Photochemical Transformations, 75[1a]

The Azo/Nitrene Route to *cis,cis*-Trialkyltriaziridines, 2[1b]

Photolysis of *syn*-Azo Azides of Defined Proximity – Attempts for $N_3 \rightarrow N_3X$ Ring Enlargement

Wolfgang Marterer, Otmar Klingler, Regina Thiergardt, Eberhard Beckmann, Hans Fritz, and Horst Prinzbach*

Chemisches Laboratorium der Universität Freiburg i. Br., Institut für Organische Chemie und Biochemie, Albertstraße 21, D-7800 Freiburg i. Br., F.R.G.

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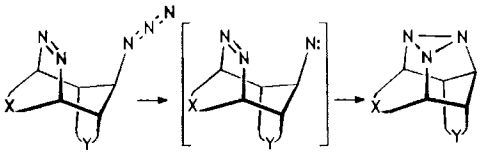
The as yet unknown route to triaziridines by the addition of nitrenes to the π side of the N=N bond is achieved intramolecularly by the photolysis (thermolysis) of *syn*-azo azide substrates with high proximity; the yields reflect the sterical (and possibly inductive) influences of the skeleton. The product composition is rather independent of the exciting light; intramolecular azo → azide energy transfer is assumed. The kinetic skeleton stabilization of the triaziridines permits the synthesis of **17** (**18**) by the thermolysis of **7** (**8**) at 200°C with the product composition deviating only marginally from that of the photolysis. Attempts towards enlargement of the triaziridines to N_3X rings (X = CHR, O, NR) lead exclusively to products of intramolecular fragmentation.

The route to *cis,cis*-trialkyltriaziridines **C** as delineated in the preceding paper[1b] encompasses the intramolecular cycloaddition of photochemically or thermally generated, unstabilized "discrete" secondary alkyl nitrenes **B** to unstabilized (dialkyl) azo units **A**. Yet, this route – with its obvious



A **B** **C**

analogy to the intramolecular three-membered ring construction by carbene[2] and nitrene[3] addition to C=C bonds[4] – has its intrinsic drawbacks: (i) Upon photoexcitation of secondary alkyl azides imine formation is generally very fast and may take place via discrete nitrenes or electronically excited azides[2,5]; (ii) N=N bonds are recognized as poor π_2 components in cycloaddition reactions[6] with the consequence of even more severe stereoelectronic requirements for nitrene/N=N than e. g. for nitrene (carbene)/C=C additions; (iii) there is an omnipresent competitive process due to N_2 elimination upon photoexcitation of azo systems, even though bi- and polycyclic azo compounds with skeletons similar to that of the azo azides considered for this study (Table 1) are found to be rather "reluctant" [7], the elimination of N_2 being not generally a (very) fast process. Consequently, irrespective of the actual course of the nitrene generation, proper and as proximate and rigid as possible placement of the potential nitrene nitrogen atom with respect to the π plane of the azo unit is mandatory for triaziridine formation. Thus, conformational and strain implications which often hamper intramolecular nitrene (carbene) additions to C=C bonds should be minimized[8]; (iv) intramolecular cycloaddition reactions between azide and N=N units yielding pentazolines should cause no complications, since the steric prerequisites for this ring formation are only met in severely distored excited states. In fact, such N_5 rings have only been postulated as rate-determining transients in the unusually rapid thermolysis of *o*-azidoazobenzenes[9].

In this paper we present (i) the MMX-derived structural and energetic details of representative *syn*-azo azide substrates **1**–**7** and of the respective triaziridines **11**–**17**; (ii) the results of the photolysis study on eight such *syn*-azo azide substrates (**1**, **2**, **5**, **6**–**10**; **3** and **4** are not yet available); (iii) some properties of the derived *cis,cis*-trialkyltriaziridines **12**, **15**–**20**; and (iv) the outcome of first attempts towards enlargement of the N_3 rings.

Calculated (MMX) Structures and Energies

To allow for a realistic judgement of the structural and energetic changes involved in the conversion of the *syn*-azo azides (as models for the respective nitrenes) into the corresponding triaziridines, force-field calculations have been performed[10] by making use of an MMX force-field program which has recently been reparametrized for such azo systems[11] and which has now been adapted to the given azide and amine functions (Table 1). A comparison with experimental structural data ensures a degree of reliability which is regarded sufficient for semiquantitative purposes. According to our experiences with N=N/N=N(O) photocycloadditions[6], the calculated *d* (ω) values of 2.7–3.0 Å (150–162°) are insofar promising for the aspired transan-

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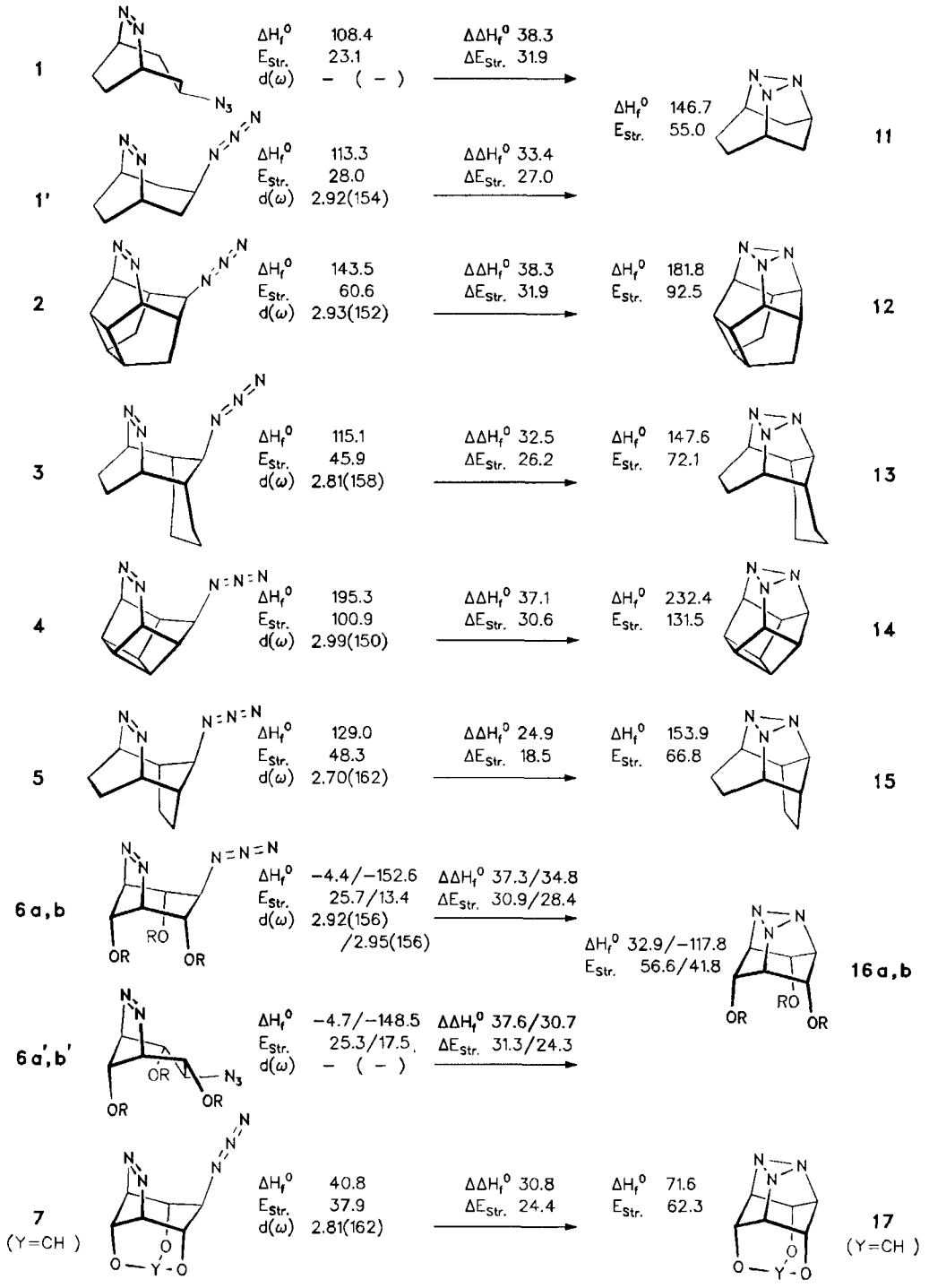
Table 1. Selected structural/energetic data (MMX) for *syn*-azo azides and triaziridines (*d*, ω as defined in the formula of Table 2); the N–N–C angles at the azido group are generally between 117 and 119°

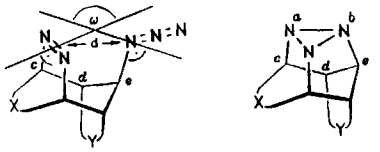


	8(18)	9(19)	10(20)
Y	CCH_3	PO	P

ular additions, as for intramolecular nitrene (carbene)/olefine additions a δ,ε orientation of the double bond relative to the nitrene and comparable transanular distances have been found to be favorable[9]. Clearly, both the degree of endothermicity and the increase in skeletal strain on the way to the triaziridines generally appear as not prohibitively high[12]. With $\Delta E_{str} < 25$ kcal/mol specifically the transformations **5** → **15** and **7** → **17** seem to profit from the release

of steric compression and/or antibonding π/n-electron interaction in the starting compounds. As a qualitative measure of the (relatively small) geometrical changes produced in these cycloadditions, the interplanary H/H angles (MMX) around the basic cyclohexane/cycloheptane rings, referred to in the NMR analyses, are given in Table 2.

