206. The Azo(Azoxy) Functionality as a π_2 Component in Photo [2 + 2] Cycloadditions *'syn'*- and *'anti'*-3,4-Diazatricyclo[4.2.2.$2^{2,5}$]dodeca-3,7-diene, Syntheses, Photolyses, X-Ray-Structure Analysis, and PE Spectra

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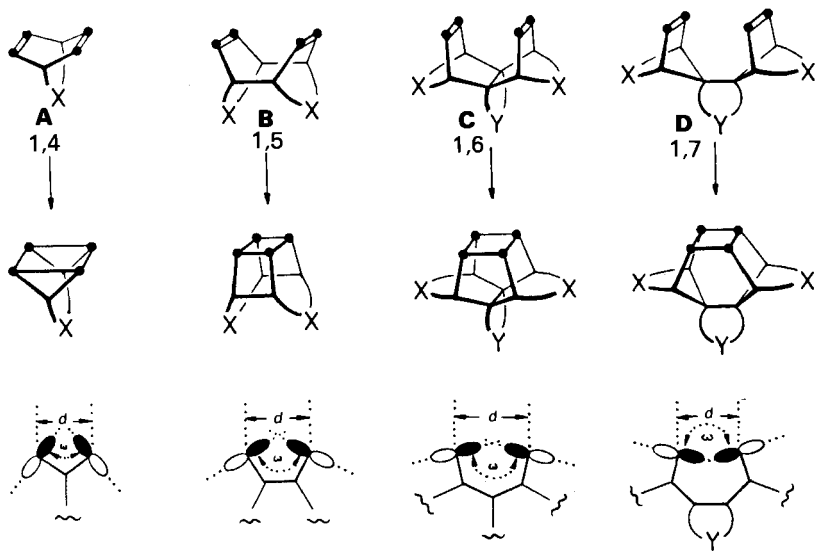
The propensity of the N=N bond to undergo photo [2 + 2] cycloadditions has been further explored. In the specifically designed 1,5-azo/enes **1–3**, no [2 + 2] cycloaddition has been observed upon either direct or sensitized excitation with light of various wave lengths at temperatures down to 77 K, in line with expectations based on X-ray (**1**: $d = 2.71$ Å, $\omega = 129°$) and PE measurements (**1**: $I_1 = 8.0_0$, $I_2 = 9.0_5$ eV; **2**: $I_1 = 8.0_0$, $I_2 = 9.2_5$ eV). The steric/stereoelectronic demands for the participation of the N=N bond in pericyclic reactions are clearly more stringent than those for the C=C bond.

Introduction. – Bichromophoric systems of the general structures **A–D** *(Scheme 1)* are proven suitable substrates for the investigation of proximity effects [1] and for preparative purposes, *e.g.* the extension of the classical [2 + 2]-photocycloaddition concept from olefins [2] to skeletons with three-membered ring [3] and benzenoid [4] functionalities. By different rigid connections (X, Y) between the chromophoric subunits, various [2 + 2]/[6 + 2]/[6 + 6] cycloaddition situations are approximated. Differences in photoreactivity are generally attributed to particular geometrical (transannular distance *d*, interorbital angle ω), thermodynamic (*e.g.* strain energy [5]), and electronic (through-space, through-bond coupling [1] [6]) parameters. For good reasons, examples with participation of N=N bonds [7–11] are relatively rare: Compared with ene/ene cycloadditions the azo/ene or azo/azo reactions are much more unfavorable thermodynamically ($\Delta\Delta H° \approx$ 20–25 and 50–80 kcal/mol, resp.), they should tolerate only a much narrower range of interorbital and shear angles (smaller π orbitals, n-electron repulsion), and N_2 elimination is an omnipresent competition.

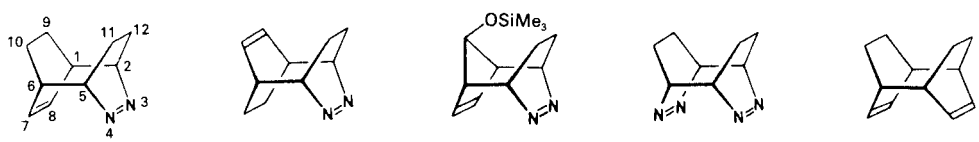
To broaden the experimental basis for a more reliable judgement of such limiting factors, our research program, originally centered upon azo/azo(azo/ene) cycloadditions of type **C** [11], was extended into the **B** series. In this paper, we describe the syntheses of azo/enes **1**/**2** with *'syn/anti'* (= *cis*-1-*cisoid*-1,6-*cis*-6/*trans*-1-*cisoid*-1,6-*trans*-6) configu-

Scheme 1[a])



[a]) ●● = CH=CH, ⟨⟩, N=N. [b]) X = CH_2. [c]) X = CH=CH. [d]) Y = CH_2. [e]) Y = $(CH_2)_3$.

ration and of **3** with *'syn'* configuration, the photolyses of **1** and **3** as well as an evaluation of the C=C/N=N interactions based on X-ray and spectral data and on PE investigations. As a result, there were no good reasons any more to pursue the synthesis of the corresponding azo/azo compound **4** further.



1 **2** **3** **4** **5**

The [2 + 2] photoreactivity of carbocyclic 1,5-dienes of type **B**, *e.g.* of **5** [12], is well studied [13]. Thus, with a few exceptions[1]), the corresponding cage compounds are available. Generally, however, in analogous 1,5-azo/ene and 1,5-azo/azo compounds **B**, the stereoelectronic and thermodynamic situation for intramolecular exciplex formation and for [2 + 2] cycloaddition is less favorable than in 1,6-skeletons **C**: At similar transannular distances *d*, the π orbitals deviate substantially (up to 50°) from the optimal

[1]) Compare the relevant discussion in the cases of cubane [14], pentaprismane [15], and hexaprismane [16].

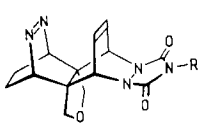
coplanar alignment (see *Scheme 1*), and four-membered ring formation is accompanied by considerable increase in strain.

The few known azo/ene and azo/azo cycloadditions have been realized in 1,6-bichromophoric skeletons **C**. Here, the disadvantage of a relatively large *d* value (2.8–3.0 Å) is more than offset by the nearly colinear π/π orientation ($\omega \approx 170°$). Independent of substitution and bridging (X, Y), diazetidines are formed upon excitation of the long-wavelength azo-n,π^* transition [7–11]; still, variations of bridge Y cause significant changes in selectivity[2]). Diazetidine formation is particularly surprising for substrates with the very photolabile diazabicyclo[2.2.1]heptene partial chromophor [7] [9]. In the carbocyclic 1,6-diene series **C**, the decrease in transannular reactivity with increasing length of bridge X is attributed to strain-energy differences. It is noteworthy that in the structure-analogous bisazo skeletons, cycloaddition is surpassed by N_2 elimination and that only after N-oxidation, azo/azoxy [2 + 2] cycloaddition (with subsequent $N{=}N/N_2O$ metathesis) becomes competitive [11]. Mainly thermochemical arguments are put forward to account for benzo/azo cycloaddition occurring in systems **C** featuring diazabicyclo[2.2.1]heptene units [18], but not in the less strained homologues with the corresponding [2.2.2] units [19]. In the structurally similar benzo/ene skeletons, [6 + 2] addition is observed independently of the length of the bridge X [20]. The 1,4-azo/enes of type **A** are not known; due to the favorable alignment of C–N bonds and C=C π orbitals, concerted [4 + 2] cycloeliminations proceed extremely rapidly [21][3]). The quantum yields for N_2 elimination from the dihydro derivatives, ranging from $\Phi = 1$ to $\Phi \approx 0$, mirror a delicate structural interdependence [25]. First efforts to construct 1,7-azo/ene or azo/azo substrates **D** with best possible d/ω values have remained so far unsuccessful [26].

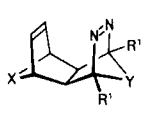
Synthesis. – As a variable approach to azotricycles **B**, [4 + 2] cycloaddition between readily available bicyclo[4.X.Y]dienes and 4-methyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (MTAD) was pursued. Complications had to be expected under two aspects: early *Diels-Alder* transition states are very sensitive to steric as well as electronic perturbations, and rather large diene 1,4-distances (3.2–3.5 Å) favor routes *via* polar intermediates.

In a pilot study, the regioselectivity of such MTAD additions was checked also with regard to 'second-order orbital interactions' [27] making use of the substrates **6–13**. The results with no direct relation to the target substances **1–3** are collected in the *Appendix*. Generally, [4.X.Y]dienes are approached by the azo dienophile from the diene's *exo*-face, in line with expectation (**6**, **7**, **8a**, **9**, **12**); it needs severe steric hindrance on the *exo*-side to

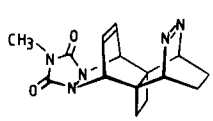
[2]) While in the furane-bridged 1,6-azo/ene substrate **i** [11] and in several unbridged analogues **ii** [7], diazetidine formation is generally highly selective, in the cyclobutane-bridged derivative **iii** [17], N_2 elimination becomes a noticcable side reaction.



