procedures are given in the Supporting Information.

Deprotonation of **1**·HX with sodium hydride in inert solvents gave **1** as low-melting, hygroscopic, colorless crystals in high yields. ^{1}H and ^{13}C NMR spectra of **1a** showed temperature-dependent ring methyl signals due to exchange by inversion of

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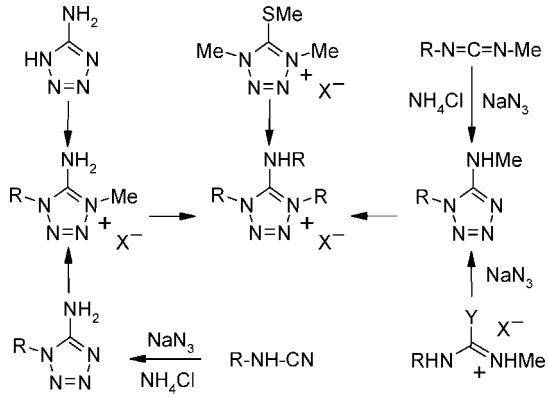
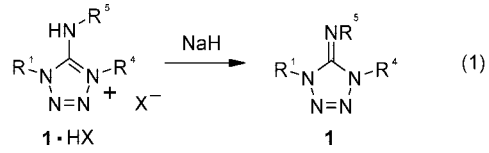
(21) For a summary of general routes to 5-aminotetrazoles, see: Katritzky, A. R.; Rogovoy, B. V.; Kovalenko, K. V. *J. Org. Chem.* **2003**, *68*, 4941.

SCHEME 2. Synthetic Routes to 1,4-Dialkyl-5-(*N*-alkylamino)tetrazolium Salts



the imino group (T_c = 28 °C at 60 MHz in [D_8]THF; $\Delta\nu$ = 34 Hz at −50 °C; $\Delta G^{\ddagger}_{28°C}$ = 62.6 kJ/mol). In contrast, **1d** did not show splitting of the *N*-methyl ^{1}H NMR singlet down to −70 °C. The asymmetrically ring-substituted imines **1e** and **1f** exist as single diastereomers to which we attribute the *E*-configuration.



(1)

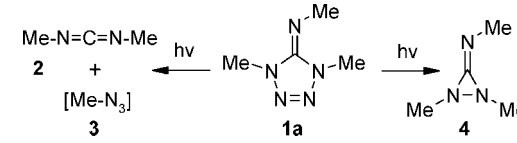
1·HX **1**

1a, **1a**•HBF_4, **1a**•$HClO_4$	$R^1 = R^4 = R^5$ = Me
1b, **1b**•HBF_4	$R^1 = R^4$ = Me; $R^5 = CD_3$
1c, **1c**•HBF_4	$R^1 = CD_3$; $R^4 = R^5$ = Me
1d, **1d**•$HClO_4$	$R^1 = R^4$ = Me; R^5 = *t*-Bu
(*E*)-**1e**, **1e**•HBF_4	R^1 = *t*-Bu; $R^4 = R^5$ = Me
(*E*)-**1f**, **1f**•HBF_4	R^1 = *t*-Bu; $R^4 = CD_3$; R^5 = Me

Photolysis experiments were performed by direct irradiation, using Corex-filtered (λ > 255 nm)[23] light of a medium-pressure mercury arc lamp. Without Corex filter, slow [2 + 1] cycloelimination of the iminodiaziridines afforded methyl or *tert*-butyl isocyanide as indicated by the characteristic 1:1:1 triplet ^{1}H NMR signals. Both *E*/*Z* diastereomerization and valence isomerization of iminodiaziridines appear to be catalyzed by acid. Hence it was essential for the observation of unaltered primary photoproducts to avoid any traces of acid at the walls of the NMR sample tubes. Otherwise, equilibrated mixtures were obtained. The irradiation experiments took a very clean course up to high conversion. Monitoring by ^{1}H NMR spectroscopy allowed complete conversion to be approached, which minimized signal overlap, and irradiation to be terminated, before isomerization of primary products became noticeable. The ^{1}H NMR spectra were integrated many times on an expanded scale by using both the high → low field and the low → high field sweep direction. The yields given in Schemes 4−6 represent average values from at least two independent experiments. The error was estimated at 1−2%, which is a size that compels neglect of remote deuterium isotope effects.