Table 2. Selected H/H interplanary angles [°] (MMX) for representative *syn*-azo azides and triaziridines (as defined in the formula)



	c,d	*d,e*	*c,x*		*c,d*	*d,e*	*c,x*
1	75(40)	166(51)	45(73)				
2	33	68	31	**12**	36	39	30
5	17	57	48(67)	**15**	24	38	49(65)
6a	51	79	46	**16a**	49	50	49
6b	53	79	45	**16b**	49	47	49
7	44	67	47	**17**	45	45	45

Photolysis of the *syn*-Azo Azides 1, 2, 5–10

The *syn*-azo azide substrates are bichromophoric[13]: the $n \rightarrow \pi^*$ absorption of N=N bonds in (strained) five-(six-)membered rings is found around λ = 350 (390) nm with ε values of ca. 100; alkyl azides generally cause a weak absorption band around λ = 280 nm ($\varepsilon \approx 30$)[14] with tailing to $\lambda \approx 320$ nm. In connection with the question of selective excitation of one of these two chromophores, the UV spectra (Table 3) have been inspected for signs of transanular interactions between the azo/azide subunits. There is a close correspondence between the flexible bicycle **1** and the rigid tricycle **5** with respect to wavelength and intensity of the N=N $n \rightarrow \pi^*$ as well as N_3 absorption, leaving not much room for proximity effects. It has been speculated, however, whether the redshift of the $n \rightarrow \pi^*$ maximum by 10–15 nm and especially the significant increase in extinction on going from **6a, b** to **7–10** reflects intramolecular azo/azide interaction in the trioxaadamantanoid skeletons[1]. Generally, the form

Table 3. UV data of *syn*-azo azides in CH_3CN; λ[nm] (ε)

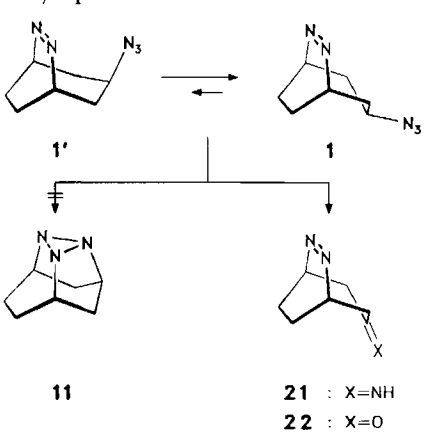
1	**2**	**5**	**6a**	**6b**
393 sh (77)	397 sh (168)	395 (89)	349 (129)	346 (152)
388 (79)	391 (175)	388 sh (78)		
288 (31)		285 sh (42)	296 (50)	290 sh (50)
ε_{254} = 22	ε_{254} = 740	ε_{254} = 125		ε_{254} = 25
7	**8**	**9**		**10**
361 (530)	360 (580)	358 (590)		360 (570)
352 sh (380)	331 sh (400)	335 sh (400)		354 sh (390)
ε_{254} = 400	ε_{254} = 320	ε_{254} = 200		ε_{254} = 324

and relative position of the absorption bands of the two chromophores endanger a selective excitation, even in the absence of proximity between the two groups. Furthermore, reactions in vibronically excited "hot" ground states have to be considered.

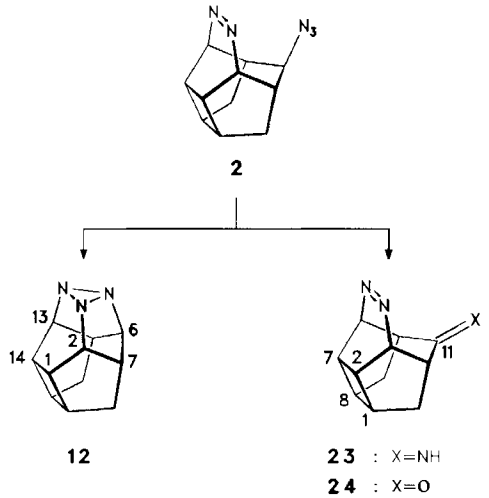
The irradiation experiments have been carried out in dry $< 10^{-2}-10^{-4}$ M solutions, thoroughly purged with argon, by using (in a Rayonet reactor) RPR monochromatic 254-nm low-pressure Hg lamps or RPR 350-nm phosphorus conversion lamps (spectral distribution λ = 300–400 nm) or (in a conventional photoreactor) a Hanau TQ 150 high-pressure Hg lamp [Pyrex (Solidex) filter, polychromatic light of $\lambda > 280$ or > 360 nm, 2 M $Cu(NO_3)_2$ filter solution][15]. It must be stressed, however, that our primary interest has been to demonstrate the applicability of this route to the preparation of *cis,cis*-trialkyltriaziridines, and that only limited efforts have been made to elucidate the nature and efficiency of competing reaction channels and other photomechanistic details.

By photolysis of the mobile azo azide **1**[16], we hoped to obtain information on a reaction proceeding in a situation highly unfavorable for triaziridine formation. In fact, transanular nitrene addition to yield triaziridine **11** is possible only within the limits set by the population of the nitrene derived from the thermodynamically unfavorable 3-axial conformation **1'** ($\Delta\Delta H_f^0$ = 4.9 kcal/mol, Table 1) and is therefore a priori highly unlikely. And indeed, independent of the exciting light (λ = 254 nm; 300–400 nm), with strict exclusion of moisture, according to continuous reaction control by TLC and NMR, no triaziridine **11**, but mainly colored, strongly absorbing oligomers are produced causing the reaction to stop already after ca. 50% conversion. There are only up to 5% of a new monomeric component, which has been identified as ketone **22**, arising from imine **21** and traces of water. Especially in the 254-nm irradiation experiments, the yield of **22** increases with rising water content of the reaction medium which is an indication of **21** being at least partly responsible for the oligomer fraction. In the same manner as in the following photolyses, a coloration of the higher molecular-weight products may suggest the intervention of diradicals resulting from α cleavage in the azo part and oligomerization being faster than N_2 elimination[7].

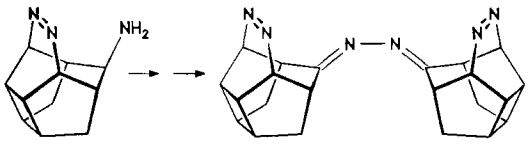
In the case of *syn*-azo azide **2**[17], the expectation – naively based on the *d*/ω parameters of Table 1 – that the addition



of nitrene yields triaziridine **12** has a plausible chance. Upon irradiation with the RPR 350-nm lamp, TLC and ^{1}H-NMR monitoring of the increasingly yellowish-colored solution reveal the parallel formation of two components in a ca. 1:10 ratio which have been identified as triaziridine **12** and imine **23**. Because of incomplete exclusion of moisture, **23** is slowly hydrolyzed to give ketone **24**. For the ^{1}H-NMR monitoring of the reaction it is beneficial that at 400 MHz ($CDCl_3$) prominent ^{1}H signals of the four components **2**, **12**, **23**, and **24** are sufficiently separated to allow their reliable integration. After total conversion and filtration, the ca. 50% CH_2Cl_2-soluble material consists of ca. 10% **12** and 90% **23**/**24** (ca. 1:1). By medium-pressure chromatography and crystallization triaziridine **12** and ketone **24** [m.p. 245°C (dec.); $\nu_{C=O}$ = 1690 cm^{-1}; $\delta_{C\text{-}11}$ = 207.5] are isolated as colorless crystals. **12** shows in the near UV only end absorption with ε_{220} = 900 and $\varepsilon_{254} \approx 0$. ^{1}H- and ^{13}C-NMR spectra confirm the C_s-symmetrical structure. The changes in vicinal H/H coupling constants around the cycloheptane ring on going from **2** ($J_{c,d} = J_{d,e}$ = 2.3 Hz) to **12** ($J_{c,d}$ = 3, $J_{d,e}$ = 7.5 Hz) are in line with the respective calculated interplanary angles (Table 2). In the mass spectrum the M^+ signal [m/z (%) = 187 (11] is very weak presumably as a result of the high strain energy in the neutral molecule (E_{str} = 92.5 kcal/mol, Table 1). The rates of azide consumption and product composition are not significantly different when **2** is irradiated with monochromatic 254-nm light (quartz vessel) or with the Hanau TQ 150 lamp (Pyrex vessel).

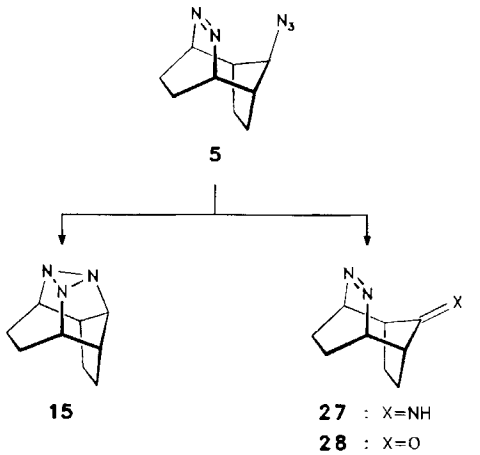


For **25**[1b] as a prototype it has been checked whether amine oxidation with $Pb(OAc)_4$ – successfully applied to intramolecular nitrene/ene cycloadditions[9] – may serve as an alternative to azide photolysis. Under proven conditions[9] the *meso*-/D,L-azines **26** are the only monomers which can be separated in ca. 50% yield from polymeric material; they crystallize from ethyl acetate/methanol (1:1) as a ca. 1:1 mixture and are characterized by their significantly different ^{1}H- and ^{13}C-NMR spectra. Dimerization by oxidation of imine **23** is plausible; triaziridine **12** has proved to be stable towards $Pb(OAc)_4$.