i

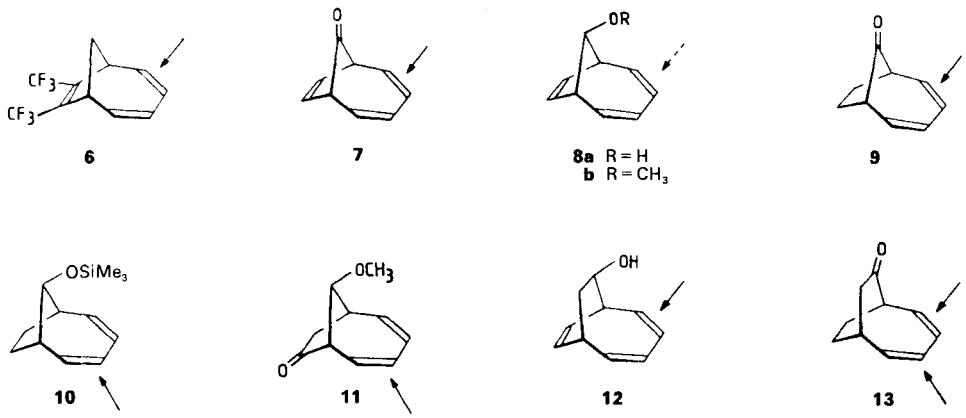


ii



iii

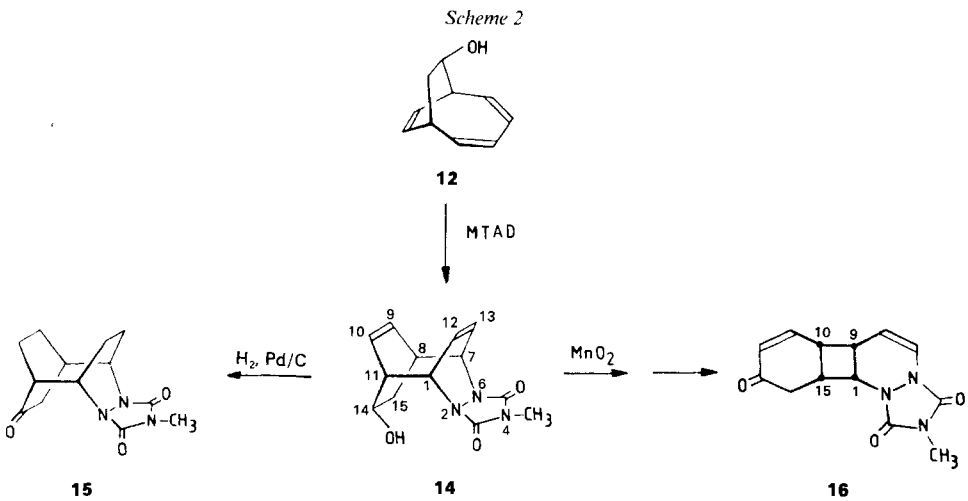
[3]) Also in thermally more stable 1,4-azo/cyclopropane (*'exo'*) derivatives [22], for which the presence of homoconjugative interactions is proven [23], $[_\pi 2 + _\sigma 2]$ cycloaddition – well documented in analogous ene substrates [3] – has no chance against N_2 elimination. $[_\pi 2 + _\sigma 2]$ Photocycloadditions in isodrin-like azoalkenes **C** were reported recently [24].



direct the attack to the *endo*-face (**10**, **11**). No addition is achieved when adverse electronic and steric effects on the diene's diastereotopic sides are operative (*e.g.* **8b**).

When the routes to **B** skeletons from [4.2.1]dienes proved to be preparatively unattractive, the [4.2.2]trienol **12** [28] and the [4.2.2]dienone **13** became the most promising candidates for stable MTAD adducts with proper configuration. In **12**, the ethylene bridge [27] as well as the OH group were expected to exert a directing effect towards **14**.

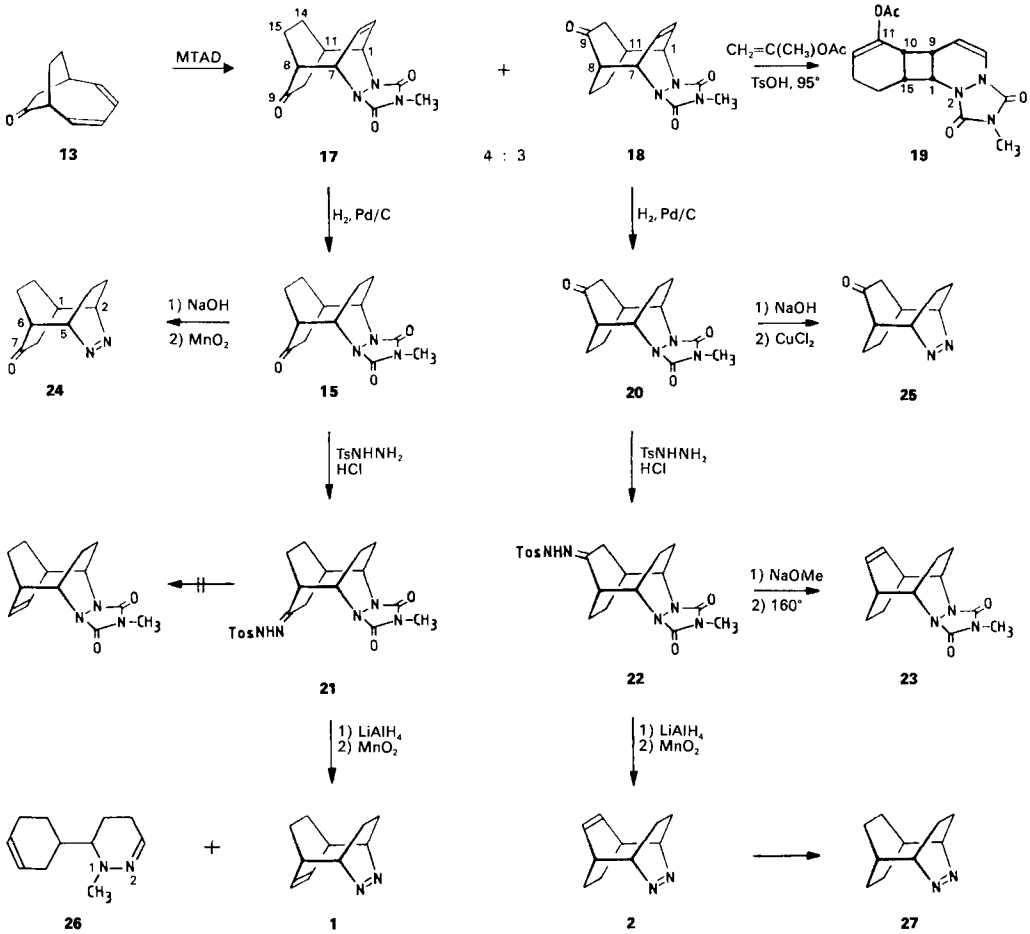
Scheme 2



Indeed, a single 1:1 adduct **14** (^{1}H-NMR) resulted from the reaction of **12** with MTAD in $CHCl_3$ between 20° and 60°, the yield, however, never exceeded 20%, presumably because of polar side reactions. The *'syn'* configuration of **14** was verified by hydrogenation and subsequent MnO_2 oxidation to the key intermediate **15**; in addition, after MnO_2 oxidation at 20°, rapid *Cope* rearrangement (**14**→**16**) occurred *(Scheme 2)*.

Dienone **13** was readily prepared from **9** [29] by ring enlargement with diazomethane/LiCl [28] (80%). MTAD addition was, however, not side-selective; the exothermic reaction (*e.g.* at *ca.* 20° in acetone) provided a 4:3 mixture (83%) of 1:1 *'syn'*- and

Scheme 3



'anti'-adducts **17**/**18** *(Scheme 3)*. Their assignment was primarily based on the upfield shift for the ^{1}H-NMR signals of the 'inside'-bridge protons facing the C=C bond. In accordance, **18** but not **17** rearranged in isopropenyl acetate/TsOH (95°), *via* its enol, into **19** (65%). Pd/C hydrogenation of **17** to *'syn'*-ketone **15** (97%) and of **18** to *'anti'*-ketone **20** was straightforward. For the conversion of ketones **15** and **20** to olefins, methodologies were favored starting from tosylhydrazones [30] [31]. With *p*-toluenesulfonic hydrazide in THF under acid catalysis, **21** (85%) and **22** (84%) were slowly but selectively formed. The thermolysis of the Na salt of **22** (diglyme, 160°) yielded the olefin **23** fairly efficiently (43%); under the same (and varied) conditions, the Na or Li salt of **21** decomposed in a complex manner with olefinic products being negligible.

Alternatively, olefination to **1** was probed in *'syn'*-azo ketone **24**. Saponification of **15** with NaOH in boiling i-PrOH led to a semicarbazide (^{1}H-NMR) which proved inert towards the usual oxidation conditions (aq. $CuCl_2$ solution, pH ≈ 5), but was readily transformed to **24** by MnO_2 (74%). Presumably, hemiaminal formation supported by the favorable alignment of the N with the CO orbitals and lacking solvation prevented the *Cu(II)*

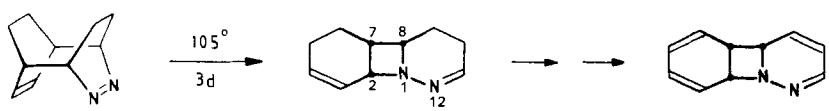
oxidation. Indeed, oxidative saponification of the *'anti'*-isomer **20** using the Cu(II) variant afforded directly the *'anti'*-azo ketone **25** (67%). All efforts to transform ketone **24** into a tosylhydrazone or an enol phosphate (lithium diisopropylamide (LDA; −78°)/diethyl chlorophosphate) failed; on the other hand, on prolonged heating with D_2O/NaOD, H_β–C(8) was exchanged almost completely (^{1}H-NMR).

Finally, $LiAlH_4$ reduction of **21** and subsequent MnO_2 oxidation were successful; thus, transformation of the urazole to the azo unit [32] and of the hydrazone to the ene functionality [33] could be brought about in 'one pot'. On heating **21** with $LiAlH_4$ in THF overnight at 55°, after hydrolysis and MnO_2 oxidation, *'syn'*-azo/ene **1** (23%) was easily separated chromatographically from **26** (43%) and other components[4]). Similarly, after $LiAlH_4/MnO_2$ treatment of **22**, the *'anti'*-azo/ene **2** (25%) could be isolated from a mixture of several compounds.