Irradiation of degassed solutions of **1a** in [D_8]tetrahydrofuran, enclosed in sealed NMR sample tubes, gave 83−87% **4** along with

SCHEME 3. Products Formed During Irradiation of 1a



13−17% dimethylcarbodiimide (**2**),[7a,9] which was identified by comparison of its IR and ^{1}H NMR spectra with those reported in the literature (Scheme 3). Methyl azide (**3**) is expected to arise by 1,3-dipolar cycloreversion of **1a** along with **2** but escaped detection, most probably, because it was photolyzed and the product formed a polymer $(CH_2NH)_n$.[24] No attempts were made to separate **4** from the solvent because of the high volatility of **4** and its propensity to undergo nucleophilic ring opening. The same properties frustrated attempts to isolate the other iminodiaziridines in pure form. However, NMR spectra and the very characteristic IR bands around 1800 cm^{-1} of iminodiaziridines[25] permitted unequivocal identification. In particular, observation of a long-range ^{1}H,^{1}H coupling of ^5J = 0.5 Hz between the protons of the ring methyl groups of **4** and **7** left no doubt about these structures.

The objective of the present study necessitated that several conditions were met. (i) Except for photochemical decomposition, the iminotetrazoles **1b**−(*E*)-**1f** remained unchanged on irradiation, i.e., they neither rearranged to turn-around isomers nor showed photochemical inversion of predominant configurations. (ii) Iminodiaziridines are known to undergo inversion of the imino group and valence isomerization, which interchanges one of the ring nitrogens and the exocyclic nitrogen.[25b,c] Consequently, irradiation was performed at −60 °C, at which temperature both isomerizations were slow so that the ratios of the iminodiaziridines remained unaltered for days. (iii) When irradiated samples were allowed to attain room temperature in the cavity of the NMR spectrometer, rapid *E*/*Z* equilibration permitted unequivocal assignment of NMR signals to a certain diastereomer. In contrast, thermal valence isomerization was slow at room temperature.[26] (iv) Persistence of the iminodiaziridines toward irradiation could not be anticipated since their photochemistry has not yet been investigated. However, irradiation of **1** at −60 °C showed that the compositions of the resulting mixtures remained essentially unaltered as long as significant amounts of **1** were still present. Thereafter, the iminodiaziridines underwent slow photochemical *E*/*Z* diastereomerization and valence isomerization.[27]

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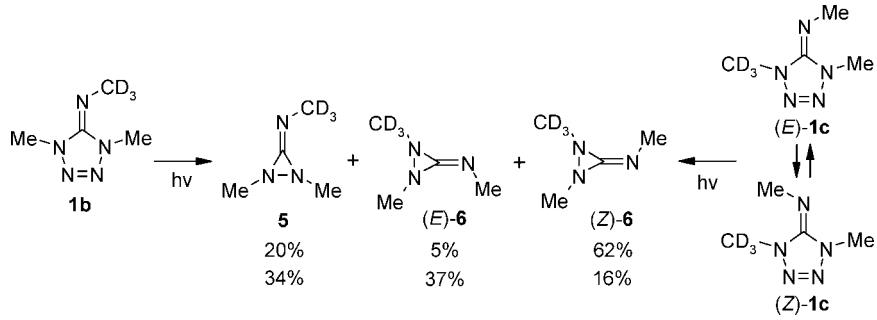
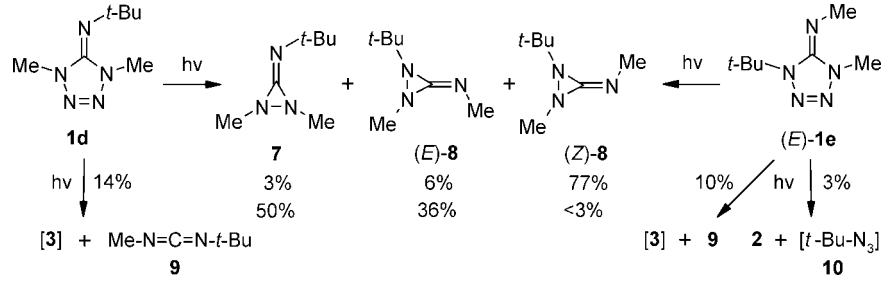
(26) Thermal equilibration of a mixture of (*E*)-, (*Z*)-**11**; (*E*)-, (*Z*)-**12**; and (*E*)-, (*Z*)-**13** required several days and gave a mixture in which (*E*)-, (*Z*)-**12** made up only 3−4%.