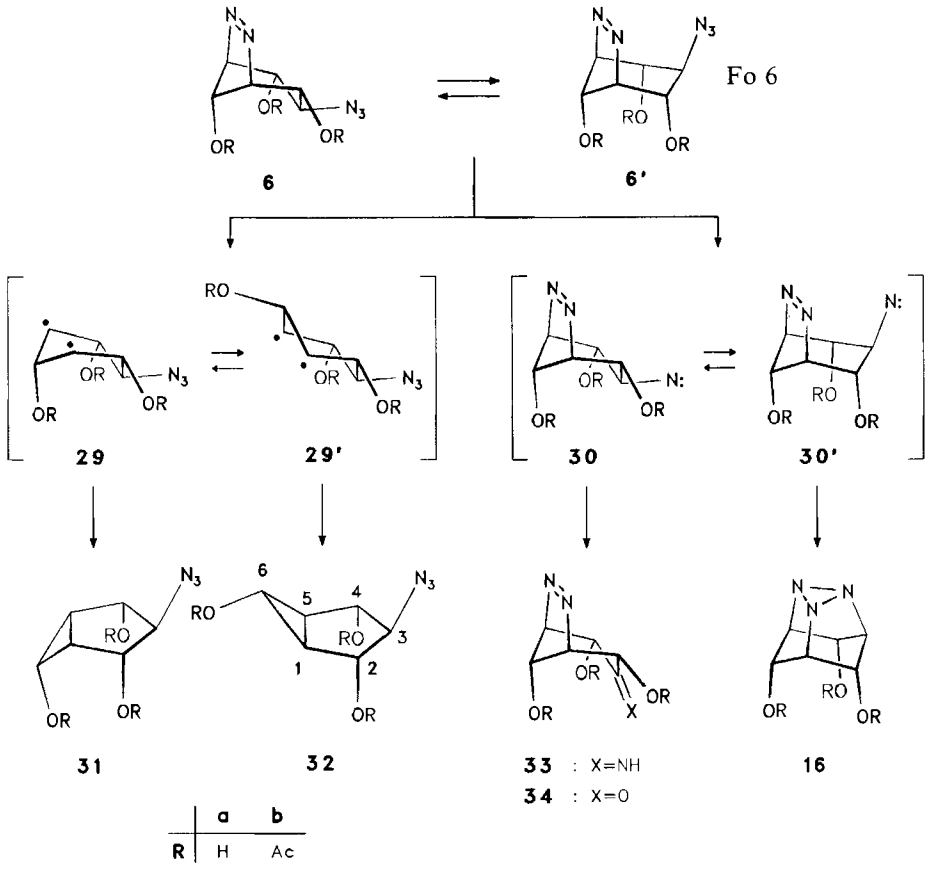


25 **26**

Both the geometrical and the energetic data for *syn*-azo azide **5** and triaziridine **15** suggest a favorable situation (Table 1)[16]. When exposed to the 300–400-nm light (RPR 350), a 10^{-4} M solution of **5** remains "transparent" (only slight coloration) with total conversion being reached after ca. 2 h. The crude material is chromatographically fractionated on silica gel; with acetone, after possible traces of **5**, 25% of triaziridine **15**, then with CH_2Cl_2/methanol (9:1) 35% of another C_s-symmetrical component are collected. Colorless, crystalline **15** is purified by sublimation at 80°C/10^{-2} Torr. Being transparent in the pertinent section of the UV spectrum (end absorption with ε_{220} = 310, ε_{254} = 37), this compound is not affected under the irradiation conditions. In the ^{1}H- ($CDCl_3$) and ^{13}C-NMR spectrum – when compared with the assignments in the spectrum of **12** – the reversal in chemical shifts of two signals is primarily attributed to the given structural (hybridizational) differences. The two ^{15}N resonance lines (2:1) are found at δ = 184.3 and 160.6 (C_6D_6), significantly downfield from the ^{15}N signals of *cis,trans*-triaziridines (δ = 140–90)[18], presumably as a consequence of the *all-cis* arrangement of the three n-electron pairs. The fact that in the mass spectrum the M^+ peak (100%) is so much more intensive than in the case of **12** probably manifests the much lower strain energy (E_{str} = 66.8 kcal/mol, Table 1). From the second isolated component up to 25% of ketone **28** are liberated upon stirring in the presence of silica gel/water. The formation of a cyclic oligomer (trimer?) of imine **27** is in agreement with the ^{1}H-NMR data.

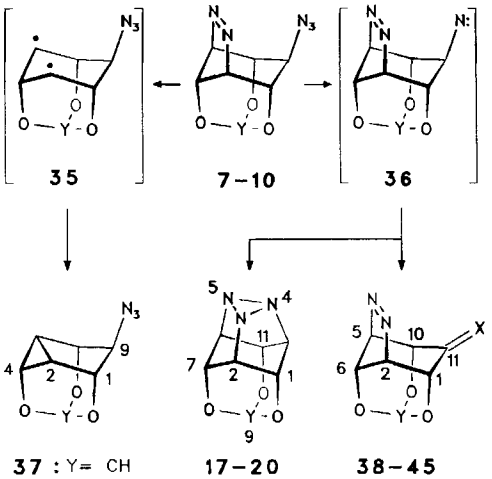


Of the cyclohexane-based, semirigid *syn*-azo azides **6a,b**, only triacetate **6b** has been studied[19]: For **6a** the 3-equatorial/3-axial conformations **6a**/**6a'** are of comparable energy, whilst for **6b**/**6b'** the necessary 3-axial conformation **6b'**, though somewhat flattened, is by far more populated



($\Delta\Delta H_f^0$ ca. 4 kcal/mol, Table 1). Direct excitation of **6b** with the RPR 350 lamp induces relatively fast conversion (90% after 80 min) ending up, however, in a very complex mixture of products. By TLC, ^{1}H-NMR and GC/MS monitoring, besides slightly colored oligomers, acetic acid, and various amino phenols, ca. 5% of the two bicyclic azides **31b/32b** (ca. 2:1) have been identified. With monochromatic 254-nm light the reaction proceeds much slower and more selectively insofar as besides polymers 36% of **31b/32b** (2:1) and up to 5% of triaziridine **16b** (vide infra) are formed, with the latter being lost, however, during the isolation procedure. The fact that neither imine **33b** nor ketone **34b** is present at any stage of the photoreaction (up to 5% might have been overlooked) is taken as an indication of the deazatization **6b** → diradical **29b** being fast with respect to **6b** → nitrene **30b**. In control experiments triaziridine **16b** (isolated via **19**) as well as azides **31b/32b** have been found to be relatively stable towards the applied light.

In the rigid adamantanoid *syn*-azo azide **7**, the prospect for triaziridine formation[19] should be significantly improved, though adverse transanular interactions inhibit optimal axial orientation of the azido function (ω = 162° instead of 180°, Table 1). During monochromatic 254-nm irradiation (1.5 mmol, 200 ml of CH_3CN, room temp., ε_{254} = 400), high-field ^{1}H-NMR monitoring allows a distinction and integration to be made of five components, i.e. besides the starting compound **7**[1] triaziridine **17**, azide **37**, imine **38**, and ketone **39** with the relative proportion of imine **38**[1] decreasing with irradiation time. Under strictly anhydrous conditions, ketone **39** is not formed. After 90% conversion (60 min) chromatographic workup yields (based on conversion) 47% triaziridine **17**, 11% **7**, 7% **37**, and 4% **39**. When the progress of the photoreaction is followed by UV spectroscopy in anhydrous CH_3CN, a new, redshifted maximum



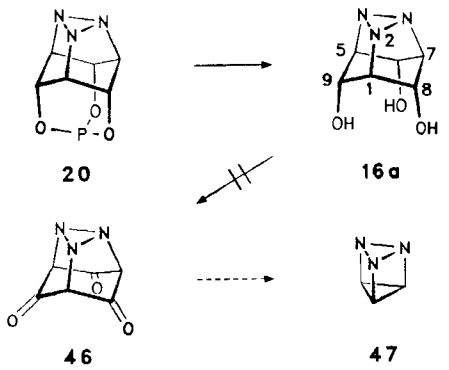
	7(17)	8(18)	9(19)	10(20)
Y	CH	CCH_3	PO	P

	38	39	40	41	42	43	44	45
Y	CH	CH	CCH_3	CCH_3	PO	PO	P	P
X	NH	O	NH	O	NH	O	NH	O

(λ = 395 nm) is rapidly built up and disappears on prolonged irradiation which is presumably a direct sign for the photochemical and/or thermal consumption of imine **38**[1]. The outcome of the irradiation with 300–400-nm light (RPR 350) is somewhat different: In a typical run with 90% conversion, **37** is not produced, and the yield of **17** has increased to 62% (ca. 5% **39**).

Triaziridine **17** crystallizes from ethyl acetate as colorless needles with the expected weak end absorption in the UV spectrum (ε_{220} = 250). C_{3v} symmetry is reflected in the ^{1}H-, ^{13}C-, and ^{15}N-NMR spectra[18].

Experiments with the *syn*-azo azides **8**–**10**[19] have been restricted to explorative, nonoptimized 300–400-nm irradiations (1.0–2.5 mmol, ca. 90% conversion). After chromatography, from **8** 38% of triaziridine **18**, from **9** 27% of triaziridine **19** (which seems to be partially destroyed in the separation procedure), and from **10** 20% of triaziridine **20** are obtained besides varying, not exactly determined amounts of imines and ketones (**40**–**45**). Phosphite **20** is oxidized to phosphate **19** in the two-phase system CH_2Cl_2/20% aqueous H_2O_2, under which conditions the N_3 ring is not tangled. MS, ^{1}H- and ^{13}C-NMR confirm the C_{3v} structures **18**–**20**.



Hydrolysis of the heteroadamantanoid esters **17**–**20** should, in principle, open access to the triaziridines **16a,b** [functionalized "triazatriaxanes" ("triaza[3]peristylanes")[20]], not available from the mobile *syn*-azo azides **6(a),b** in significant, isolable quantities. For well established reasons[21], the acid hydrolysis of trioxaadamantanes of type **17/18** needs rather drastic conditions, and indeed, **18** has proved stable towards 0.2 N HCl/CH_3CN/25°C, the application of more vigorous conditions (80°C, 2 N HCl/25°C) causes unspecific transformations. Bicyclic orthophosphates like **19** are known to be rapidly hydrolyzed in aqueous NaOH[22]. Yet, under varied alkaline conditions, **19** cannot be cleaved selectively to **16a**. Under acid catalysis, phosphite[23] esters are hydrolyzed up to 10^{12} times faster then the corresponding phosphates[21]. And indeed, in CH_3CN/1 N HCl at 25°C, **20** is hydrolyzed slowly with only partial decomposition (dark red solution). After acetylation and chromatography, crystalline triacetate **16b** (m.p. 203°C) is isolated in 65% yield. A partial flattening of the cyclohexane chair in the C_{3v}-symmetrical **16a,b** is deduced inter alia from the vicinal H/H coupling constants of J = 5.0–5.5 Hz (Table 2).

Attempts to oxidize the three axial hydroxy groups in **16a** to triaziridinetrione **46**, which is considered as a potential intermediate on the way to triazaprismane **47** as a very special *cis,cis*-trialkyltriaziridine, have been unsuccessful so far under various sets of conditions.

Thermal Stability of *cis,cis*-Trialkyltriaziridines 12 and 15–20

The degree of kinetic stabilization of the triaziridines **12**, **15**–**20** with strain energies ranging from 41.8 to 92.5 kcal/mol has been a major point of interest. **12**, when heated in degassed benzene solution, remains unchanged up to 140°C and decomposes at 200°C with a half-life of 1.5 h. **15** is comparatively stable [$t_{1/2}$ (130°C) $\approx$ 22 h]. At first sight, a surprise has been the significantly higher stability of **16b**; thus, when heated in dilute CH_3CN solution at 200°C, **16b** remains unchanged; at 250°C the half-life is ca. 3.5 h. In the mass spectrum, however, the M^+ signal is no more the most intensive one [*m/z* (%) = 297 (14), 226 (16), 43 (100)], the fragmentation being governed by the substituents. In the triaziridines **17**–**20**, the rigid trioxaadamantanoid corset confers an additional (small) increase in stability. Thus, these compounds only slowly decompose during melting at temperatures between 220 and 245°C. In the mass spectra of **17** and **19**, the M^+ signal runs up to 100% intensity. Clearly, in these threefold annulated triaziridines **12** and **15**–**20**, the increase in stability as already observed on going from *cis,trans*-di(tri)alkyltriaziridines to monoannulated ones[24,25] continues, the scission of one of the N–N bonds is increasingly prohibited by the molecular skeleton.