In the rather similar ^{1}H-NMR spectra of **1** and **2**, only a small diamagnetic shift for the signals of the vinylic protons in **1** ($\Delta\delta \approx 0.15$ ppm) is indicative of the *'syn'*-geometry. Notable differences are found in the UV spectra (MeCN). In comparing first the absorption of **1** ($\lambda_{max}(\varepsilon)$ 392 nm (76); $\varepsilon_{254} = 236$) with that of derivative **27** (prepared from **2** by Pd/C hydrogenation and subsequent MnO_2 oxidation; $\lambda_{max}(\varepsilon)$ 401 (sh, 71), 396 (73); $\varepsilon_{254} = 303$), no bathochromic shift of the long-wavelength n,π^* transition in **1**, which could be ascribed to the proximity of the ene to the azo unit, is revealed. In the *'syn'*-1,6-azo/ene series **C**, such bathochromic shifts are pronounced and show a marked dependence on bridge length [7–11]. In contrast, the n,π^* transition of **2** ($\lambda_{max}(\varepsilon)$ 419 (sh, 38), 411 (47); $\varepsilon_{254} = 171$) is considerably red-shifted compared with that of **1**, presumably due to stronger π/σ coupling in the *'anti'*-geometry [35].

syn-Azo/ene **1** is rather stable thermally; in toluene at 105°, the (irreversible) *Cope* rearrangement to **28** is still slow (conversion after 62 h > 85%; 34% isolated; *Scheme 4*). The expected *cis-cis* configuration in the azetidine moiety of **28** shows up in the vicinal H,H-coupling constants ($J(2,7) \approx J(7,8) \approx 7$ Hz). In analogous *'syn'*-1,5-dienes **B** (*e.g.* **5** [12]), the activation barrier of the [3,3] sigmatropic process is markedly lower. Recently, additional 1,2-diaza *Cope* rearrangements were published [36]; sigmatropic [3,3] shifts in 2,3- 2,5-, and 3,4-diazahexadienes are well known [37]. Currently, it is being investigated whether **28** and similar substrates (*e.g.* **16**) can be exploited for the preparation of *'syn'*-(hetero) benzene dimers [38] (*e.g.* **29**) which are of considerable interest as substrates in our study on domino *Diels-Alder vs.* pincer additions *(Scheme 4)*.

Scheme 4



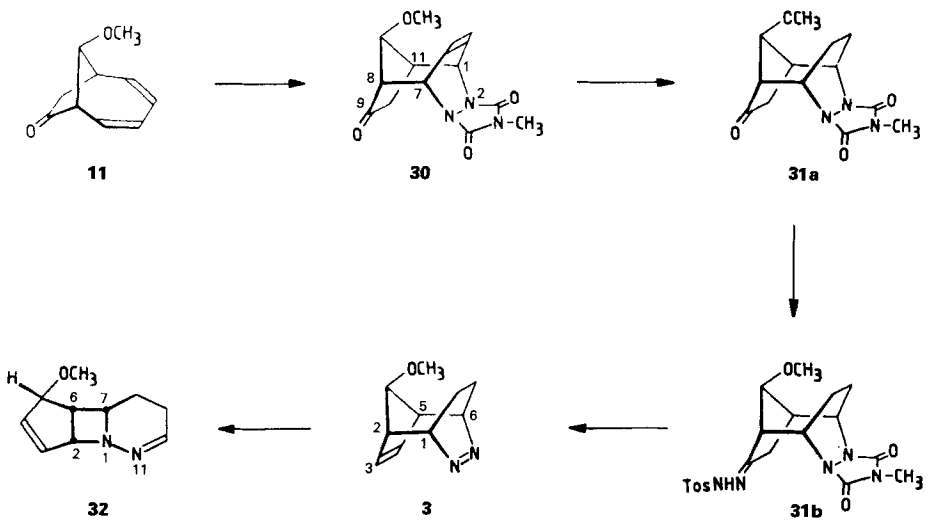
1 **28** **29**

According to MM2 force-field calculations, the thermodynamic and stereoelectronic situation for [2 + 2] cycloaddition in type-**B** compounds should be improved by shortening the bridges X, *i.e.* compound **3** would be a better substrate than **1**. Key step for the synthesis of such a substrate **3** is the (mainly) sterically guided MTAD addition to the

[4]) For TLC detection, advantage was taken of the fact that azo compounds, on treatment with ethanolic Cu(II)-salt solutions, form brownish-red complexes [34].

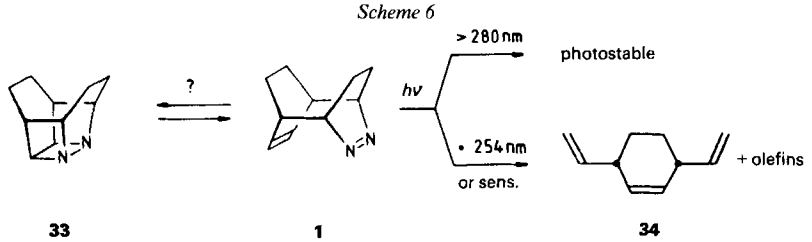
methoxy dienone **11**, which was available from **8b** [28] by hydroboration (BH_3·THF, H_2O_2; 77%) and subsequent *Swern* oxidation (96%). MTAD attacked **11** selectively on the *endo*-face (88% of **30**). After Pd/C hydrogenation (99% of **31a**) and (rather slow) conversion into its tosylhydrazone (64% of **31b**), the azo/ene **3** (12%) was set free according to the $LiAlH_4/MnO_2$ procedure worked out for **1** and **2**. The 1,2-diaza-*Cope* rearrangement of **3** to **32** (refluxing xylene, 3 d; 52%), manifesting the *'syn'*-geometry in **3**, required considerably rougher conditions than in **1**, presumably because of a more strained transition state *(Scheme 5)*.

Scheme 5



Photolyses of Azo/ene 1. – Upon n,π* excitation of *ca.* 10^{-3} M degassed solutions of **1** *(Hanau TQ 150; Pyrex)*, independent of the solvent, conversion was very slow (< 20% at −60° after 6.5 h), and no monomeric products were found (UV, DC, ^{1}H-NMR). An EPA solvent mixture (Et_2O/isopentane/EtOH 5:5:2) was used to obtain rigid glassy solutions for photolyses at 77 K. In the long-wavelength photolysis at 77 K (monochromatic 365-nm light), UV monitoring did not indicate any change after 1.5 h irradiation. Excited-state deactivation *via* a thermally labile diazetidine **33** was considered to be improbable *(Scheme 6)*, since the n,π*-absorption band of **1** did not increase in intensity when the photolyzed solution was thawed.

Scheme 6



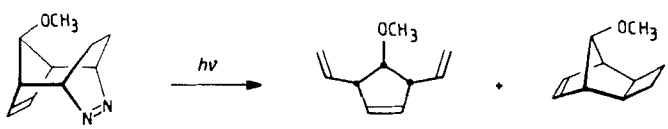
In contrast, with monochromatic light of 254 nm, rapid deazotation of **1** occurred, independent of the medium, even at 77 K. Primary product was the triene **34** which was recognized easily by (it's?) intense UV absorption. A quantitative analysis was complicated, however, by the photoreactivity of **34** as well as its high volatility (it codistilled with the solvent; conversion of **1**, 39%). The same holds for the benzophenone-sensitized reaction ($\lambda = 300$ nm; room temperature; (D_6)benzene; *Rayonet* photoreactor), though deazotation of **1** to **34** proceeded more cleanly (conversion 60%; estimated yield 30%).

In no photolyses of **1**, any indications for diazetidine formation (see **33**), *Cope* rearrangement (see **28**), or [1,3] shift (see **42**) could be detected. In control experiments, **28** (λ_{max} 251 (4550)) was decomposed on 254-nm excitation and remained unchanged on irradiation with light of $\lambda > 280$ nm.

On direct excitation, the azo compounds **2** and **27** were qualitatively as photoreluctant as **1**, while benzophenone-sensitized deazotations were markedly slower; presumably the less rigid skeletons support non-productive deactivation processes through torsional relaxation.

Photolyses of Azo/ene 3. – The results of these experiments closely resemble those of **1**. In the relatively rapid N_2 eliminations, the only monomeric products were the olefins **35** and **36** which appeared in a *ca.* 10:1 ratio on direct and a *ca.* 100:1 ratio on triplet-sensitized (acetone, benzophenone, benzil) excitation, respectively *(Scheme 7)*.