(27) For example, irradiation for 3 d at −60 °C converted about half of (*E*)-**8** into (*Z*)-**8**. Under these conditions, **13** [(*E*):(*Z*) ca. 1:1] underwent degenerate valence isomerization to **11** [(*E*):(*Z*) ca. 1:1]. Similar photochemical rearrangements of methylenecyclopropanes are known, see: Creary, X.; Losch, A; Sullivan, W. *J. Org. Chem.* **2007**, *72*, 7930. and references cited therein.

SCHEME 4. Iminodiaziridines Formed During Irradiation of 1b (First Row) and 1c (Second Row)



SCHEME 5. Iminodiaziridines and Carbodiimides Formed During Irradiation of 1d (First Row) and (*E*)-1e (Second Row)

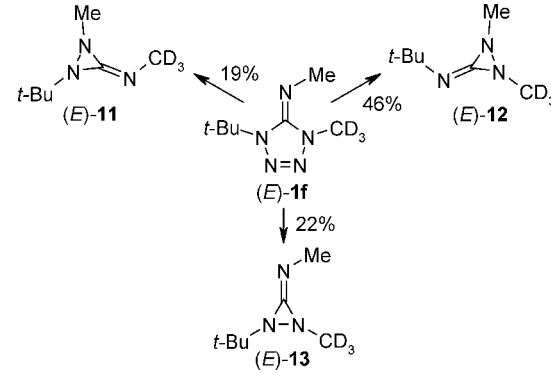


By contrast to the iminodiaziridines **4**, **5**, and **7**, whose structures can be immediately read from the ^{1}H NMR spectra, the iminodiaziridines **6**, **8**, and **11**−**13** exist as pairs of *E*/*Z* diastereomers. Provided that both diastereomers can be observed, a most convenient and reliable criterium for the configuration of *N*-alkylimines is the relative asymmetric solvent-induced shift (ASIS).[28] Asymmetric solvation by aromatic solvents shifts resonances of protons at the side of the imino alkyl group stronger to high field than those of protons at the side of the lone pair.[29] Therefore, we irradiated **1** not only in [D_8]THF but also in [D_8]toluene as solvent. The nature of the solvent hardly influenced the differential chemical shifts of the imino methyl signals of the *E*- and *Z*-diastereomers but strongly influenced those of their ring methyl signals (Table 1). Thus each diastereomer could be assigned the *E*- or *Z*-configuration.[30] Very similar ratios of photoproducts were observed in both solvents, except that the ratios in [D_8]toluene were somewhat shifted toward those of the room temperature equilibria (hence they are only reported in the Supporting Information).

Irradiation of the isotopomers **1b** and **1c** gave the iminodiaziridines **5**, (*E*)-**6**, and (*Z*)-**6** in total yields of 87% (Scheme 4) along with 13% dimethylcarbodimides [D_3]**2** and (**2** + [D_3]**2**), respectively. When the main photoproduct arises from **1b**, the Me−N−C−N−Me moiety, fixed in the tetrazole ring of **1b**, mutates into the Me−N−C═N−Me partial structure of (*Z*)-**6**, i.e., *without change of the original geometry*. In the minor product (*E*)-**6**, this geometry has been inverted. We are reluctant, however, to attribute this *N*-inversion to an intermediate, because we cannot exclude that a small fraction of (*Z*)-**6** underwent light-induced *N*-inversion.

Irradiation of the 1:1 mixture of (*E*)-**1c** and (*Z*)-**1c** furnished yields of **5**, (*E*)-**6**, and (*Z*)-**6** that strongly differed from those obtained from **1b**. Iminodiaziridine **5** arises from both diastereomers by bond formation between the nonlabeled nitrogens. Provided that light-induced *N*-inversion is unimportant, (*E*)-**1c** affords exclusively (*E*)-**6**, while (*Z*)-**1c** may yield (*E*)-**6** as well as (*Z*)-**6**. This explains why (*E*)-**6** predominates.

SCHEME 6. Iminodiaziridines Formed During Irradiation of (*E*)-1f



Formal exchange of the [D_3]methyl groups of **1b** and **1c** for *tert*-butyl groups leads to **1d** and **1e**, respectively, and strongly altered the results. The *tert*-butyl group of **1e** coerces the molecule into adopting exclusively the *E*-configuration. Irradiation of **1d** and (*E*)-**1e** afforded the expected iminodiaziridines **7** and **8** along with small amounts of carbodiimides **2** and **9** (Scheme 5). Most probably, the missing 1,3-dipoles methyl azide (**3**)[24] and *tert*-butyl azide (**10**)[31,32] were photolyzed and hence could not be detected.