The thermal stability of triaziridines **16**–**20** exceeds that of alkyl azides and polycyclic azo compounds[26]. Thus, it is possible to compare the product distribution with that observed during thermal "nitrene" generation. When samples of **7** (**8**) are heated to 200°C (degassed solutions in benzonitrile) the **17/18** (**39**) [**18/40** (**41**)] ratio and the yield of **17** (**18**) after 90% conversion have been found similar to that of the photochemical reaction.

N-Electron Interaction – PE Spectra

The stability of the "clamped" triaziridines presented in this paper has allowed us to study experimentally the interaction between the three *syn*-oriented nitrogen lone pairs by PE spectroscopy (Gleiter and Sigwart)[27] using **15**, **17**, and **18** as representative examples. A comparison of the reported vertical ionization energies of **15** (8.5, 8.9 eV), **17** (9.4, 9.8, 10.5, 10.8 eV), and **18** (9.4, 9.7, 10.4, 10.7 eV) and the orbital energies calculated (MNDO) for the hypothetical *cis,cis*-trimethyltriaziridine allow the assignment of the first two peaks in the spectrum of **15** and of the first three peaks in the spectra of **17/18**. The following conclusions are relevant: (i) The energy difference between bonding (n^+) and antibonding (n^-) molecular orbitals (ca. 2.5 eV) manifest strong lone-pair interactions in all three cases; (ii) splitting between the two first bands (0.3–0.4 eV), due to a Jahn-Teller effect, is an indication of the high skeletal strain; and (iii) the energy differences for the highest occupied orbitals of **15** and **17**

(**18**) exhibit the strong inductive effect exerted by the three oxygen functions of the latter compound. Effects of this sort might favor the release of 1,3-diradicals by N_2 elimination (**29**, **35**) and thus the occurrence of the corresponding bicyclo[3.1.0]hexane products **31**, **32**, and **37**.

X-ray Structural Analysis – Deformation Density

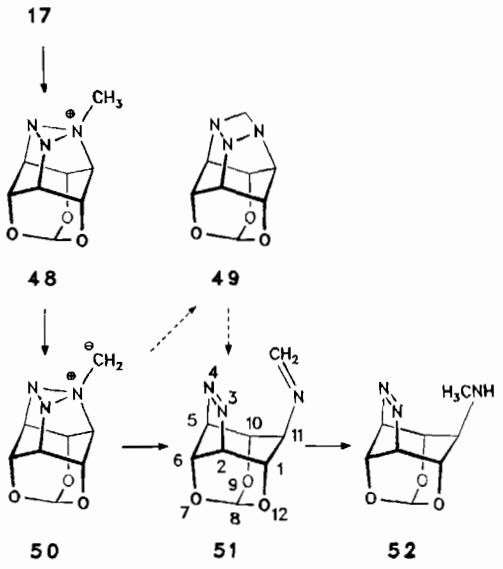
Irngartinger and Gries have determined the X-ray structure of **16b**[27] and the deformation densites from low-temperature X-ray data (105 K)[28]. As expected, the N–N bonds have been found to be bent, and also stretched by the repulsive interactions along these bonds; for reasons inherent in the applied methodology, only very low electron-density peaks for N–N bonds are seen, however. Yet, the maxima of the nitrogen lone pairs can be clearly recognized, lying 0.5 Å above the N_3 plane and being 2.1 Å apart from each other.

By a comparison of the experimental structural data of **16b** with the calculated ones the reliability of our MMX calculations (Tables 1, 2), at least with respect to the geometrical details, is demonstrated.

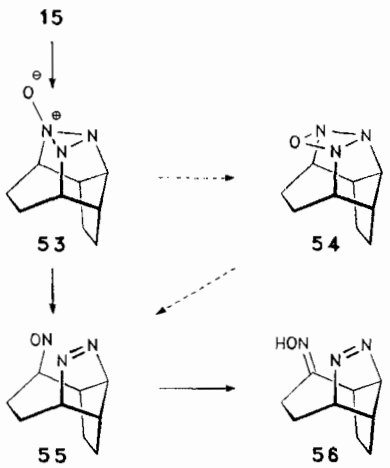
Attempts for $N_3 \rightarrow N_3X$ Ring Enlargement

In a more preparative synthetic context, *syn,syn*-trialkylated triaziridines have been valued as potential intermediates in the synthesis of kinetically stabilized N_3X four-membered rings[1b]. It is understood a priori that for any ylide generated by the addition of a carbene (nitrene) to a triaziridine or by oxidation of the latter, ring enlargement has to compete with highly exothermic (cheletropic) fragmentation. In this section we shortly summarize some pertinent, though mostly preliminary, results which might, however, help to better define the prerequisites for molecular corsets which would be sufficiently rigid to allow access to these elusive N_3X ring systems.

The triaziridines are generally very weak bases (pK_a of *trans*-diisopropyltriaziridine: < 2[29]); **17** e.g. is not protonated in trifluoroacetic acid, it reacts, however, quickly with Meerwein salt (trimethyloxonium tetrafluoroborate, 1 equiv.) at room temperature[30]. After crystallization from methanol, 67% colorless monomethyl salt **48** [m.p. 105°C (dec.)] is isolated with a static C_s-symmetrical methyltriaziridinium unit according to ^{1}H-NMR analysis. For deprotonation, to provide in situ the ylide **50**, and hopefully triazetidine **49**, a CD_3CN solution of **48** is treated with aqueous K_2CO_3 (0–20°C); the only monomeric, highly reactive component (up to 80%) has been shown to be azo aldimine **51** on the basis of spectral (UV, IR, ^{1}H-NMR) data ($\nu_{C=N}$ = 1644 cm^{-1}; δ_{CH_2} = 7.58). After reduction of the crude product mixture with $NaBH_4$ and filtration through silica gel, crystalline C_s-azo methylamine **52** (72%, m.p. 186°C) is obtained.

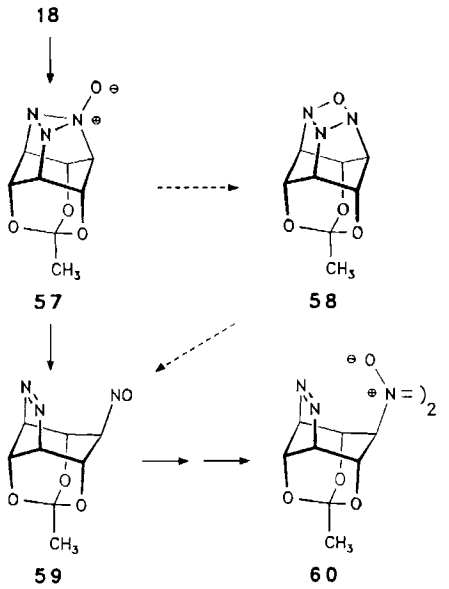


Access to oxatriazetidine rings (e.g. **54**, **58**) has been sought by starting from **15** and **18** via the respective triaziridine *N*-oxides (e.g. **53**, **57**[31]). **15** with its relatively low ionization potential[27] is oxidized by *m*-chloroperbenzoic acid (1.0 equiv.; $CDCl_3$) already at –30°C, the deeply blue color manifesting the presence of azo nitroso isomer **55**, which is at equilibrium with its azo dioxide dimer[32]. ^{1}H-NMR spectra taken at this temperature do not hint at the formation of either of the two possible triaziridine *N*-oxides (e.g. **53**) – cf. the fragmentation of 1,2-diazetidine *N*-oxides[33] – or oxatriazetidines (e.g. **54**). However, after warming up to room temperature, the peracid and not **15** is consumed. This is in line with the faster oxidation of the products. Careful TLC and spectroscopic analyses reveal the presence of only one new monomeric component, which, after chromatographic separation, is isolated as colorless crystals and identified spectroscopically (UV, ^{1}H-, ^{13}C-NMR) as azo oxime **56** [31%, (*E*)/(*Z*) = 5:3; m.p. 86°C; λ_{max}(methanol) = 340 nm], presumably generated by acid-catalyzed isomerization of **55**. Within the limits of the material balance, the two sorts of nitrogen atoms in **15** are obviously discriminated in this oxidation, with only the N-1 (–12) atoms being attacked. This is in line with the calculated geometrical situation/hybridization at these centers.

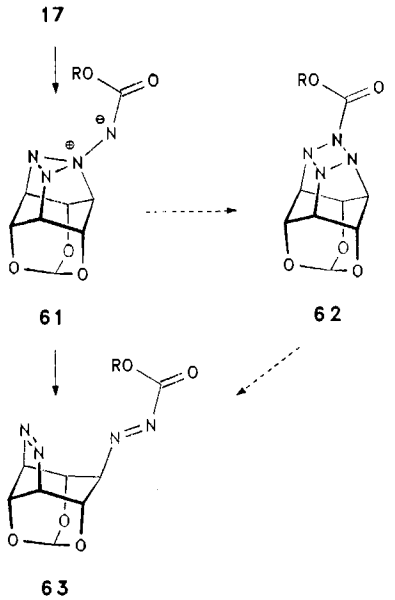


The analogous oxidation of inductively stabilized **18** occurs only at room temperature with no ensuing blue coloration and again no spectral indication of an *N*-oxide (**57**) or an oxatriazetidine (**58**) formation. Of the at least six new

components, besides ca. 35% of **18**, only the major component (11%) has been isolated and spectroscopically identified as C_s-symmetrical, colorless azo dioxide **60**, the dimer of **59**.



For nitrene addition to triaziridines as a potential route to tetrazetidines **62**, a CH_2Cl_2 solution of **17** in the presence of a vast excess of methyl azidoformate (1:1000) is irradiated (254 nm, room temp.). A deepening of the coloration of the increasingly complex reaction solution (TLC) prevents conversion beyond ca. 50%. Chromatographically, the only monomeric product (TLC, ^{1}H NMR) is separated together with **17** (1:2 ratio, ca. 20% based on conversion) and only inefficiently obtained in a pure form (1%!) by complexation with CuCl. The crystalline compound, available in only minute amount, is assigned the structure **63** on the basis of spectral data. Thus, the formation of triaziridine N-ylide **61** rests on indirect evidence.