Scheme 7

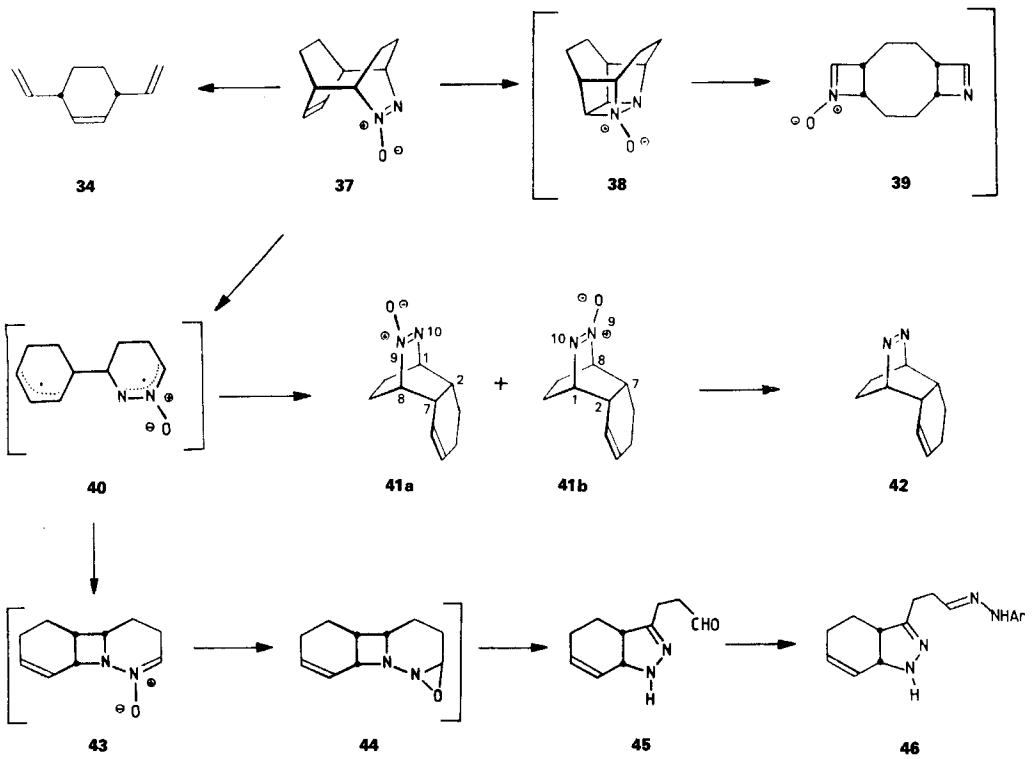


3 **35** **36**

Photolyses of Azoxy/ene 37. – In azoxy compounds, photochemical N_2O elimination is often rather slow. In fact, our experiments with isodrin-like 1,6-azoxy/azo and 1,6-azoxy/ene arrangements (upon selective excitation of the azoxy chromophors) had led to metathesis products arising presumably from tetra- and diazetidine *N*-oxide intermediates, respectively [11]; the typical photoprocesses of azoxy chromophores [39] – oxadiaziridine formation, deoxygenation, N_2O elimination – are of no importance here. It had to be examined whether in the azoxy/ene **37** (obtained from **1** by *m*-chloroperbenzoic-acid oxidation in CH_2Cl_2 at 0°; 93%), a similar preference exists for [2 + 2] photocycloaddition to give **38**, or possibly *via* **38** the metathesis isomer **39** *(Scheme 8)*.

Direct excitation of **37** (λ_{max} 237 (3520) nm) with 254-nm light under various conditions (*i.a.* MeOH, MeCN, EPA glass (77 K)) generally resulted in complex mixtures (UV, DC, ^{1}H-NMR); even in the initial stages of the irradiation, no isosbestic points emerged in the UV control spectra. The rate of the photolysis gradually diminished (in MeOH at 20°, 90% conversion after *ca.* 17 h). After short irradiation periods (1–5 min), triene **34** was the first observable product (UV), whose concentration decreased with irradiation time. It is not clear, whether **34** originates from N_2O elimination or deoxygenation/deazo-

Scheme 8



tation of **37**. The 254-nm irradiation in MeOH at 20° yielded, besides residual starting material (9%), two fractions which could be separated chromatographically from high-molecular-weight material. The second consisted of a 1:1 mixture of the diastereoisomeric azoxytricycles **41a**/**41b** (26%), the first of at least three components which were not separable and were spectroscopically characterized as the aldehyde **45** (additionally characterized as 2,4-dinitrophenylhydrazone **46**), azo compound **42**, and a MeOH adduct of unknown structure. Formation of **41** and **45** can be rationalized assuming the intermediates **40**, **43**, and **44**. As in the case of **1**, low-temperature experiments (77 K, EPA) confirmed the rapid formation of **34**; any indication for the [2 + 2] adduct **38**, which would have to revert thermally to **37** but not to **39**, is lacking. On benzophenone sensitization, **37** seemed to become efficiently deactivated by photophysical processes; at generally low conversions (< 20%, 20 h), there were only traces of **41a**/**41b**.

X-Ray Crystallographic Analysis of *'syn'*-Azo/ene 1. – *Crystal Data:* $C_{10}H_{14}N_2$, monoclinic, space group $P2_1/c$, $a = 6.095(3)$ Å, $b = 9.730(4)$ Å, $c = 13.932(4)$ Å, $\beta = 96.6(2)°$, $Z = 4$. A *Philips PW 1100* automatic diffractometer was used for data collection with Mo$K\alpha$ radiation and graphite monochromator. The intensities of 2182 independent reflections with $\theta < 28°$ were measured, of which 1757 were classified as observed with $I > 2\sigma(I)$. The structure was solved by direct methods. All H-atoms were found from a difference *Fourier* map. The structure was refined by full-matrix least-squares calculations with anisotropic (isotropic for H-atoms) thermal parameters to a final R value of 0.047. Final fractional coordinates are given in *Table 1*.

Table 1. *Fractional Coordinates of* **1**

Atom	*x*	*y*	*z*	*B*(A2)[a])
C(1)	0.7258(4)	0.3677(3)	0.6561(2)	2.75(4)
C(2)	0.8038(4)	0.2648(3)	0.7406(2)	3.05(5)
N(3)	1.0256(3)	0.2044(3)	0.7305(2)	3.58(5)
N(4)	1.0368(3)	0.1094(2)	0.6714(2)	3.52(5)
C(5)	0.8295(4)	0.0612(3)	0.6151(2)	3.04(5)
C(6)	0.7560(4)	0.1588(3)	0.5270(2)	2.87(5)
C(7)	0.9073(4)	0.2806(3)	0.5226(2)	3.07(5)
C(8)	0.8929(4)	0.3814(3)	0.5845(2)	3.06(5)
C(9)	0.5024(4)	0.3313(3)	0.5984(2)	3.12(5)
C(10)	0.5192(4)	0.2158(3)	0.5252(2)	3.21(5)
C(11)	0.6487(4)	0.1466(3)	0.7590(2)	3.38(5)
C(12)	0.6626(4)	0.0302(3)	0.6864(2)	3.49(5)
H(13)	0.697(5)	0.460(4)	0.691(2)	4.4(9)*
H(14)	0.839(5)	0.321(4)	0.800(2)	4.4(9)*
H(15)	0.878(5)	–0.027(4)	0.590(2)	4.4(9)*
H(16)	0.747(5)	0.105(4)	0.466(2)	4.4(9)*
H(17)	1.003(6)	0.283(4)	0.473(2)	4.4(9)*
H(18)	0.994(5)	0.464(4)	0.588(2)	4.4(9)*
H(19)	0.444(5)	0.417(4)	0.565(2)	4.4(9)*
H(20)	0.375(5)	0.305(4)	0.642(2)	4.4(9)*
H(21)	0.410(5)	0.133(4)	0.530(2)	4.4(9)*
H(22)	0.468(5)	0.248(4)	0.457(2)	4.4(9)*
H(23)	0.496(6)	0.179(4)	0.760(3)	4.5(9)*
H(24)	0.691(5)	0.111(4)	0.829(2)	4.4(9)*
H(25)	0.703(5)	–0.059(4)	0.722(2)	4.4(9)*
H(26)	0.512(5)	0.007(4)	0.653(2)	4.5(9)*

[a]) Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
$(4/3)\cdot[a^2\cdot B(1,1) + b^2\cdot B(2,2) + c^2\cdot B(3,3) + ab(\cos\gamma)\cdot B(1,2) + ac(\cos\beta)\cdot B(1,3) + bc(\cos\alpha)\cdot B(2,3)]$.

Perspective views of the molecule **1** with the atomic numbering scheme and the packing of **1** are shown in *Figs. 1* and *2*, respectively, bond lengths and bond and dihedral angles are given in *Table 2*. There is no manifestation for significant through-space π,π

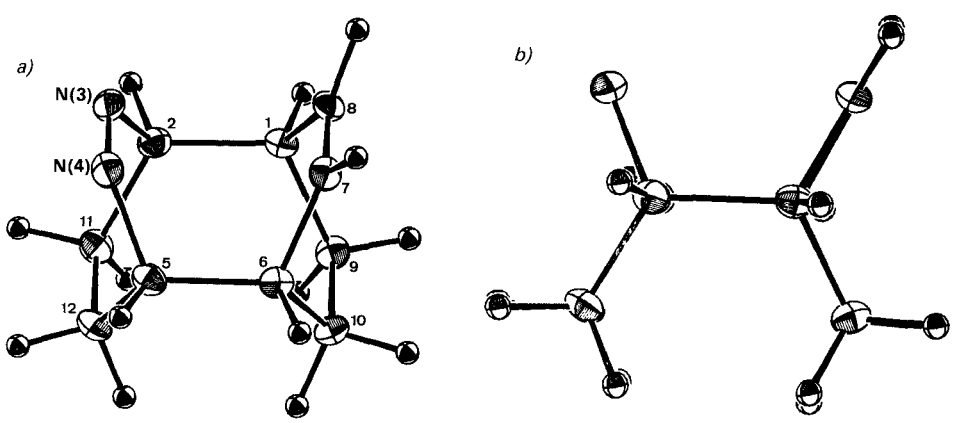


Fig. 1. *Structure of* **1**. *a)* Side/top view; *b)* side view.