Small amounts of photoproducts, viz., (*E*)-**8** from **1d** and (*Z*)-**8** from (*E*)-**1e**, had inverted imino groups. As before, this can be rationalized in terms of light-induced *E*/*Z* isomerization of the

(28) Quast, H.; Aldenkortt, S.; Freudenreich, B.; Schäfer, P.; Hagedorn, M.; Lehmann, J.; Banert, K. *J. Org. Chem.* **2007**, *72*, 1659.

(29) (a) Karabatsos, G. J.; Lande, S. S. *Tetrahedron* **1968**, *24*, 3907. (b) Karabatsos, G. J.; Taller, R. A. *Tetrahedron* **1968**, *24*, 3923. (c) Rummens, F. H. A.; Krystynak, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 6914.

(30) Surprisingly, (*E*)-**8** is slightly *less* stable than (*Z*)-**8** [(*E*):(*Z*) = (47.5 ± 0.5):(52.5 ± 0.5)]. Each diastereomer is more stable than **7** [**7**:**8** = (3.5 ± 0.5):(96.5 ± 0.5) at 25 °C].

(31) Photolysis of **10** yields *N*-isopropylidene-*N*-methylamine,[32] which shows three multiplets in the ^{1}H NMR spectrum.[33] In view of the low yield of the 1,3-dipolar cycloreversion, these could not be expected to emerge from the noise.

(32) (a) Solar, S.; Koch, E.; Lietich, J.; Margaretha, P.; Polansky, O. E. *Monatsh. Chem.* **1973**, *104*, 220. (b) Dunkin, I. R.; Thomson, P. C. P. *Tetrahedron Lett.* **1980**, *21*, 3813.

TABLE 1. Chemical Shifts [ppm] (Relative to TMS) and ^{1}H,^{1}H Coupling Constants ^5J [Hz] in 60 or 90 MHz ^{1}H NMR Spectra

compd	=N−R	δ_H	>N−R$_{syn}$	δ_H	>N−R$_{anti}$	δ_H	*a*
4	Me	3.04	Me	2.79[b]	Me	2.68[b]	A
		3.03		2.58[c]		2.55[c]	B
7	*t*-Bu	1.18	Me	2.80[b]	Me	2.64[b]	A
(*E*)-**8**	Me	3.05	Me	2.79	*t*-Bu	1.08	A
		3.02		2.58[c]		1.10	C
(*Z*)-**8**	Me	3.05	*t*-Bu	1.13	Me	2.69	A
		3.03		1.04		2.56[c]	C

[a] Solvent: A = [D$_8$]THF, B = [D$_6$]benzene, C = [D$_8$]toluene. [b] Quartet, ^5J = 0.5 Hz. [c] The chemical shifts may be exchanged.

prevailing diastereomers. The origin of **7** by bond formation between the two methyl-substituted nitrogens of **1d** and (*E*)-**1e** is obvious. Likewise, the two possible routes to the major product of **1d**, (*Z*)-**8**, are straightforward. However, the second product of (*E*)-**1e**, (*E*)-**8**, may arise on two different routes, viz., by bond formation between the two ring nitrogens and between the *tert*-butyl-substituted and the exocyclic nitrogen. To distinguish these paths, we labeled the ring methyl group of (*E*)-**1e** and obtained (*E*)-**1f**. As expected, the product distribution for (*E*)-**1f** in Scheme 6 closely resembles that for (*E*)-**1e** in Scheme 5, except that all iminodiaziridines **11**−**13** revealed their mode of formation and adopted the *E*-configuration, which portrays the geometry of the precursor (*E*)-**1f**. Only tiny amounts, if any, of **11** and **13** possessed the *Z*-configuration. Besides the iminodiaziridines, [D$_3$]dimethylcarbodiimide ([D$_3$]**2**, 4%) and **9** (8%) made their appearance in the ^{1}H NMR spectra.