Conclusion

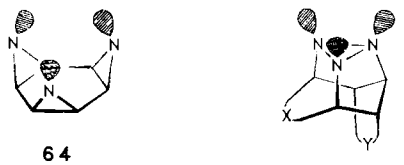
The primary goal of this project, the preparation of stable and chemically manipulable *cis,cis*-trialkyltriaziridines, has been achieved by photolysis (or thermolysis) of rigid, suitably aligned and "proximate" *syn*-azo azides. More effectively than expected are these triaziridines stabilized by their molecular corsets. Though the photolysis experiments are of more exploring than systematic nature, they document the preparatively rather limiting (stereoelectronic) prerequisites of this approach. Without invoking a strict correlation with the relative alignment of the reactive centers as defined by the d/ω parameters, the yields of 5% **12**, 25% **15**, and 62% **17** suggest that the preparative utility of this route is bound to $d \leqslant 2.8$ Å and $\omega \geqslant 160°$. Similar limiting geometrical parameters have been stated within related contexts, e.g. intramolecular hydrogen abstraction by alkoxide radicals[34] or [6 + 6] benzo/benzo photocycloadditions[35]. (Photo)mechanistically intriguing questions intimately connected with the unusually proximate arrangement of the azo/azido functions and the triaziridine formation remain unanswered, e.g.: What is the nature of the product-determining excited states? Are there discrete nitrene or exciplex intermediates[36]? An admittedly qualitative argument could be seen in the thermolysis of **7**/**8**: The temperature necessary for the decomposition of this azo azide (> 200 °C) is considered typical of azides, which are fragmented to nitrenes[37] whithout anchimeric assistance. The formation of triaziridines **12** and **15** from **2** and **5**, respectively, through the action of daylight has provoked the speculation about an intramolecular energy transfer from the azo to the azido unit. In a control experiment, **2** has been photolyzed by light with $\lambda > 365$ nm in order to guarantee selective azo $n \rightarrow \pi^*$ excitation; no significant differences in the reaction rate and product composition compared to that in the 254-(300–400-)nm irradiations[17] have been noted. Nitrene generation by intramolecular (triplet) energy transfer from the oxo to the azido function with γ-hydrogen abstraction as the main competitive process has been established[38]. Low-temperature matrix and strictly monochromatic photolysis studies with azo azides **1**–**10** should provide deeper insight[36,39].

Not totally unexpected, yet somewhat disappointing in view of the initial hopes[1b], is the failure to observe any N_3X four-membered rings generated from the respective triaziridine ylides. Still, their intermediacy on the way to the final products – without any skeletal enforcement prima facie admittedly a rather remote alternative to the highly exothermic fragmentation – cannot be ruled out with certainty. The decrease in stability on going from the triaziridine C- (**50**) to O- (**53**, **57**) and N-ylides (**61**) is in line, e.g., with findings in the aziridine and 1,2-diazetidine series[31,33].

A comment is necessary regarding the nature of substrates and methodologies applied in this project. The decision to make use of secondary (azo) azides with the generally very fast imine formation (hydrogen migration) as detracting competitive process is simply based on the more convenient accessibility of these substrates. Needless to stress the point that triaziridine formation should become (even) more pre-

ponderant by starting from the corresponding tertiary (azo) azides (c.f. **H, I**; R = alkyl in ref.[1b]). The generation of "nitrenes" by azide photolysis has been chosen as the method which is considered to comply best with the needs of the produced triaziridines. When the latter turned out to withstand rather high reaction temperatures and to be resistant to oxidizing agents like $Pb(OAc)_4$, alternatives as, e.g., the oxidation of the more readily available *syn*-azo amines may be taken into account. In the one case (**25**) studied, however, triaziridine formation (**12**) has not been observed, which probably again confirms the restricted propensity of N=N bonds to participate in cycloaddition reactions.

An intriguing aspect in the chemistry of the *cis,cis*-trialkyltriaziridines connected with the *syn* orientation of the three nitrogen lone pairs is their potential as tridentate ligands. The *cis*-benzene trisimine **64** (d_{N-N} = 2.97–3.13 Å), a prominent member of the class of *cis*-tris-σ-homobenzenes[40], has been shown to act – like the analogous *cis*-benzene trioxide[41] – as a very special tridentate ligand. Because of its unique geometry, with large metal ions (e.g. $La^{3\oplus}$) 4:1 complexes featuring nearly ideal icosahedral MeN_{12} coordination spheres have become available[42]. It will be exciting to find out whether *cis,cis*-trialkyltriaziridines can enter into similar high coordination compounds.



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Experimental*)

Melting points (m.p.): Bock-Monoscop M. – Anal. TLC: Merck silica-gel plates with F_{254} indicator. – Flash chromatography: 0.04–0.06 mm silica gel, Macherey-Nagel. – Anal. GC: Varian 3700, glass capillary column 25 m, OV 17, FID; integrator Varian CDS 111. – ^1H NMR: Bruker WM 250, WM 400; ^{13}C NMR: Bruker WP 80, WM 250, WM 400. Chemical shifts in ppm relative to TMS and coupling constants in Hz. – ^{15}N NMR: Bruker WM 400 [^{15}N]nitromethane (δ = 380.2) as external standard. *Indicated assignments are interchangeable. – IR: Perkin-Elmer 457, Philips PU 9706. – UV: Perkin-Elmer Lambda 15. – MS: Finnigan MAT 44 S. – The photolyses were carried out in dry solutions, thoroughly purged with argon, using RPR 254-nm low-pressure Hg lamps or RPR 350 phosphorus conversion lamps in a Rayonet reactor or a Hanau TQ 150 high-pressure mercury lamp in a conventional photoreactor.

Photolysis of **1**: 206 mg (1.25 mmol) of **1** in 200 ml of acetonitrile was irradiated with RPR 350-nm lamps (room temp.), the solution becoming rapidly colored. After 2.5 h (conversion ca. 35%), the solvent was evaporated in vacuo and the residue containing besides **1** only one monomeric component (TLC) subjected to flash chromatography on silica gel (elution with ethyl acetate). 118 mg (57%) of **1** (R_f = 0.42) and 9 mg (5%) of **22** (R_f = 0.33) were separated from polymers.

6,7-Diazabicyclo[3.2.2]non-6-en-3-one (**22**): Yellowish crystals, m.p. 125°C. – IR (KBr): $\tilde{\nu}$ = 1705 cm^{-1}, 1547. – ^1H NMR ($CDCl_3$): δ = 5.30 (m, 1-, 5-H), 2.67–2.49 (m, 4H), 1.86–1.68 (m, 4H). $C_7H_{10}N_2O$ (138.2) Calcd. C 60.85 H 7.29 N 20.28 Found C 60.58 H 7.22 N 20.06

With the RPR 254-nm lamps (quartz vessel, room temp.) the rate of conversion and product composition do not differ significantly.

Photolysis of **2**: 100 mg (0.47 mmol) of **2**[1b] in 90 ml of acetonitrile was irradiated with an RPR 350-nm lamp for 45 min (room temp., total conversion, TLC). After concentration in vacuo, the residue was extracted with CH_2Cl_2; after concentration, 51 mg (51%) of a colorless solid mixture of **12** and **23/24** (10:51:39) was obtained. By allowing the NMR sample to stand for 2 h, imine **23** was hydrolyzed quantitatively to ketone **24**. Triaziridine **12** was obtained in pure form by rapid chromatography (column 15 × 1 cm, ethyl acetate/methanol): TLC monitoring with $CuCl_2$: **12** (R_f = 0.11) causing green and **24** (R_f = 0.36) brown coloration.

With the monochromatic 254-nm (quartz vessel) or Hanau TQ 150 lamp (Solidex vessel, room temp.) practically the same product composition was found.

3,4,5-Triazaheptacyclo[7.5.0.0^{2,7}.0^{3,5}.0^{4,13}.0^{6,12}.0^{10,14}]tetradecane (**12**): Colorless crystals, decomposition beginning at 212°C. – IR (KBr): $\tilde{\nu}$ = 1468 cm^{-1}. – UV (CH_3CN): ε_{254} = 0, ε_{220} = 900. – ^1H NMR ($CDCl_3$): δ = 4.16 (m_c, 2-, 13-H), 3.82 (m, 7-, 12-H), 3.38 (t, 6-H), 3.03 (m, 9-, 10-H), 2.59 (m, 1-, 14-H), 1.75 (m, 8-, 11-H)*, 1.47 (m, 8′-, 14′-H)*; $J_{6,7(6,12)}$ = 7.5; (C_6D_6, 400 MHz): δ = 3.80 (m_c, 2-, 13-H), 3.27 (dd, 7-, 12-H), 2.91 (t, 6-H), 2.34 (m_c, 9-, 10-H), 2.02 (m_c, 1-, 14-H), 1.03 (d, 8′-, 11′-H), 0.70 (m, 8-, 11-H); $J_{2,7(12,13)}$ = 3; $J_{6,7(6,12)}$ = 7.5; $J_{7,8(11,12)}$ = 6.75; $J_{8,8'(11,11')}$ = 15. – ^{13}C NMR ($CDCl_3$): δ = 63.0 (C-2, -13), 62.8 (C-6), 61.9 (C-7, -12), 40.1 (C-9, -10), 27.6 (C-1, -14), 23.5 (C-8, -11). – MS (EI, 70 eV): *m/z* (%) = 187 (11) [M^+], 120 (100); [CI (isobutane), 170 eV]: *m/z* (%) = 188 (100) [M^+ + 1], 160 (9), 120 (7). – In degassed ca. $2 \cdot 10^{-2}$ M C_6D_6 solution a half-life at 200°C of ca. 1.5 h was determined.

4,5-Diazapentacyclo[6.5.0.0^{2,7}.0^{3,12}.0^{6,10}]tridec-4-en-11-imine (**23**): UV (CH_3CN): λ_{max} = 392 nm. – ^1H NMR ($CDCl_3$): δ = 6.54 (m_c, 3-, 6-H), 3.35 (m_c, 10-, 12-H), 3.22 (m_c, 1-, 8-H), 2.63 (m_c, 2-, 7-H), 1.94 (m, 9-, 13-H)*, 1.80 (m, 9′-, 13′-H)*. – ^{13}C NMR ($CDCl_3$): δ = 180.4 (C-11), 70.1 (CX-3, -6), 57.6 (C-10, -12), 40.1 (C-1, -8), 34.8 (C-2, -7), 29.9 (C-9, -13).

4,5-Diazapentacyclo[6.5.0.0^{2,7}.0^{3,12}.0^{6,10}]tridec-4-en-11-one (**24**): Colorless crystals, m.p. 245°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1690 cm^{-1}, 1454. – UV (CH_3CN): λ_{max} (ε) = 393 (46); ε_{220} = 620. – ^1H NMR ($CDCl_3$): δ = 5.71 (m_c, 3-, 6-H), 3.35 (m_c, 10-, 12-H), 3.30 (m_c, 1-, 8-H), 2.72 (m_c, 2-, 7-H), 1.94 (m, 9-, 13-H), 1.86 (d, 9′-, 13′-H); $J_{9,9'(13,13')}$ = 14. – ^{13}C NMR ($CDCl_3$): δ = 207.5 (C-11), 69.4 (C-3, -6), 57.6 (C-10, -12), 39.9 (C-1, -8), 34.9 (C-2, -7), 28.6 (C-9, -13). – MS [CI (isobutane), 170 eV]: *m/z* (%) = 188 (5) [M^+], 149 (5), 132 [$M^+ - N_2 - CO$] (5), 105 (13), 66 (100).