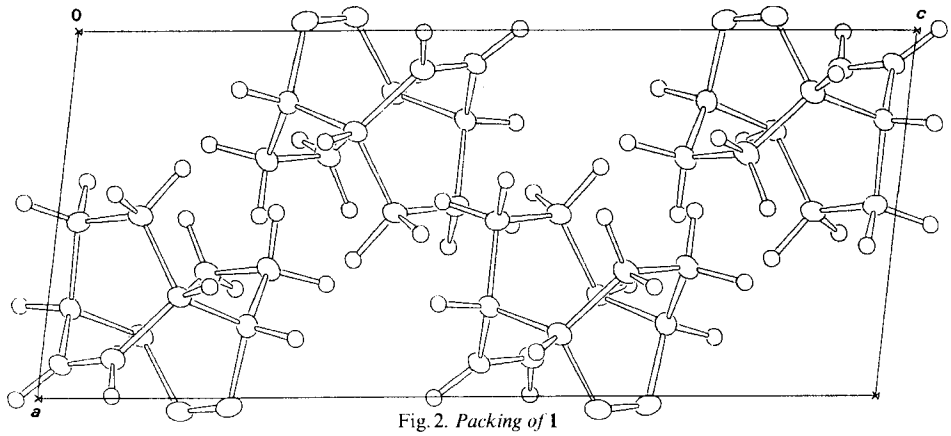


Fig. 2. *Packing of* **1**

Table 2. *Bonds Lengths* [Å] *and Bond and Dihedral Angles* [°] *of* **1**[a])

Bond length			
C(1)–C(2)	1.576(3)	C(5)–C(6)	1.576(3)
C(1)–C(8)	1.512(4)	C(5)–C(12)	1.532(4)
C(1)–C(9)	1.540(3)	C(6)–C(7)	1.507(4)
C(2)–N(3)	1.495(3)	C(6)–C(10)	1.544(3)
C(2)–C(11)	1.529(4)	C(7)–C(8)	1.316(4)
N(3)–N(4)	1.245(3)	C(9)–C(10)	1.529(4)
N(4)–C(5)	1.484(3)	C(11)–C(12)	1.527(4)
Bond angles			
C(2)–C(1)–C(8)	112.4(2)	C(6)–C(5)–C(12)	118.3(2)
C(2)–C(1)–C(9)	114.6(2)	C(5)–C(6)–C(7)	112.7(2)
C(8)–C(1)–C(9)	107.3(2)	C(5)–C(6)–C(10)	114.2(2)
C(1)–C(2)–N(3)	112.2(2)	C(7)–C(6)–C(10)	107.0(2)
C(1)–C(2)–C(11)	117.7(2)	C(6)–C(7)–C(8)	118.2(2)
N(3)–C(2)–C(11)	107.7(2)	C(1)–C(8)–C(7)	117.9(2)
C(2)–N(3)–N(4)	118.3(2)	C(1)–C(9)–C(10)	113.2(2)
N(3)–N(4)–C(5)	118.4(2)	C(6)–C(10)–C(9)	112.9(2)
N(4)–C(5)–C(6)	111.6(2)	C(2)–C(11)–C(12)	111.4(2)
N(4)–C(5)–C(12)	108.0(2)	C(5)–C(12)–C(11)	112.0(2)

Dihedral angles	
C(2)–C(11)–C(12)–C(5)/C(2)–N(3)–N(4)–C(5)	54.0(1)
C(2)–C(11)–C(12)–C(5)/C(2)–C(5)–C(6)–C(1)	60.3(1)
C(2)–C(5)–C(6)–C(1)/C(2)–N(3)–N(4)–C(5)	65.7(1)
C(1)–C(8)–C(7)–C(6)/C(2)–N(3)–N(4)–C(5)	50.8(1)
C(2)–C(5)–C(6)–C(1)/C(1)–C(8)–C(7)–C(6)	63.5(1)
C(2)–C(5)–C(6)–C(1)/C(1)–C(6)–C(10)–C(9)	62.6(1)
C(1)–C(8)–C(7)–C(6)/C(1)–C(6)–C(10)–C(9)	53.8(1)

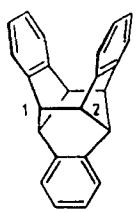
Non-bonding distances

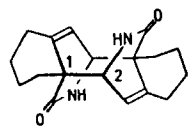
N(3)–C(8) 2.716(3) N(4)–C(7) 2.705(3)

[a]) Numbers in parentheses are estimated standard deviations in the last significant digits.

repulsion: no deviation from C_s symmetry, no pyramidalization of the olefinic positions, and no widening of interplanar angles. The closest transannular N–C distance amounts to 2.710 Å (av.), the interorbital angle ω to 129°. The bisallylic C–C bonds are slightly elongated to 1.58 Å (av.), but still significantly shorter than in related, strongly σ-coupled 1,5-dienes [40]. These structural details come very close to the ones calculated for the carbocyclic *'syn'*-diene **5** (MM2: $d = 2.67$ Å, $\omega = 130°$, C(1)–C(2) = 1.55 Å). The good agreement especially between the d distances, for which the MM2 method predicts in general too short values because of underestimation of π,π repulsion, must be taken as another criterion for the 'isolation' of the *'syn'*-azo/ene subunits in **1**. For comparison, the relevant structural data for several annellated derivatives of **5** are given in *Table 3*.

Table 3. *X-Ray Data of Model Compounds* **I–IV**





		I [41]	**II** [42]	**III** [43]		**IV** [44]
				$n = 1$	$n = 2$	
C(1)–C(2)	[Å]	1.61	1.59_5	1.63	1.62	1.62_3
d	[Å]	–	2.72	2.80	2.71	–
ω	[°]	–	136	129	130	–

PE-Spectra. – The He(Iα) photoelectron (PE) spectra of compounds **1**, **2**, and **37** are displayed in *Fig. 3*. The positions I_j^m of the band maxima (which are close to the vertical ionization energies I_j^v) and the band assignment in terms of *Koopmans'* theorem have been collected in *Table 4*.

The assignment of the PE spectra is rather straightforward. Previous investigations of azo compounds [45] [46], in particular of numerous mono- and polycyclic ones containing a *cis* configurated azo group [47] [51], suggest that the sequence of the outer valence shell orbitals is (in descending order of energy) $\varphi_{HOMO} \approx n_-$, $\varphi_{HOMO\text{-}1} \approx \pi_{NN'}$, $\varphi_{HOMO\text{-}2} \approx n_+$, with the notable exception of molecules in which the azo group is part of a four-membered ring [49]. In the latter case, the orbitals of π_{NN} and n_+ character are interchanged. If the alkyl moiety of the molecule is large, the bands corresponding to the π_{NN}^{-1} and n_+^{-1} ionization processes are imbedded in the σ-band system of the PE spectrum, making it rather difficult to identify them. The results reported in the references quoted above leave no doubt that band ① in the PE spectra of **1** and **2** is due to the ejection of an electron which is dominantly of n_- character which means that the positive hole is mainly localized in the region occupied by the N lone-pairs. Both the ionization energy I_1^m and the halfwidth of band ① are unaffected by the relative positions assumed by the N=N and C=C bonds in **1** and **2**. The bands corresponding to ionization processes which could be labeled π_{NN}^{-1} and

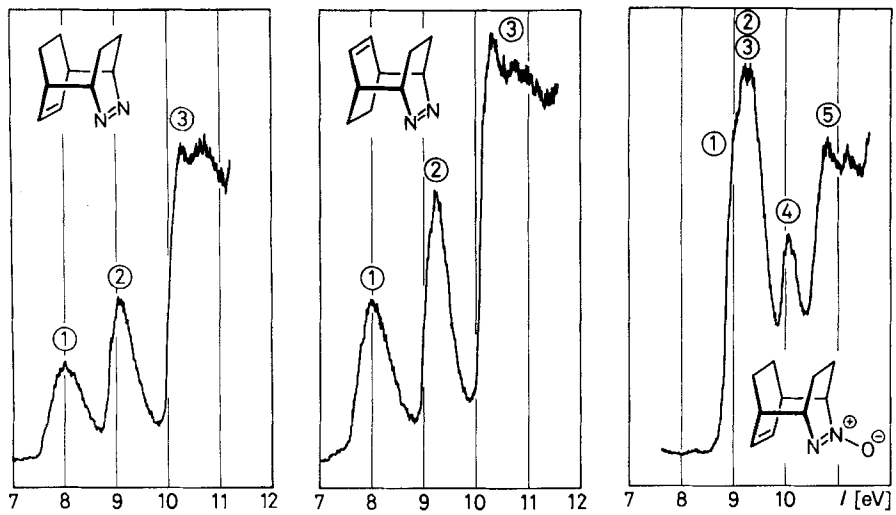


Fig. 3. *PE spectra of* **1**, **2**, *and* **37**

Table 4. *Position* I_j^m *and Assignment of the Bands in the PE Spectra of Compounds* **1**, **2**, *and* **37**. The band numbers refer to those given in *Fig. 3*.

ⓙ	**1**		**2**		**37**	
	I_j^m [eV]	Assignment	I_j^m [eV]	Assignment	I_j^m [eV]	Assignment
①	8.0_0	n_-	8.0_0	n_-	9.1[a])	π_{CC}
②	9.0_5	π_{CC}	9.2_5	π_{CC}	9.3[b])	π_{NNO}[c])
③	10.3		10.3			$n_{NNO,+}$[c])
④					10.0_5	$n_{NNO,-}$
⑤					10.8	?

[a]) Shoulder.
[b]) Slightly split by $\Delta I \approx 0.2$ eV.
[c]) Order uncertain.

n_+^{-1} are both expected to occur in the interval *ca.* 10.5–11.4 eV, *i.e.* close to the position I_3^m of band ③. It is not possible, however, to deconvolute this part of the PE spectrum in a meaningful way. Accordingly, band ② has to be assigned to the removal of an electron from the π_{CC} orbitals of **1** and **2** which, of course, hyperconjugate extensively with the σ orbitals of the molecular framework. The observed values I_2^m (**1**) = 9.0_5 eV and I_2^m (**2**) = 9.2_5 eV are in perfect agreement with the considerable body of information about π ionization energies of unsaturated hydrocarbon-related systems (*e.g.* [52] and ref. given therein).

The PE spectra of cyclic [53] and bicyclic azo *N*-oxides (and azo *N*,*N'*-dioxides) [54] have been reported previously (*cf.* also [57]). The low-energy part of the spectrum of the

N-oxides of 2,3-diazabicyclo[2.2.*n*]alk-2-enes consists of a double band ①, ② in the interval $I^m_{1,2} \approx 9.2$–9.7 eV followed by a single band ③ at $I^m_3 \approx 10.7$–10.0 eV, depending on the size *n* of the second methylene chain. In particular, one finds for $n = 2$ [54] $I^m_1 = 9.3$ eV, $I^m_2 = 9.4$ eV, $I^m_3 = 10.3$ eV. According to the assignment given in [54], the first two bands are associated with electron ejection from the orbitals π_{NNO} and $n_{NNO,+}$ (order uncertain, the third one with $n_{NNO,-}$). Combining this information with that derived from the analysis of the PE spectra of **1** and **2** leads to the following assignment of the spectrum of **37** *(cf. Fig. 3)*. Bands ② and ③ at 9.3 eV are due to the π^{-1}_{NNO} and $n^{-1}_{NNO,+}$ ionization processes, not necessarily in this order. The split $I^m_3 - I^m_2 \approx 0.2$ eV is typical for azo *N*-oxides [54]. Consequently, the shoulder ① at $I^m_1 = 9.1$ eV must be due to electron ejection from π_{CC} which agrees with the expectation that this ionization energy should be the same as that of band ② in the PE spectrum of **1**, within the limits of error. Band ④ at $I^m_4 = 10.0_5$ eV corresponds to the process $n^{-1}_{NNO,-}$, and finally the band system starting with band ⑤ ($I^m_5 \approx 10.8$ eV) contains again the bands associated with electron ejection from lower-lying NNO and σ-frame orbitals.