Discussion

In the absence of photophysical and computational evidence, an interpretation of the photolysis of iminodihydrotetrazole **1** must remain tentative, in particular, since even the type of excitation, n,π^* and/or π,π^*, is unknown. Triplet species do not appear to be involved in the formation of iminodiaziridines, because these arise at a temperature as low as 12 K,[9a] while triplet triazaTMMs are persistent at 77 K.[14]

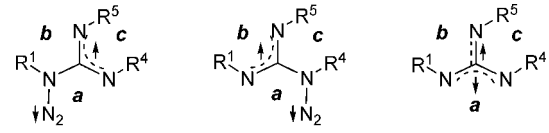
The observed bifurcation in photodenitrogenation and light-induced 1,3-dipolar cycloreversion of **1** is found in organic solvents at room temperature as well as in nitrogen matrix at 12 K.[9] The share of the latter reaction remained unchanged in the presence of *tert*-butyl substituents. In the 1,3-dipolar cycloreversions, the NN bonds by the side of the *tert*-butyl groups of (*E*)-**1e** and (*E*)-**1f** were broken more readily (→**9**) than the NN bonds alongside of the ring methyl groups (→**2**). This could be explained if strongly asynchronous or even stepwise mechanisms via diazenyl 1,3-diazaallyl diradicals **14** and **15** would be postulated. Following each of the two mechanistic alternatives, formation of **9** would be more favorable compared to **2** because the onset of NN bond breaking that affords **9** develops less allylic strain.

The regio- and stereoselectivity of the photochemical formation of iminodiaziridines indicate that any conceivable intermediates do not exist long enough to attain equilibrium structures. Instead short-lived intermediates retain geometries that closely resemble those of the iminodihydrotetrazoles **1**.[34] This is particularly obvious from Scheme 4 where neglect of remote deuterium isotope effects allows the different diradicals that may originate from **1b**, (*E*)-**1c**, and (*Z*)-**1c** to be considered degenerate with respect to their energy.

TABLE 2. Ratios of Yields y_i of Iminodiaziridines That Were Obtained From Iminodihydrotetrazoles 1 by Cyclizations of Intermediate Diradicals at Their Sites *a*, *b*, and *c*

compd	ratios of Yields	
1b	y_a: (y_b + y_c) = 23:77	Scheme *4*
1d	y_a: (y_b + y_c) = 4:96	Scheme *5*
(*E*)-**1e**	(y_a + y_b): y_c = 42:58	Scheme *5*
(*E*)-**1f**	y_a:y_b:y_c = 26:21:53	Scheme *6*

Singlet triazaTMMs **16** may be invoked as intermediates. In principle, they may arise by concerted or stepwise photodenitrogenation. The latter mechanism would involve diazenyl 1,3-diazaallyl diradicals **14** and **15**. These could not only form triazaTMMs **16** but also cyclize directly to iminodiaziridines by radical substitution of the diazenyl group, or close again the tetrazole ring affording turn-around isomers, which were not observed, however. We note that both types of hypothetical intermediates, **14/15** and **16** (see below; for the substituent key, see **1**), differ by their propensities to undergo changes of



14 **15** **16**

geometry. The former possess a CN single bond with a probably low rotational barrier while **16** resembles the guanidinium ion. A priori, the diradicals may close the diaziridine ring at each of their three sites, referred to as *a*, *b*, and *c*. These differ by the degree of repulsion between the substituents and, in case of **14** and **15**, by the mechanisms of cyclization. To support a choice between **14/15** and **16**, we assigned the yields given in Schemes 4−6 to the corresponding sites and compiled the ratios of these yields in Table 2.

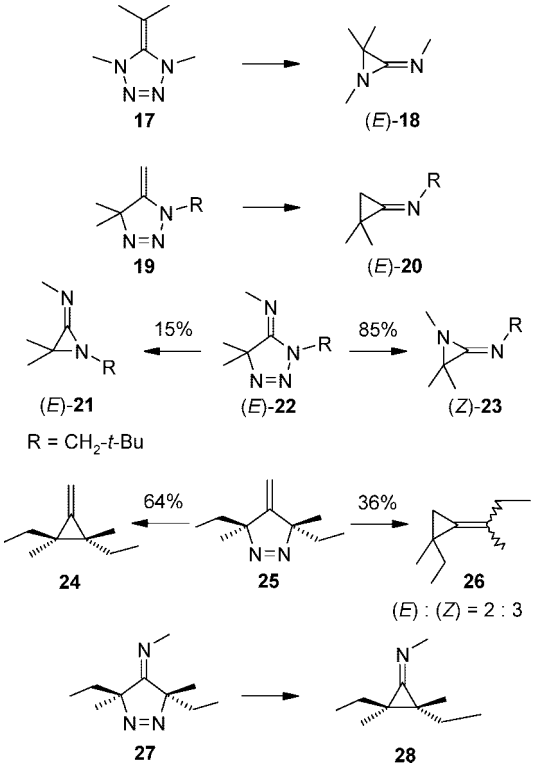
Inspection of the results listed in Table 2 shows that they are consistent with intermediate diazenyl 1,3-diazaallyl diradicals **14** and **15** only on the basis of a number of questionable assumptions. Therefore, we propose singlet triazaTMM diradicals **16** as crucial intermediates en route from iminodihydrotetrazoles **1** to iminodiaziridines.