$C_{11}H_{12}N_2O$ (188.2) Calcd. C 70.19 H 6.43 N 14.88 Found C 70.08 H 6.39 N 14.85

$Pb(OAc)_4$ Oxidation of Amine **25**: A suspension of 90 mg (0.48 mmol) of **25**[1], 161 mg (1.92 mmol) of $NaHCO_3$ and 211 mg (0.48 mmol) of $Pb(OAc)_4$ in 3 ml of CH_2Cl_2 was stirred at room temp. (N_2) for 3 h (total conversion). TLC monitoring indicated the pres-

*) See corresponding footnote in ref.[1b].

ence of only one new component. After concentration in vacuo, chromatography [silica gel, ethyl acetate/methanol (2:1), R_f = 0.30], and crystallization 90 mg (51%) of colorless crystals of a ca. 1:1 mixture of *meso-/DL-4,5-diazapentacyclo[6.5.0.0^{2,7}.0^{3,12}.0^{6,10}]tridec-4-en-11-one Azine* (**26**) was obtained: m.p. >260°C (ether). – IR (KBr): $\tilde{\nu}$ = 1616 cm^{-1}, 1449. – UV (CH_3CN): λ_{max} (ε) = 392 nm (355), 235 (5130; sh); ε_{254} = 2760. – ^{1}H NMR ($CDCl_3$): δ = 5.65/5.52 (m_c, 3-, 3′-, 6-, 6′-H), 4.05/3.58 (dd, 10-, 12-H), 3.50/3.49 (m_c, 10′-, 12′-H), 3.19 (m_c, 1-, 1′-, 8-, 8′-H), 2.69 (m_c, 2-, 2′-, 7-, 7′-H), 1.96/1.77 (m, 2CH$_2$), 1.82/1.62 (m, 2CH$_2$); J_{gem} = 14. – ^{13}C NMR ($CDCl_3$): δ = 162.8/159.5 (C-11), 70.2/70.0 (C-3, -3′, -6, -6′), 50.9/50.6 (C-10, -12), 42.5/42.3 (C-10′, -12′), 40.1/40.0/39.9 (C-1, -1′, -8, -8′), 34.9/34.86/34.81/34.7 (C-2, -2′, -7, -7′), 30.6/30.0/29.4/28.8 (C-9, -9′, -13, -13′). – MS [CI (isobutane), 170 eV]: *m/z* (%) = 372 (17) [M$^+$], 344 (19) [M$^+$ – N$_2$], 316 (6) [M$^+$ – 2N$_2$], 158 (62), 131 (64), 92 (99), 66 (100).

Photolysis of **5**: A solution of 511 mg (2.67 mmol) of **5** in 400 ml of dry THF was exposed to irradiation with a RPR 350-nm lamp (room temp.). After ca. 90% conversion (2 h), the orange solution was concentrated in vacuo and the solid residue separated by chromatography on silica gel. With acetone first 15 mg (3%) of **5** (R_f = 0.53), then 109 mg (25%) of **15** (R_f = 0.25) were eluted. By changing to CH_2Cl_2/methanol (9:1) 127 mg of a uniform component (R_f = 0.17, 25–30%, cyclic oligomer of **27**?) was eluted [λ_{max}(methanol) = 385 nm (sh), <270 (end absorption); ^{1}H NMR ($CDCl_3$): δ = 5.42 (d, $n\cdot$2H), 2.72 (m, $n\cdot$2H), 2.16–1.92 (m, $n\cdot$4H), 1.82 (m, $n\cdot$2H), 1.32 (m, $n\cdot$2H)]. On stirring this component in the presence of silica gel/water the ketone **28** was slowly formed.

1,2,12-Triazapentacyclo[6.4.0.0^{2,12}.0^{3,7}.0^{4,11}]dodecane (**15**): After sublimation at 80°C/10^{-2} Torr, colorless crystals of **15** were obtained, m.p. 214°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1473 cm^{-1}. – UV (CH_3CN): $\varepsilon_{254} \approx 37$; $\varepsilon_{220} \approx 310$. – ^{1}H NMR ($C_6D_6$): δ = 3.66 (t, 3-H), 3.47 (m, 8-, 11-H), 2.87 (m, 4-, 7-H), 1.48 (m, 9β-, 10β-H), 1.18–1.00 (m, 5α/β-, 6α/β-, 9α-, 10α-H); $J_{3,4(3,7)}$ = 6.5; $J_{7,8(4,11)}$ = 10; $J_{8,9\beta(10\beta,11)}$ = 3; ($CDCl_3$): δ = 4.06 (t, 3-H), 3.85 (m, 8-, 11-H), 3.45 (m, 4-, 7-H), 1.93–1.58 (m, 8H). – ^{13}C NMR (C_6D_6): δ = 75.5 (C-3, J_{CH} = 152), 57.3 (C-8, -11, J_{CH} = 146), 57.2 (C-4, -7, J_{CH} = 136), 25.5 (C-5, -6, J_{CH} = 132), 15.1 (C-9, -10, J_{CH} = 131 Hz). – ^{15}N NMR (C_6D_6): δ = 184.3 (N-1, -12), 160.6 (N-2). – MS (EI, 70 eV): *m/z* (%) = 164 (11) [M$^+$ + 1], 163 (100) [M$^+$], 135 (46), 134 (16), and other fragments.

Photolysis of **6b**: a) A solution of 250 mg (0.77 mmol) of **6b** in 100 ml of dry acetonitrile was irradiated with RPR 350-nm lamps (room temp.). After 80 min, the solvent was evaporated in vacuo, the oily residue (smelling like acetic acid) partitioned between CH_2Cl_2/$NaHCO_3$ solution. The dried organic extract ($MgSO_4$) was concentrated in vacuo to give 162 mg of a red oil which could be separated partially by chromatography on silica gel [cyclohexane/ethyl acetate (1:1)] to yield 16 mg (ca. 6%) of **31b/32b** (ca. 2:1), 20 mg (ca. 8%) of **6b**, and 110 mg of a red oil, which presumably consisted of several aniline derivatives (^{1}H NMR, MS). **16b** (≤2%) could be detected only spectroscopically.

b) A solution of 280 mg (0.86 mmol) of **6b** in 100 ml of acetonitrile was irradiated with monochromatic 254-nm light (quartz vessel, room temp.). After 13 h (TLC, the reaction had virtually stopped), the solvent was removed in vacuo and the residue subjected to chromatography on silica gel [cyclohexane/ethyl acetate (2:1)]. 80 mg (36% based on conversion) of **31b/32b** (2:1) was obtained as a colorless oil, besides 35 mg (11%) of **6b**. Triaziridine **16b**, observed, in the ^{1}H-NMR spectrum of the crude photolysis mixture (ca. 5%), was lost during isolation procedures.

(1α,2β,3α,4β,5α,6β- and (1α,2α,3β,4α,5α,6α)-3-Azidobicyclo[3.1.0]hexane-2,4,6-triyl Triacetate (**31b/32b**). – IR (film): $\tilde{\nu}$ = 2100 cm^{-1}, 1740, 1425. – ^{1}H NMR (C_6D_6): **31b**: δ = 5.26 (m, 2-, 4-H), 4.09 (t, 6-H), 3.86 (t, 3-H), 1.70 (m, 1-, 5-H), 1.69–1.58 (9H, CH_3); $J_{1,6(5,6)}$ = 7.5; $J_{2,3(3,4)}$ = 6.8; **32b**: δ = 4.96 (s, 2-, 4-H), 4.15 (t, 6-H), 3.77 ("s", 3-H), 1.86 (t, 1-, 5-H), 1.69–1.58 (9H, CH_3); $J_{1,6(5,6)}$ = 1.5. – MS [CI (ammonia), 170 eV]: *m/z* (%) = 315 (100) [M$^+$ + NH_4], 272 (44), 270 (36); [CI (methane), 170 eV]: *m/z* (%) = 298 [M$^+$ + 1] (2), 238 (46), 153 (100).

(1α,2β,3α,4β,5α,6β)- and (1α,2α,3β,4α,5α,6α)-3-Azidobicyclo[3.1.0]hexane-2,4,6-triol (**31a/32a**): Through a stirred solution of 20 mg (0.07 mmol) of **31b/32b** (2:1 mixture) in 20 ml of methanol dry gaseous ammonia was bubbled for 15 min; after 2 h at room temp. and solvent evaporation in vacuo, 11 mg (91%) of **31a/32a** (ca. 2:1) was isolated as a colorless oil. – ^{1}H NMR (D_2O): **31a**: δ = 4.39 (m, 2-, 4-H), 3.94 (t, 6-H), 3.77 (t, 3-H), 1.59 (m, 1-, 5-H); $J_{1,6(5,6)}$ = 7.5; $J_{2,3(3,4)}$ = 7.0; **32a**: δ = 4.06 ("s", 2-, 4-H), 3.78 ("s", 6-H), 3.30 ("s", 3-H), 1.77 ("s", 1-, 5-H).

Photolysis of **7**: a) A solution of 300 mg (1.43 mmol) of **7** in 200 ml of acetonitrile was irradiated with monochromatic 254-nm light (quartz vessel, room temp.). After ca. 90% conversion (60 min), the solvent was evaporated in vacuo, the solid residue separated by chromatography on silica gel [cyclohexane/ethyl acetate (2:1)] to yield 17 mg (7% based on conversion) of **37**, 33 mg (11%) of **7**, 109 mg (47%) of triaziridine **17**, and 10 mg (4%) of **39** (yield scattered markedly). ^{1}H-NMR analysis of a typical raw photolysis mixture revealed **17** and **38** in a 3:1 ratio.

b) A solution of 150 mg (0.72 mmol) of 7 in 100 ml of acetonitrile was irradiated with 350-nm lamps for 50 min (room temp.). After solvent evaporation in vacuo, the residue was separated by chromatography on silica gel [cyclohexane/ethyl acetate (2:1)] to afford 14 mg (9%) of **7** and 73 mg (62%) of **17** besides ca. 5% of **39**. ^{1}H-NMR analysis of the raw photolysis mixture revealed ca. 20% of **38**.

8,10,13-Trioxa-3,4,5-triazahexacyclo[7.3.1.0^{2,7}.0^{3,5}.0^{4,12}.0^{6,11}]tridecane (**17**): Colorless crystals, m.p. 233°C (dec.) (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 1380 cm^{-1}. – UV (CH_3CN): ε_{220} = 250. – ^{1}H NMR ($CDCl_3$): δ = 5.68 (s, 9-H), 5.07 (m, 1-, 7-, 11-H), 4.05 (2-, 6-, 12-H). – ^{13}C NMR ([D$_6$]DMSO): δ = 100.3 (d, J_{CH} = 206, C-9), 77.9 (d, J_{CH} = 165, C-1, -7, -11), 52.5 (d, J_{CH} = 161, C-2, -6, -12). – ^{15}N NMR ([D$_6$]DMSO): δ = 180.6. – MS [CI (isobutane), 170 eV]: *m/z* (%) = 182 (100) [M$^+$ + 1], 110 (23), 108 (76), and other fragments.