One of the questions that seems to suggest itself is, whether there is a noticeable 'through-space' interaction between the π_{CC} and π_{NN} orbitals in **1** which would be absent in **2**, or in other words, whether the small shift of −0.2 eV of band ② ongoing from **2** to **1** (*cf. Fig. 3* and *Table 4*) could be interpreted in these terms. Although such an interpretation has been attempted in a similar case [50], we are of the opinion that this cannot be done with confidence for the following reasons.

Whatever the size of the 'through-space' coupling term $\langle \pi_{CC}\, H\, \pi_{NN} \rangle$ is, it must be much smaller than the π_{CC} and π_{NN} orbital energy shift due to the 'through-bond' interaction with the 16 framework σ orbitals of A' symmetry within the group C_s. For instance, the latter type of interaction shifts the π_{CC} orbital by *ca.* 1.5 eV from its basis energy −10.5 eV to *ca.* −9.0 eV. A similar displacement in energy is expected for π_{NN}. In view of the large number and dense population of the 16 relay σ orbitals, it is by no means obvious whether the π_{CC} and π_{NN} basis orbitals are in-phase or out-of-phase in the linear combination giving rise to band ② in the PE spectrum of **1**. Accordingly it is an open question whether a 'through-space' interaction would lead to a positive or negative shift of the band position.

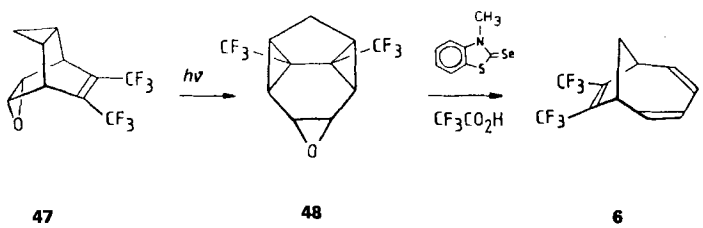
Quite apart from this, the size of the 'through-space'-conditioned shift must be small because of the following reasons. The cross-term $\langle \pi_{CC}\, H\, \pi_{NN} \rangle$ is much smaller than $\langle \pi_{CC}\, H\, \pi_{CC} \rangle$ in the case of polycyclic dienes with similar spatial relationship of two double bonds, due to the contraction of the π_{NN} basis orbital. Furthermore, because of the large separation in energy of the π_{CC} and π_{NN} basis orbitals, the contribution of π_{NN} to the linear combination associated with band ② is very small, which further reduces the size of a potential 'through-space'-induced shift. In fact, rather simple *Hückel*-type calculations suggest that the 'through-space' interaction can be neglected. It is much more probable that the observed difference of 0.2 eV in the positions of band ② in **1** and **2** is due to changes in 'through-bond' interaction. Anyway, no one in its right mind would bother about it.

Conclusion. – Why do **1**, **3**, and **37**, in contrast to 1,6-azo/enes **C** and to analogous carbocyclic 1,5-dienes **B**, not undergo [2 + 2] photocycloadditions? Are the reasons – non-concerted pathways excluded *a priori* – 'electronic' (mainly 'through-bond' effect with

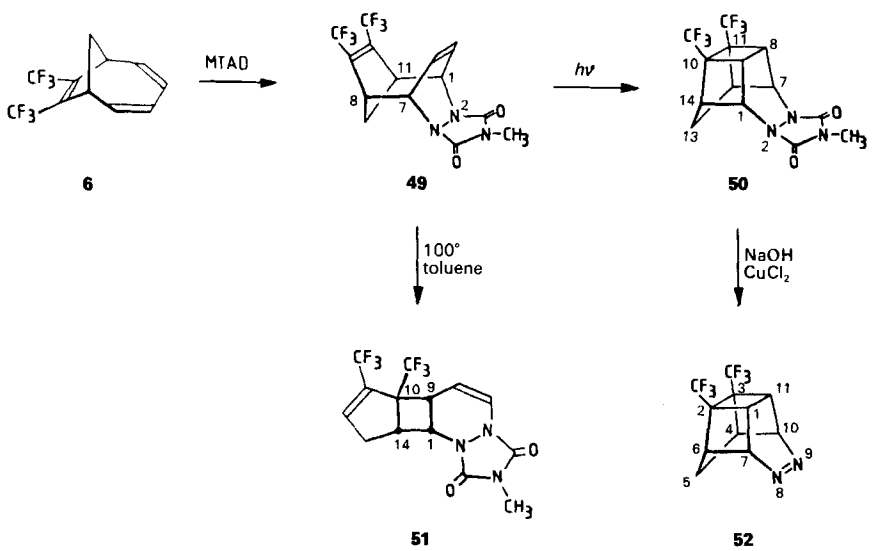
reversal of the orbital ordering and transannular antibonding LUMO π^*-linear combination), 'stereoelectronic' (insufficient π,π interaction), or 'thermodynamic' (the pericyclic minimum lies too high energetically) parameters? Whatever the reasons are, as quintessence it can be stated, that for [2 + 2] cycloadditions the steric/stereoelectronic demands of the N=N functionality are significantly more stringent than that of the C=C bond and that in 1,5-azo/ene skeletons of type **B**, these conditions are not sufficiently met. It should be mentioned that in a parallel study for the mono- and bisbenzo-annellated, variably X,X-bridged dienes **B**, no [6 + 2]/[6 + 6] cycloaddition could be brought about photochemically [31] – with the very same uncertainties as to a rational explanation.

Appendix. On the Stereochemistry of MTAD Additions to Bicyclo[4.2.1]nona-2,4,7-triene Skeletons. – The bis(trifluoromethyl)[4.2.1]triene **6** became available *via* [$_\pi$2 + $_\sigma$2] photoaddition **47**→**48** [56] and subsequent deoxygenation with 3-methylbenzothiazole-2-selone/CF_3COOH [57] *(Scheme 9)*. With MTAD, the *'syn'*-1,5-diene **49** was formed in almost quantitative yield. The configuration was derived from efficient acetone-sensitized [2 + 2] cycloaddition to the hexacycle **50** (80%) and *Cope* rearrangement to **51** (toluene, 100°, 80%). Oxidative saponification of **50** (NaOH; $CuCl_2$; NH_3) led to the thermally labile azo compound **52** in modest yield (31%; *Scheme 9*).