Ring-closure of **16b** at site *a* is less favorable than cyclizations at sites *b* and *c* (1st entry). The ratio of yields of the *tert*-butyl-substituted iminodiaziridines **7** and **8**, formed from iminodihydrotetrazole **1d**, reflects the relative stabilities of **7** and **8** (2nd entry),[30] while this ratio, observed for the isomeric precursor (*E*)-**1e**, does not (3rd entry). Cyclization of **16d** at site *a* (→**7**) is strongly disfavored compared to that at sites *b* and *c* [→(*Z*)-**8**]. Presumably, cyclizations at the latter two sites are more rapid, because the *tert*-butyl-substituted nitrogen of **16d** is predisposed to ring closure owing to twisting of the *tert*-butyl group from the molecular plane. Ring closure of **16e** at site *c* predominates but yields the less stable isomer **7**; cyclizations at both sites *a* and *b* afford the minor but more stable product (*E*)-**8** (3rd entry). However, all three sites become distinguishable when the labeled diastereomer (*E*)-**1f** is irradiated. Diradical **16f** cyclizes at cites *a*, *b*, and *c* in the approximate ratios 1:1:2 (4th entry). The preference for cyclization at site *c* of all diradicals **16** indicates that relief of allylic strain is an important factor.

(33) Colebourne, N.; Foster, R. G.; Robson, E. *J. Chem. Soc. (C)* **1967**, 685.

(34) It goes without saying that the stereochemical information of the two nitrogens is lost when they close the diaziridine ring, and only the *E*/*Z* ratios of the iminodiaziridines **6**, **8**, and **11**−**13** reveal the reluctance of the intermediates to undergo change of configuration.

SCHEME 7. Three-Membered Rings Formed During Irradiation of Some Heterocyclic Azo Compounds with Unconjugated Exocyclic Double Bonds



We restrain ourselves from detailing speculations about the timing of the two rotations around CN bonds involved in the ring closure of **16** assumed to be planar. However, a *stepwise* process via mono-orthogonal triazaTMMs that arise by 90° rotation of one of the two sterically interacting imino groups at site *c* seems reasonable. It explains, for example, the nearly statistical ratio 1:1:2 of the ring closure at sites *a*, *b*, and *c* of **16f**. In contrast to a stepwise process, two *concerted* rotations in **16f** should occur only at site *c*, but would be unlikely at site *a*.

It is interesting to compare the present results with those from photodenitrogenations of related heterocyclic azo compounds (Scheme 7). The two alkylidene heterocycles **17** and **19** afford exclusively the three-membered ring imines (*E*)-**18**[7b] and (*E*)-**20**,[2b] respectively, certainly because the alternative paths of cyclization would lead to much less stable three-membered rings. The same is true for the photolysis of iminodihydrotriazole (*E*)-**22**. However, (*E*)-**22** yields isomeric iminoaziridines (*E*)-**21** and (*Z*)-**23**, which immediately reveal the site of ring-closure.[7c] All photoproducts of **17**, **19**, and (*E*)-**22** portray the geometries of their precursors. This indicates that hypothetical intermediate azaTMM and diazaTMM diradicals retain the inherited configurations, just like the triazaTMM intermediates **16** of the present study. Likewise, bisorthogonal TMMs, which have been advocated by Andrews and Day[1d,e] and Bushby et al.,[1n,p,20d] and monoazaTMM diradicals with persistent configurations are to be invoked as intermediates to explain stereoretention on product formation from the dihydropyrazoles **25**[1w] and **27**.[2c]

Conclusion

The present study describes the photolysis of the last type of heterocyclic azo compounds that is represented by the general structure in Scheme 1 where each letter X, Y, and Z stands for carbon or nitrogen. The results depicted in Scheme 7 and those of this investigation indicate that both photochemical generation and cyclization of intermediates are stereochemically well-defined. As inferred from the structures of the photolysis products, configuration and geometric features inherent in the heterocyclic azo precursors translate to intermediates that maintain the configuration during their lifetime and cyclize regio- and stereoselectively to three-membered rings with exocyclic double bonds. Details of photochemical generation, structures, and cyclization of these intermediates, which most probably are singlet TMM-type diradicals, may be challenges for photophysical and computational research. Finally, we note that the photolyses described here offer a convenient access to sensitive iminodiaziridines.