$C_7H_7N_3O_3$ (181.2) Calcd. C 46.41 H 3.89 N 23.19
Found C 46.26 H 3.80 N 23.34

(1α,9α)-9-Azido-5,7,10-trioxatetracyclo[4.3.1.0^{2,4}.0^{3,8}]dodecane (**37**): Colorless crystals, m.p. 82°C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 2100 cm^{-1}, 1400. – ^{1}H NMR ($CDCl_3$): δ = 5.39 (s, 6-H), 4.77 (m, 1-, 8-H), 4.30 (m, 9-H), 4.18 (dt, 4-H), 1.99 (m, 2-, 3-H); $J_{2,4(3,4)}$ = 7. – MS [CI (methane), 170 eV]: *m/z* (%) = 182 (12) [M$^+$ + 1], 139 (18), 83 (96), 80 (100).

$C_7H_7N_3O_3$ (181.2) Calcd. C 46.41 H 3.89 N 23.19
Found C 46.40 H 3.94 N 23.04

7,9,12-Trioxa-3,4-diazatetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodec-3-en-11-imine (**38**): ^{1}H NMR ($CDCl_3$): δ = 5.69 (s, 8-H), 5.44 [m, 2(5)-H], 4.77 [m, 1(10)-H], 4.37 (m, 6-H).

Thermolysis of **7**: 5.0 mg (0.024 mmol) of crystalline **7** was heated to 200°C. ^{1}H-NMR analysis after 30 (60) min showed a **7**:**17**:**38** ratio of 20:5:2 (6:3:1).

Photolysis of **8**: A solution of 200 mg (0.9 mmol) of **8** in 150 ml of acetonitrile was irradiated with an RPR 350-nm lamp for 60 min

(room temp.). After solvent evaporation, the residue was separated by chromatography on silica gel [cyclohexane/ethyl acetate (1:1)] to give 22 mg (11%, based on conversion) of **8**, 58 mg (38%) of triaziridine **18**, and 13 mg (9%) of **41**.

9-Methyl-8,10,13-trioxa-3,4,5-triazahexacyclo-[7.3.1.0^{2,7}.0^{3,5}.0^{4,12}.0^{6,11}]tridecane (**18**): Colorless crystals, m. p. 220°C (dec.) (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 1400 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 5.08 (m, 1-, 7-, **11**-H), 3.96 (m, 2-, 6-, 12-H), 1.49 (s, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 107.4 (C-9), 80.6 (C-1, -7, -11), 52.8 (C-2, -6, -12), 23.9 (CH_3). – MS (EI, 70 eV): *m/z* (%) = 195 [M$^+$] (22), 166 (32), 43 (100).

$C_8H_9N_3O_3$ (195.2) Calcd. C 49.23 H 4.65 N 21.53
Found C 48.68 H 4.51 N 21.40

8-Methyl-7,9,12-trioxa-3,4-diazatetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodec-3-en-11-one (**41**): ^{1}H NMR ($CDCl_3$): δ = 5.45 (dd, 2-, 5-H), 4.63 (d, 1-, 10-H), 4.52 (t, 6-H), 1.56 (s, CH_3); $J_{1,2(5,10)}$ = 4.5; $J_{2,6(5,6)}$ = 5.5. – MS (EI, 70 eV): *m/z* (%) = 196 [M$^+$] (14), 97 (100).

Thermolysis of **8**: A degassed solution of 22 mg (0.1 mmol) of **8** in 2 ml of benzonitrile was heated to 200°C for 9.5 h. After solvent evaporation, ^{1}H-NMR analysis revealed **8/18/40** in a ratio of 2:12:25. Chromatography on silica gel [cyclohexane/ethyl acetate (1:1)] afforded 8 mg (42%) of **18**.

Photolysis of **9**: cf. **8**: 283 mg (1.16 mmol) of **9**, 200 ml of acetonitrile. After irradiation for 60 min and chromatography [silica gel, cyclohexane/ethyl acetate (1:2)], 100 mg of a mixture of **9** and **19** (ratio 7:3) and 23 mg (25% based on 75% conversion) of pure **19** were obtained. The high-field ^{1}H-NMR spectrum of the raw photolysis product revealed the imine **42** and subsequently the ketone **43**.

8,10,13-Trioxa-3,4,5-triaza-9-phosphahexacyclo-[7.3.1.0^{2,7}.0^{3,5}.0^{4,12}.0^{6,11}]tridecan-9-one (**19**): Colorless crystals, m. p. 245°C (dec.) (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 1330 cm^{-1}. – ^{1}H NMR ([D$_6$]acetone): δ = 5.79 (m, 1-, 7-, 11-H), 4.44 (m, 2-, 6-, 12-H); $J_{1,P(7,P;11,P)}$ = 20. – MS (EI, 70 eV): *m/z* (%) = 215 (20) [M$^+$], 81 (100); [CI (methane), 170 eV]: *m/z* (%) = 216 (100) [M$^+$ + 1].

$C_6H_6N_3O_4P$ (215.1) Calcd. C 33.50 H 2.81 N 19.53
Found C 33.62 H 2.70 N 19.18

Photolysis of **10**: cf. **8**: 545 mg (2.4 mmol) of **10** in 400 ml of actonitrile. After 60 min chromatography on silica gel [cyclohexane/ethyl acetate (1:1)] yielded 122 mg (22%) of **10** and 74 mg of triaziridine **20** (20% based on conversion). A further fraction (ca. 82 mg) contained a varying mixture of **44** and **45** as revealed by ^{1}H-NMR analysis.

8,10,13-Trioxa-3,4,5-triaza-9-phosphahexacyclo-[7.3.1.0^{2,7}.0^{3,5}.0^{4,12}.0^{6,11}]tridecane (**20**): Colorless crystals, m. p. 230°C (dec.) (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 1380 cm^{-1}, 1360. – ^{1}H NMR ($CDCl_3$): δ = 4.86 (m, 1-, 7-, 11-H), 4.17 (m, 2-, 6-, 12-H); $J_{1,P(7,P;11,P)}$ = 7. – MS (EI, 70 eV): *m/z* (%) = 199 [M$^+$] (10), 106 (100).

$C_6H_6N_3O_3P$ (199.1) Calcd. C 36.19 H 3.03 N 21.10
Found C 36.31 H 2.97 N 20.94

Oxidation of **20**: A solution of 6.0 mg (0.03 mmol) of **20** in 2 ml of CH_2Cl_2 was treated with 1 ml of aqueous 20% H_2O_2 solution and stirred at room temp. for 1 h. After solvent evaporation in vacuo at 20°C, ca. 6.0 mg (93%) of **19** was obtained.

Hydrolysis of **20**: A solution of 270 mg (1.36 mmol) of **20** in 100 ml of acetonitrile was treated with 19 ml of 1 N HCl and kept at room temp. for 2 d. After neutralization with aqueous $NaHCO_3$ solution, the mixture was concentrated in vacuo to dryness, the residuc acetylated by stirring with 5 ml of pyridine and 5 ml of acetic anhydride at room temp. for 2 d. After concentration in vacuo, the residue was filtered through a short pad of silica gel [cyclohexane/ethyl acetate (1:1)]. From ethyl acetate 263 mg (65%) of **16b** was isolated.

(6α,8α,9α)-2,3,4-Triazatetracyclo[3.3.1.0^{2,4}.0^{3,7}]nonane-6,8,9-triol (**16a**): ^{1}H NMR (D_2O): δ = 4.80 (m, 6-, 8-. 9-H), 3.96 (m, 1-, 5-, 7-H).

(1α,5α,6β,8β)-2,3,4-Triazatetracyclo[3.3.1.0^{2,4}.0^{3,7}]nonane-6,8,anti-9-triyl Triacetate (**16b**): Colorless crystals, m. p. 203°C. – IR (KBr): $\tilde{\nu}$ = 1730 cm^{-1}, 1360. – UV (CH_3CN): ε_{220} = 240. – ^{1}H NMR ($CDCl_3$): δ = 5.27 (m, 6-, 8-, 9-H), 4.42 (m, 1-, 5-, 7-H), 2.07 (s, 9H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 169.1 (C=O), 76.1 (C-6, -8, -9), 57.1 (C-1, -5, -7), 20.3 (CH_3). – MS (EI, 70 eV): *m/z* (%) = 297 [M$^+$] (14), 226 (16), 43 (100).

$C_{12}H_{15}N_3O_6$ (297.3) Calcd. C 48.49 H 5.09 N 14.14
Found C 48.31 H 5.01 N 13.94

3-Methyl-8,10,13-trioxa-4,5-diaza-3-azoniahexacyclo-[7.3.1.0^{2,7}.0^{3,5}.0^{4,12}.0^{6,11}]tridecane Tetrafluoroborate (**48**): A solution of 51 mg (0.28 mmol) of **17** in 60 ml of CH_2Cl_2 was added dropwise to 41 mg (0.28 mmol) of trimethyloxonium tetrafluoroborate. After vigorous stirring at room temp. for 4 h, it was filtered and the solution concentrated in vacuo. The residue was crystallized from methanol to give 53 mg (67%) of **48** as pale brown crystals, m. p. 105°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1638 cm^{-1}, 1438, 1387. – ^{1}H NMR (CD_3CN): δ = 5.86 (s, 9-H), 5.63 (m, 1-, 7-H), 5.34 (m, 2-H), 5.00 (t, 11-H), 4.74 (dd, 6-, 12-H), 3.60 (s, 3H, CH_3); $J_{1,12(6,7)} \approx J_{6,11(11,12)} \approx$ 5.6.

$C_8H_{10}BF_4N_3O_3$ (283.0) Calcd. C 33.95 H 3.56 F 26.85 N 14.85
Found C 33.83 H 3.52 F 26.63 N 14.97

(1α,11α)-11-(Methylenamino)-7,9,12-trioxa-3,4-diazatetracyclo-[6.3.1.0^{2,6}.0^{5,10}]dodec-3-ene (**51**): To a solution of 10 mg (0.035 mmol) of **48** in 1 ml of acetonitrile 1 ml aqueous K_2CO_3 solution was added. After stirring for 24 h at room temp., the solution was treated with 10 ml of water and extracted with 50 ml of CH_2Cl_2. The dried ($MgSO_4$) organic extract was concentrated in vacuo to give 10 mg of **51**, a colorless oil contaminated with oligomeric material. The product was used without further purification. – IR (KBr): $\tilde{\nu}$ = 1644 cm^{-1}, 1511. – UV (CH_3CN): λ_{max} = 360 nm, strong absorption at $\lambda \leqslant$ 300 nm. – ^{1}H NMR (CD_3CN): δ = 7.58 (m, 2H, CH_2), 5.71 (s, 8-H), 5.42 (m, 4H), 4.61 (m, 1H), 4.39 (m, 1H). – No correct analysis was obtained because of the instability of **51**.