Scheme 9



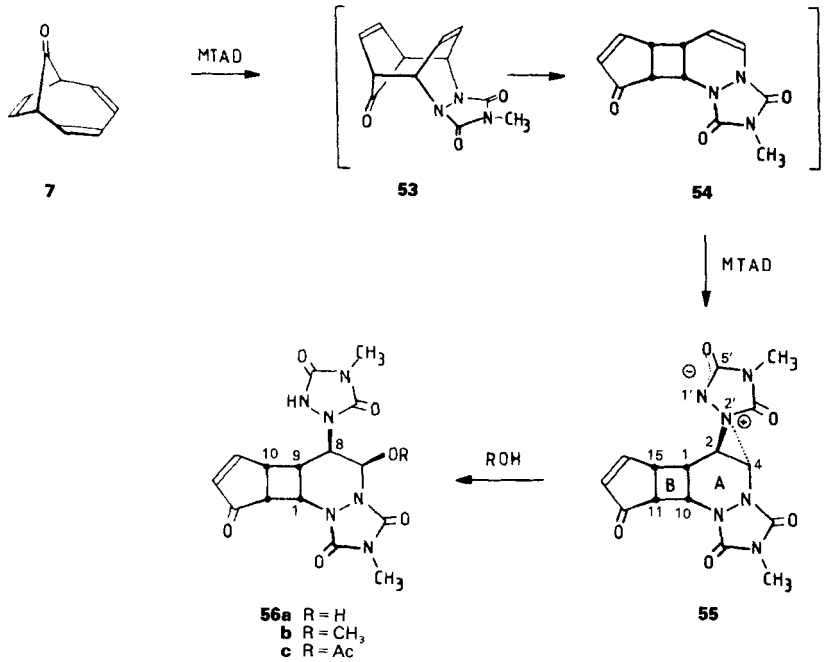
47 **48** **6**



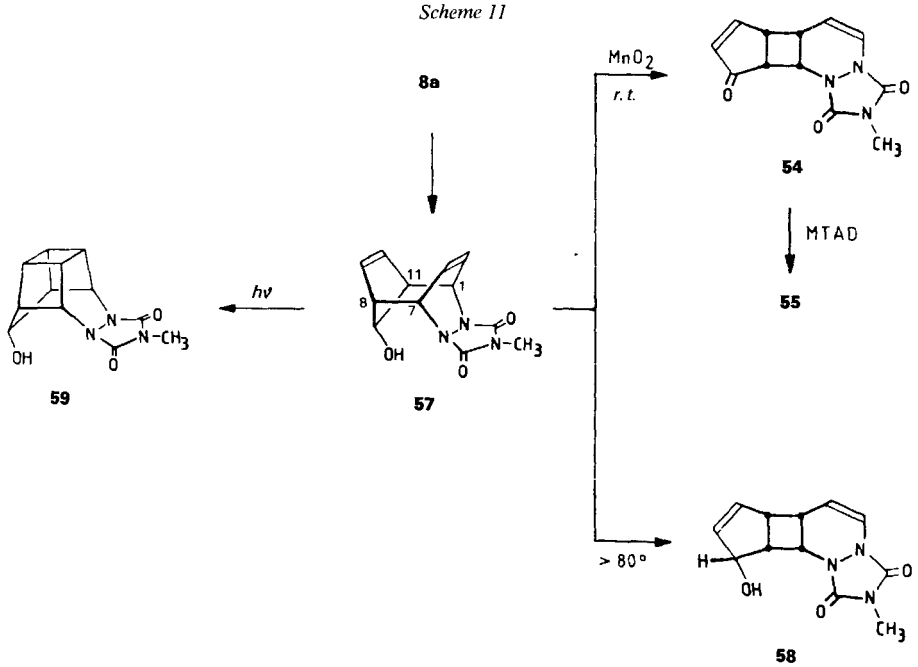
6 **49** **50**

51 **52**

Scheme 10



Scheme 11

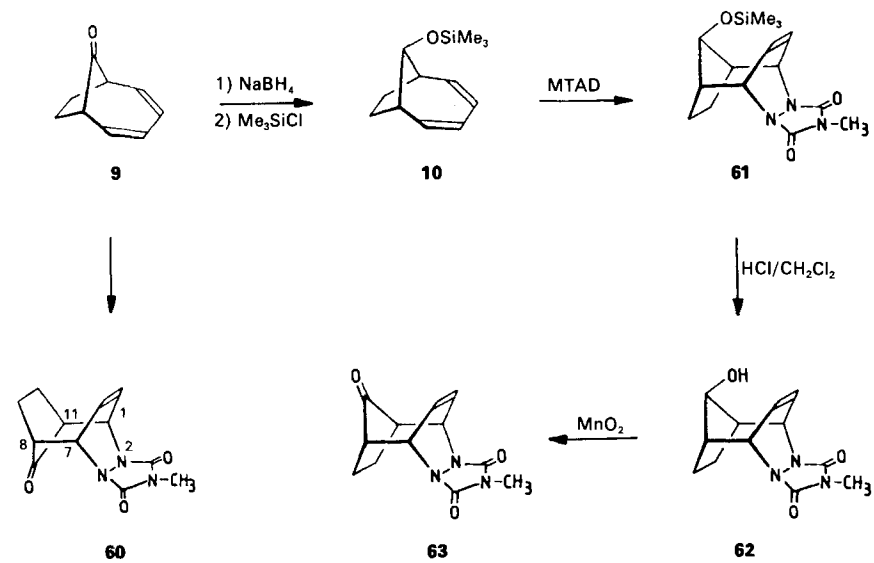


The trienone **7** – readily available from cyclooctatetraene [28] – reacted with an excess of MTAD (> 2 equiv.) in acetone at 20° to furnish almost quantitatively a hardly soluble, mesoionic 1:2 adduct **55** which was sensitive to moisture or protic solvents (formation of corresponding adducts **56a–c**; *Scheme 10*). Though there are still uncertainties with regard to the exact ylide substructure in **55**, we prefer the formulation as an aziridinium ylide [58]. The primary [4 + 2] addition to the diene's *exo* face is the slowest step, since **55** was formed irrespectively of MTAD equivalents present. Clearly, the high rate of the *Cope* rearrangement in the 1:1 adduct **53** limitates the preparative exploitation with regard to the actual target molecule **1**; the literature offers several analogies [59], as well as for the rapid [2 + 2] MTAD addition to the electron-rich 'ene-amid' double bond in **54** [58] *(Scheme 10)*.

syn-Alcohol **8a** [28] added MTAD in CH_2Cl_2 at room temperature slowly but selectively from the *exo*-face to yield 77% of the stable 1:1 adduct **57** *(Scheme 11)*, while the methoxy derivative **8b** [28] with its effective *exo*/*endo*-shielding proved resistent towards MTAD, even on prolonged heating at 60° (AcOEt). *Cope* rearrangement to **58** (toluene, 106°, 5 h; 75%) and acetone-sensitized [2 + 2] cycloaddition (λ 300 nm; *Rayonet*, quartz) to hexacycle **59** substantiated the *'syn'*-configuration of 1,5-diene **57** (> 95%). With MnO_2 in CH_2Cl_2 at 20°, the sterically compressed OH function in **57** was readily oxidized to give **54** (82%) *via* ketone **53**; as expected, from **54** and MTAD, the adduct **55** is obtained spontaneously at 20° (83%, *Scheme 11*).

With dienone **9**, MTAD addition occurred exclusively from the *exo*-side (91% of **60**), with its Me_3Si ether **10** selectively from the *endo*-face (besides 62% of **61**, *ca.* 10% of **62**; *Scheme 12*). Ether **61** was cleaved to **62** in the two-phase system CH_2Cl_2/conc. HCl within a few min; nucleophilic transannular additions [60] did not intervene under these conditions. By MnO_2 oxidation, the ketone **63**, a regioisomer of **60**, is obtained (83%; *Scheme 12*).

Scheme 12



Attempts to transform **60** or related tricycles to key compound **15** *(Scheme 3)* had failed due to the severely reduced reactivity of the carbonyl group in nucleophilic additions. Ketone **15** was obtained, however, in a rather cumbersome multistep sequence starting from hexacyclic compound **59** [61].

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Experimental Part

General. Photolyses were routinously performed in N_2-purged, highly purified solvents; EPA glass: Et_2O/isopentane/EtOH 5:5:2 [63]. Anal. TLC: *Merck* silica gel plates with *QF-254* indicator. Flash chromatography (FC): 0.04–0.06 mm silica gel, *Macherey-Nagel.* Anal. GC: *Varian 3700,* glass capillary column 25 m, *OV17,* FID; integrator *Varian CDS 111.* M.p.: *Bock-Monoscop M;* uncorrected. UV: *Zeiss DMR 21;* λ_{max} in nm (ε). IR: *Perkin-Elmer-457* grating IR spectrometer; unless otherwise stated, KBr pellets; in cm^{-1}. ^{1}H-NMR: *Varian EM 390, 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 J in Hz. ^{15}N-NMR: *Bruker WM* 400; [^{15}N]nitromethane (δ 380.2 ppm) as external standard. Unless otherwise stated NMR spectra were taken in $CDCl_3$; the values marked with an asterisk * are interchangeable. MS: *Finnigan MAT 44S* at 70 eV.

*14-Hydroxy-4-methyl-*trans-*1-*cisoid-*1,7-*trans-*7-2,4,6-triazatetracyclo[5.4.2.2^{8,11}.0^{2,6}]pentadeca-9,12-diene-3,5-dione* (**14**). A soln. of **12** (108 mg, 0.72 mmol) [28] in $CHCl_3$ (5 ml) was stirred with MTAD [64] (80 mg, 0.71 mmol) for 15 min at 50–60°. After that time, MTAD was consumed and unsoluble material precipitated. For completion, additional MTAD (40 mg, 0.35 mmol) was added. After 10 min at 50°, solvent was evaporated to afford crude **14** containing insoluble material. ^{1}H-NMR (250 MHz): 6.09–5.86 (*m*, 4 H); 5.25–5.13 (*m*, 2 H); 4.12 (*m*, 1 H); 3.37–3.14 (*m*, 3 H); 3.07 (*s*, 3 H); 2.29 (*ddd*, 1 H); 1.90 (*dd*, 1 H).

*4-Methyl-*cis-*1-*cisoid-*1,9-*cis-*9-2,4,6-triazatetracyclo[7.6.0.0^{2,6}.0^{10,15}]pentadeca-7,11-diene-3,5,13-trione* (**16**). The crude **14** was stirred with MnO_2 (15 g, 0.17 mol) in $CHCl_3$ (20 ml) for 3 h. Solids were removed by suction filtration and the residue, after solvent evaporation, subjected to FC (CH_2Cl_2/acetone 3:1, R_f 0.32). Recrystallization from EtOH gave **16** (38 mg, 20%). M.p. 167°. IR: 1760, 1700, 1670, 1470, 1390, 1285, 1240, 750. ^{1}H-NMR (250 MHz): 6.96 (*dd*, H–C(7)); 6.63 (*ddd*, H–C(11)); 6.13 (*dd*, H–C(12)); 5.05 (*dd*, H–C(8)); 4.69 (*m*, H–C(1)); 3.69 (*m*, H–C(9)); 3.51–3.31 (*m*, H–C(10), H–C(15)); 3.09 (*s*, CH_3N); 2.77 (*dd*, H_α–C(14)); 2.42 (*dd*, H_β–C(14)); $J(1,9) = J(15,10) = 7.5$, $J(7,8) = 8.5$, $J(7,9) = 1.5$, $J(8,9) = 5$, $J(10,11) = 4.5$, $J(11,12) = 10.5$, $J(14,14) = 18$, $J(14\beta,15) = 8.5$, $J(14\alpha,15) = 3$. Anal. calc. for $C_{13}H_{13}N_3O_3$ (259.3): C 60.23, H 5.05, N 16.21; found: C 59.84, H 4.82, N 16.27.

15 *from* **14**. Crude **14** (obtained from dropwise addition of a soln. of MTAD (2.1 g, 17.7 mmol) in $CHCl_3$ (20 ml) to **12** (2.6 g, 17.5 mmol) in $CHCl_3$ (20 ml) within 2 h at 50° and solvent evaporation) was hydrogenated in MeOH in the presence of 10% Pd/C and subsequently oxidized with MnO_2 (20 g) in CH_2Cl_2 for 4.5 h at r.t.: 1.2 g (26%) of **15**. Spectral data: see below.