Experimental Section

Equivalent masses were determined by titration with 0.1 M perchloric acid in acetic acid.[35]

Irradiation experiments were performed by using NMR sample tubes whose walls had been carefully freed from traces of acids followed by drying under vacuum at 150 °C. The sample tubes were attached to a vacuum line (10^{-5} Torr) and the iminodihydrotetrazoles (kept under Ar) allowed to sublime into the tubes. This took 1−4 h at 10^{-5} Torr for a 20−50 mg sample. Deuterated solvents were kept over $LiAlH_4$, degassed by several pump−freeze–thaw cycles, and condensed into the sample tubes, which were cooled with liquid N_2 and sealed under high vacuum. A 150 W medium-pressure mercury arc lamp (TQ 150 by Heraeus, Hanau, Germany) was placed into a vacuum-insulated water-cooled quartz immersion well, which was fixed in a large Dewar vessel filled with methanol whose temperature was kept at −60 °C with the help of a stainless steel coil connected to a low-temperature thermostat. The NMR sample tube was kept in a Corex filter glass tube,[23] which was directly attached to the immersion well and suffused by a stream of cold methanol.

1,4-Dialkyl-5-(*N*-alkylimino)-4,5-dihydro-1*H*-tetrazoles (1), General Procedure. 1,4-Dimethyl-5-(*N*-methylimino)-4,5-dihydro-1*H*-tetrazole (1a). Under Ar, **1a**·HBF_4 (2.15 g, 10 mmol) or **1a**·$HClO_4$ (2.28 g, 10 mmol) was slowly added to a stirred suspension of NaH (1.2 g, 50 mmol) in dry THF (20 mL), contained in an 80 mL centrifuge tube, which was equipped with a septum and connected via syringe to an Ar supply and a vacuum line. The suspension was stirred overnight. The solid was removed with the help of a centrifuge and washed with pentane. Distillation of the solvent from the clear solution under vacuum with strict exclusion of air and moisture yielded a colorless residue. Sublimation at 30–40 °C/10^{-3} Torr into a directly attached flask, cooled to −78 °C, furnished hygroscopic colorless crystals (1.15 g, 91%), mp 52−53 °C (sealed tube) (ref 22c mp <100 °C). MS (EI 70 eV): *m*/*z* (rel intensity) 127 (32) [M^+], 126 (17), 71 (10), 70 (51) [$M^+ - CH_3N_3$], 69 (100), 44 (8), 43 (18), 42 (59). UV (hexane) λ_{max} [nm] (log ϵ) 216 (3.878), 279 (3.286) [UV (DMSO and 0.01 M aq NaOH): ref 36]. IR (Nujol) 1682 cm^{-1} (C═N). ^1H NMR ([D_8]THF, 60 MHz) δ 3.13 (s, 3 H, CH_3), 3.55 [br s, 6 H, 2 CH_3; splits into 2 signals at T_c = 28 °C, $\Delta\nu$ = 34 Hz (−50 °C), $\Delta G_c^{\ddagger}$ = 62.6 $kJmol^{-1}$]; ^1H NMR (C_6D_6, 250 MHz) δ 3.037 (s, 3 H, CH_3), 3.064 (s, 6 H, 2 CH_3). ^{13}C NMR (C_6D_6, 63 MHz) δ 31.4 (broadened by exchange, CH_3), 33.1 (CH_3), 34.7 (broadened by exchange, CH_3), 142.8 (quat C, C-5). Anal. Calcd for $C_4H_9N_5$: equivalent mass, 127.1. Found: equivalent mass, 127.9.

(35) Huber, W. *Titrations in Nonaqueous Solvents*; Academic Press: New York, 1967.

(36) Bianchi, G.; Boulton, A. J.; Fletcher, I. J.; Katritzky, A. R. *J. Chem. Soc. (B)* **1971**, 2355.

1,4-Dimethyl-5-(*N*-[D_3]methylimino)-4,5-dihydro-1*H*-tetrazole (1b). (a) **1b** was prepared from **1b**·HBF_4 (2.18 g, 10 mmol) and NaH; colorless crystals (1.16 g, 89%), mp 52–53 °C (sealed tube).