(1α,11α)-11-(Methylamino)-7,9,12-trioxa-3,4-diazatetracyclo-[6.3.1.0^{2,6}.0^{5,10}]dodec-3-ene (**52**): To a solution of 10 mg (0.035 mmol) of **51** (raw material) in 2 ml of methanol 5 mg (0.130 mmol) of $NaBH_4$ was added. After stirring at 0°C for 5 h, the solvent was removed in vacuo, the residue was taken up in 10 ml of buffer solution (Na_2HPO_4/NaH_2PO_4), and the solution extracted with 50 ml of CH_2Cl_2. The extract was dried ($MgSO_4$) and concentrated in vacuo. The residue was filtered through a short pad of silica gel [cyclohexane/ethyl acetate (1:1)] to yield 5 mg (72%) of **52** (R_f = 0.08) as colorless crystals, m. p. 186°C (methanol). – IR (KBr): $\tilde{\nu}$ = 1724 cm^{-1}, 1454. – UV (CH_3CN): λ_{max} = 368 nm. – ^{1}H NMR ($CDCl_3$): δ = 5.69 (s, 8-H), 5.29 (m, 2-, 5-H), 4.56 (m, 1-, 10-H), 4.17 (m, 6-H), 3.20 (br. s, 11-H), 2.41 (s, 3H, CH_3); $J_{1,2(5,10)} \approx J_{2,6(5,6)} \approx$ 5.3. – ^{13}C NMR ($CDCl_3$): δ = 102.3 (C-8), 72.7 (C-1, -10), 71.7 (C-11), 69.0 (C-2, -5), 61.7 (C-6), 35.0 (CH_3). – MS [CI (ammonia), 170 eV]: *m/z* (%) = 198 (100) [M$^+$ + 1].

(E)/(Z)-2,3-Diazatricyclo[6.3.0.0^{4,11}]undec-2-en-7-one Oxime (**56**): 7.0 mg (0.043 mmol) of **15** and 8.4 mg (0.043 mmol) of 85% chloroperbenzoic acid were mixed in 5 ml of $CDCl_3$ at –50°C. The

reaction was controlled by ^1H and ^{13}C NMR. Above $-30°C$ slow oxidation was indicated by the formation of a blue color. After ca. 1.5 h at room temp., all of chloroperbenzoic acid was consumed. Evaporation of the solvent in vacuo afforded a residue which was subjected to chromatography on silica gel (acetone) to yield 2.5 mg (31%) of a 5:3 mixture of **56** and smaller fractions of **15** and by-products. – UV (methanol): λ_{max} = 340 nm. – ^1H NMR ($CDCl_3$): (*E*)-**56**: δ = ca. 7.6 (br. s, OH), 5.30 (t, 1-H), 5.08 (m, 4-H), 3.53 (t, 8-H), ca. 2.6 (11-H), 2.55–1.75 (series of m, 4 CH_2); (*Z*)-**56**: δ = 7.6 (br. s, OH), 5.34 (t, 1-H), 5.00 (m, 4-H), 4.24 (t, 8-H), ca. 2.6 (11-H), 2.55–1.75 (series of m, 4 CH_2). – ^{13}C NMR ($CDCl_3$): (*E*)-**56**: δ = 91.8 (C-1), 84.0 (C-4), 47.8 (C-8), 43.8 (C-11), 31.1 (C-5*), 29.0 (C-6), 22.0 (C-8*), 20.0 (C-9*); (*Z*)-**56**: δ = 92.6 (C-1), 84.9 (C-4), 40.4 (C-8), 40.6 (C-11), 32.0 (C-5*), 26.7 (C-6), 22.1 (C-8*), 21.7 (C-9*), C-7 not visible.

(1α,1'α,11α11'α)-8,8'-Dimethyl-11,11'-azodi[7,9,12-trioxa-3,4-diazatetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodec-3-ene] N,N'-Dioxide (**60**): A stirred solution of 93 mg (0.48 mmol) of **18** in 4 ml of CH_2Cl_2 was treated with 97 mg (0.48 mmol) of 85% chloroperbenzoic acid. After 3 d at room temp. (TLC), the mixture was washed with 5 ml of $NaHSO_3$ solution and with 5 ml of $NaHCO_3$ solution. The organic layer was dried ($MgSO_4$) and concentrated in vacuo to give a complex mixture of **18**, one main product, and ca. 5 byproducts (^1H NMR). The mixture was subjected to chromatography on silica gel [cyclohexane/ethyl acetate (1:1)] to yield besides small mixed fractions 15 mg (11%, based on recovered starting material) of the main product **60** (R_f = 0.55) and 32 mg (34%) of **18**. – UV (CH_3CN): λ_{max} = 363 nm, 356 (sh), strong absorption at λ = ⩽220 nm. – ^1H NMR ($CDCl_3$): δ = 5.43 (m, 2-, 5-H), 5.24 (m, 1-, 10-H), 4.30 (m, 6-H), 3.60 (t, 11-H), 1.45 (s, 3H); $J_{1,2(5,10)} \approx 7.0$; $J_{2,6(5,6)} \approx 4.9$; $J_{1,11(10,11)} \approx 2.6$. – ^{13}C NMR ($CDCl_3$): δ = 108.4 (C-8), 76.2 (C-11), 72.1 (C-6), 71.2 (C-1, -10), 62.6 (C-2, -5), 24.1 (CH_3).

Methyl (1α,11α)-7,9,12-Trioxa-3,4-diazatetracyclo-[6.3.1.0^{2,6}.0^{5,10}]dodec-3-en-11-ylazoformate (**63**): A solution of 50 mg (0.28 mmol) of **17** and 30 ml of methyl azidoformate in 30 ml of CH_2Cl_2 was irradiated with monochromatic light (λ = 254 nm). After 2.5 h at room temp. (^1H-NMR analysis of the photolysis mixture revealed a 2:1 ratio of **17**/**63**) and evaporation of volatile contents (0.1 Torr), the red oily residue was subjected to chromatography on silica gel [cyclohexane/ethyl acetate (1:1) followed by CH_2Cl_2/methanol (10:1)] to yield 5 mg of colorless crystals **63**/**17** in a ratio of 2:1. The mixture was dissolved in 10 ml of dried methanol, and under vigorous stirring 50 mg (0.5 mmol) of CuCl was added. After 10 h at room temp. the Cu(I) complex was filtered. For decomplexation concd. NH_3 was added, and the solution was extracted with 15 ml of CH_2Cl_2. After drying of the extract ($MgSO_4$) and solvent evaporation, 1 mg (1%) of solid **63** was obtained. – IR (KBr): $\tilde{\nu}$ = 1709 cm^{-1}, 1535. – UV (CH_3CN): λ_{max} = 364 nm. – ^1H NMR ($CDCl_3$): δ = 5.70 (s, 8-H), 5.35 (dd, 2-, 5-H), 4.53 (m, 1-, 10-, 11-H), 4.21 (t, 6-H), 3.65 (s, 3H, OCH_3); $J_{1,2(5,10)} \approx J_{2,6(5,6)} \approx 5.3$; ($CDCl_3/C_6D_6$): δ = 5.56 (s, 8-H), 5.08 (t, 2-, 5-H), 4.48 (br. s, 11-H), 4.30 (d, 1-, 10-H), 3.93 (t, 6-H), 3.54 (s, 3H, CH_3); $J_{1,2(5,10)} \approx J_{2,6(5,6)} \approx 5.5$ Hz.

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Table 4. Force-field parameters[a]

Bonds	V_1	V_2	V_3	Angle	Θ	K_Θ
C_{sp^3}–C_{sp^3}–N_{sp^3}–N_{sp^3}	−0.20	0.73	0.80	C_{sp^3}–N_{sp^3}–N_{sp^3}	108.00	0.63
C_{sp^3}–C_{sp^3}–N_{sp^2}–N_{sp}	−0.10	0.00	0.15	C_{sp^3}–N_{sp^2}–N_{sp}	115.00	0.60
C_{sp^3}–N_{sp^3}–N_{sp^3}–C_{sp^3}	0.20	0.27	0.09	N_{sp^3}–N_{sp^3} Lp	128.00	0.35
C_{sp^3} N_{sp^3}–N_{sp^3}–N_{sp^3}	0.00	0.00	0.00	N_{sp^2} N_{sp^2} X	(OOP)	0.05

Bonds	V_1	V_2	V_3
C_{sp^3}–N_{sp^3}–N_{sp^3}–Lp	0.00	0.00	0.00
C_{sp^3}–N_{sp^2}–N_{sp}–N_{sp^2}	0.00	0.00	0.00
H–C_{sp^3}–N_{sp^3}–N_{sp^3}	0.00	0.00	0.52
H–C_{sp^3}–N_{sp^2}–N_{sp}	0.00	0.00	−0.20
N_{sp^3}–N_{sp^3}–N_{sp^3}–Lp	0.00	0.00	0.00
Lp–N_{sp^3}–N_{sp^3}–Lp	0.00	0.00	0.00

Bond	L_0	K_s	μ
C_{sp^3}–N_{sp^3}	1.480	5.10	0.04
N_{sp^3}–N_{sp^3}	1.500	5.00	0.00
N_{sp^3}–Lp	0.600	6.10	0.60
N_{sp}–N_{sp^2}	1.180	5.00	0.00

Bond	Heat	Atom	VDW	Hardness
N_{sp}–N_{sp^2}	29.195	N_{sp2}	2.00	0.045
N_{sp^3} N_{sp^3}	35.000	$H_{Alc.}$	1.325	0.034
C_{sp^3}–N_{sp^2}	6.500			

[a] The force field equations are those found in MMX, the force field used in PCMODEL, QCPE no. 395; V_1, V_2, V_3: first-, second-, and third-order torsion constants [kcal/mol]; K_Θ: bending constant [mdyne Å/rad^2]; Θ: minimum energy angle [°]; L_0: natural bond length [Å]; K_s: stretching force constant [mdyne/Å]; μ: bond moments [debye]; VDW: van der Waals radius [Å]; Hardness, Heat [kcal/mol]; Lp: lone pair of electrons; OOP: out-of-plane bending.

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