(b) A mixture of 5-(*N*-benzoyl-*N*-[D_3]methylamino)-1,4-dimethyltetrazolium tosylate (16.3 g, 40 mmol) and conc aq HCl (30 mL) was heated under reflux for 0.5 h. The solvent was distilled under vacuum. Aq NaOH (4 M, 30 mL) was added to the residue and the resulting mixture was extracted with CH_2Cl_2 (5 × 100 mL). The organic layers were filtered under Ar through a pad of Na_2SO_4 (4 × 10 cm) into a flask containing NaH (2–3 g). After the suspension was stirred for 1 h and the solid material filtered under Ar, the solvent was distilled under vacuum with strict exclusion of air and moisture. Sublimation as described for **1a** afforded hygroscopic colorless crystals (4.51 g, 87%), mp 52.5–54 °C (sealed tube).

1-[D_3]Methyl-4-methyl-5-(N-methylimino)tetrazole (**1c**) was obtained from **1c**·HBF_4 (2.18 g, 10 mmol) and NaH as hygroscopic colorless crystals (1.18 g, 91%), mp 52–53 °C (sealed tube).

5-(*N*-*tert*-Butylimino)-1,4-dimethyl-4,5-dihydro-1*H*-tetrazole (**1d**) was obtained from **1d**·$HClO_4$ (2.70 g, 10 mmol) and NaH as colorless crystals (1.63 g, 96%), mp 24–25 °C (sealed tube). MS (EI 70 eV) *m*/*z* (rel intensity) 169 (13) [M^+], 154 (67), 112 (1) [$M^+ - CH_3N_3$], 98 (6), 97 (100), 69 (6), 57 (13), 56 (12). UV (hexane) λ_{max} [nm] (log ϵ) 208 (3.989), 278 (3.258). IR (Nujol) 1668 cm^{-1} (C═N). ^1H NMR ([D_8]THF, 60 MHz) δ 1.28 (s, 9 H, *t*-Bu), 3.53 (s, 6 H, 2 CH_3; shows no splitting into 2 signals down to −70 °C); ^1H NMR (C_6D_6, 250 MHz) δ 1.28 (s, 9 H, *t*-Bu), 3.15 (s, 6 H, 2 CH_3). ^{13}C NMR (C_6D_6, 63 MHz) δ 33.8 (3 CH_3), 34.2 (2 CH_3), 50.2 (quat. C), 138.5 (quat. C, C-5). Anal. Calcd for $C_7H_{15}N_5$: N, 41.43; equivalent mass, 169.2. Found: N, 41.82; equivalent mass, 170.3.

1-*tert*-Butyl-4-methyl-5-(*N*-methylimino)-4,5-dihydro-1*H*-tetrazole (**1e**) was obtained from **1e**·HBF_4 (2.57 g, 10 mmol) and NaH as colorless crystals (1.45 g, 86%), mp 61–62 °C (sealed tube). MS (EI 70 eV) *m*/*z* (rel intensity) 169 (20) [M^+], 114 (100), 113 (87), 112 (46), 71 (53), 70 (51), 69 (36), 57 (100), 56 (35). UV (hexane) λ_{max} [nm] (log ϵ) 219 (3.692), 27 (3.234). IR (Nujol) 1675 cm^{-1} (C═N). ^1H NMR ([D_8]THF, 60 MHz) δ 1.53 (s, 9 H, *t*-Bu), 3.14 (s, 3 H, CH_3), 3.79 (s, 3 H, CH_3). Anal. Calcd for $C_7H_{15}N_5$: N, 41.43. Found: N, 41.78.

1-*tert*-Butyl-4-[D_3]methyl-5-(*N*-methylimino)-4,5-dihydro-1*H*-tetrazole (**1f**) was obtained from **1f**·HBF_4 (2.60 g, 10 mmol) and NaH as colorless crystals (1.48 g, 86%), mp 61–62 °C (sealed tube).

Acknowledgment. We thank Dres. Markus Heubes and Wolfgang Nüdling for recording the high-field NMR spectra and Dr. Gerda Lange for taking the mass spectra. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, Frankfurt an Main, is gratefully acknowledged.

Supporting Information Available: General experimental details; synthetic procedures, elemental analyses, and NMR spectra for 5-aminotetrazolium salts; UV and NMR spectra of iminodihydrotetrazoles; detailed results of all irradiation experiments; and IR and ^1H NMR spectra of photolysis products. This material is available free of charge via the Internet at http://pubs.acs.org.

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