Bicyclo[4.2.2]deca-2,4-dien-7-one (**13**). Into a stirred soln. of LiCl (1.1 g, 25.9 mmol) and **7** [29] (10.2 g, 76.1 mmol) in MeOH/CH_2Cl_2 3:1 (150 ml) at 0°, *ca.* 200 ml of a freshly prepared CH_2N_2 soln. in Et_2O [65] were distilled within 3 h. After 12 h, excessive CH_2N_2 was destroyed by cautiously adding HCO_2H. The org. layer was repeatedly washed with H_2O and $NaHCO_3$ soln., dried (Na_2SO_4), and evaporated. The waxy residue was distilled at 140°/10^{-2} Torr into an ice-cooled 'Säbelkolben': 10.5 g (93%) of **13** (GC purity *ca.* 90%); the product was used without further purification. ^{1}H-NMR (250 MHz): 5.95–5.64 (*m*, 4 H); 3.09 (*m*, 1 H); 2.93–1.75 (*m*, 7 H).

17 *and* **18** *from* **13**. To a stirred soln. of **13** (15.2 g, 0.103 mol; purity *ca.* 90%) in acetone (100 ml) at r.t., MTAD (11.3 g, 0.10 mol) was added within 4 h. After stirring overnight, the mixture (2 components) was diluted with CH_2Cl_2 (20 ml), filtered through a short pad of bas. Al_2O_3 (act. III, CH_2Cl_2/acetone 3:1), and evaporated. From CH_2Cl_2/hexane, **17** crystallized purely, but incompletely (7.5 g). The mother liquor was evaporated and the residue subjected to FC (CH_2Cl_2/acetone 3:1) yielding **17** (total: 12.2 g, 47%) and **18** (9.7 g, 36%).

*4-Methyl-*cis-*1-*cisoid-*1,7-*cis-*7-2,4,6-triazatetracyclo[5.4.2.2^{8,11}.0^{2,6}]pentadec-12-ene-3,5,9-trione* (**17**). R_f 0.36 (CH_2Cl_2/Aceton 3:1). M.p. 238° (subl.; from i-PrOH). IR: 2935, 1760, 1700, 1460, 1390, 1255, 1115, 1000, 807, 745. ^{1}H-NMR (250 MHz): 6.63 (*t*, H–C(12)*); 6.47 (*t*, H–C(13)*); 5.27–5.18 (*dd*, H–C(1), H–C(7)); 3.27 (*dd*, H–C(8)); 3.12 (*m*, H–C(11)); 3.02 (*s*, CH_3N); 2.88 (*dt*, H_α–C(10)); 2.31 (*dd*, H_β–C(10)); 2.04–1.87 (*m*, H_{syn}–C(14), H_{syn}–C(15)); 1.85–1.64 (*m*, H_{anti}–C(14), H_{anti}–C(15)); $J(1,11) = J(7,8) = 11.5$, $J(1,12) = J(7,13) = 7.5$, $J(10,10) = 19$, $J(10\alpha,11) = 2$, $J(10\beta,11) = 4.5$. Anal. calc. for $C_{13}H_{15}N_3O_3$ (261.3): C 59.76, H 5.78, N 16.08; found: C 59.44, H 5.70, N 15.96.

*4-Methyl-*trans-*1-*cisoid-*1,7-*trans-*7-2,4,6-triazatetracyclo[5.4.2.2^{8,11}.0^{2,6}]pentadec-12-ene-3,5,9-trione* (**18**). R_f 0.26 (CH_2Cl_2/acetone 3:1). M.p. 209° (subl.; from i-PrOH). IR: 2930, 1760, 1690, 1450, 1394, 1265, 1180, 808, 745. ^{1}H-NMR (250 MHz): 6.41–6.24 (*m*, H–C(12), H–C(13)); 5.27 (*dd*, H–C(1)); 5.10 (*dd*, H–C(7)); 3.20 (*dd*, H–C(8)); 3.10 (*s*, CH_3N); 3.02 (*m*, H–C(11)); 2.36 (*dt*, H_α–C(10)); 2.36–2.13 (*m*, H_{syn}–C(14), H_{syn}–C(15)); 2.15 (*dd*, H_β–C(10)); 1.99–1.75 (*m*, H_{anti}–C(14), H_{anti}–C(15)); $J(1,11) = 11$, $J(1,12) = 7.5$, $J(7,8) = 11.5$, $J(7,13) = 7$, $J(10,10) = 19.5$, $J(10\alpha,11) = 2$, $J(10\beta,11) = 4.5$. Anal. calc. for $C_{13}H_{15}N_3O_3$ (261.3): C 59.76, H 5.78, N 16.08; found: C 59.49, H 5.71, N 15.76.

*4-Methyl-*cis-*1-*cisoid-*1,9-*cis-*9-2,4,6-triazatetracyclo[7.6.0.0^{2,6}.0^{10,15}]pentadeca-7,11-dien-11-yl Acetate* (**19**). The soln. of **18** (1.1 g, 4.2 mmol) in isopropenyl acetate (20 ml) and TsOH (35 mg) was kept at 95° for 60 h under N_2.

After concentration, the residue was filtered through a short pad of SiO_2 with AcOEt and crystallized from Et_2O: 830 mg (65%) of **19**. M.p. 132–134°. IR: 1750, 1700, 1470, 1440, 1390, 1345, 1310, 1208, 745. ^{1}H-NMR (250 MHz): 6.91 (*dd*, H–C(7)); 5.63 (*t*, H–C(12)); 5.24 (*dd*, H–C(8)); 4.91 (*'t'*, H–C(1)); 3.39 (*m*, H–C(9)); 3.13 (*s*, CH_3N); 3.18–3.04 (*m*, H–C(10), H–C(15)); 2.14 (*s*, AcO–C(11)); 2.09 (*m*, 2 H); 1.63 (*m*, 1 H); 1.46 (*m*, 1 H); $J(1,9) \approx J(1,15) \approx J(7,8) \approx 8.5$, $J(7,9) = 2$, $J(8,9) \approx 4.5$. Anal. calc. for $C_{15}H_{17}N_3O_3$ (287.3): C 62.71, H 5.96, N 14.63; found: C 62.65, H 5.82, N 14.65.

*4-Methyl-*cis-*1-*cisoid-*1,7-*cis-*7-2,4,6-triazatetracyclo[5.4.2.2^{8,11}.0^{2,6}]pentadecane-3,5,9-trione* (**15**). A suspension of **17** (12.1 g, 46.3 mmol) in MeOH (150 ml) was hydrogenated over 10% Pd/C (*ca.* 100 mg) at 20°. The catalyst was filtered off and the residue recrystallized from i-PrOH: 11.8 g (97%) of **15**. M.p. 184°. IR: 2910, 1755, 1683, 1445, 1385, 1290. ^{1}H-NMR (250 MHz): 4.86 (*dd*, H–C(1)*); 4.75 (*dd*, H–C(7)*); 3.07 (*s*, CH_3); 3.01 (*m*, H–C(8)); 2.85 (*m*, H–C(11)); 2.63 (*dt*, H_α–C(10)); 2.38–1.71 (*m*, H_β–C(10), CH_2(12), CH_2(13), CH_2(14), CH_2(15)); $J(1,11) \approx J(7,8) \approx 10.5$, $J(10,10) \approx 18$. Anal. calc. for $C_{13}H_{17}N_3O_3$ (263.3): C 59.30, H 6.50, N 15.96; found: C 59.11, H 6.35, N 16.09.

*4-Methyl-*trans-*1-*cisoid-*1,7-*trans-*7-2,4,6-triazatetracyclo[5.4.2.2^{8,11}.0^{2,6}]pentadecane-3,5,9-trione* (**20**). As for **15** with **18** (11.2 g, 42.9 mmol), MeOH (150 ml), and 10% Pd/C (*ca.* 100 mg): 10.2 g (90%) of **20**. M.p. 204° (subl.). IR: 2930, 1748, 1685, 1460, 1389, 1318, 1300, 1190, 1004, 739. ^{1}H-NMR (250 MHz): 4.85 (*dd*, H–C(1)*); 4.75 (*dd*, H–C(7)*); 3.17 (*s*, CH_3); 2.96–2.88 (*m*, H–C(8), H–C(11)); 2.79 (*dt*, H_α–C(10)); 2.36 (*dd*, H_β–C(10)); 2.10–1.71 (*m*, CH_2(12), CH_2(13), CH_2(14), CH_2(15)); $J(1,11) \approx J(7,8) \approx 10.5$, $J(10,10) \approx 19.5$, $J(10\beta,11) \approx 4.5$, $J(10\alpha,11) \approx 2$. Anal. calc. for $C_{13}H_{17}N_3O_3$ (263.3): C 59.30, H 6.50, N 15.96; found: C 58.99, H 6.43, N 16.17.

*4-Methyl-9-[(4-methylphenylsulfonyl)hydrazono]-*cis-*1-*cisoid-*1,7-*cis-*7-2,4,6-triazatetracyclo[5.4.2.2^{8,11}.0^{2,6}]-pentadecane-3,5-dione* (**21**). A suspension of **15** (14.5 g, 55.1 mmol), $TsNHNH_2$ (11.5 g), and 5 drops of conc. HCl soln. in THF (100 ml) was stirred for 2 d at r.t. and 3 h at 60°. The colorless precipitate was dried *in vacuo* and used for the preparation of **1** without further purification: 20.3 g (85%) of **21**. M.p. 283° (from MeOH). IR: 3440, 3110, 2930, 1745, 1675, 1465, 1400, 1332, 1292, 1160, 1010, 917, 810, 733. ^{1}H-NMR (250 MHz; (*E*)/(*Z*) 5:1): 8.48 (*s*, NH (*E*)); 8.12 (*s*, NH (*Z*)); 7.87–7.80, 7.35–7.27 (*AB*, 4 H (*E*)/(*Z*)); 4.90–4.61 (*m*, 2 H (*E*)/(*Z*)); 3.18–1.52 (*m*, 12 H (*E*)/(*Z*)); 3.13 (*s*, CH_3N (*Z*)); 2.93 (*s*, CH_3N (*E*)); 2.43 (*s*, CH_3 (*Z*)); 2.42 (*s*, CH_3 (*E*)). Anal. calc. for $C_{19}H_{20}N_5O_4S$ (431.5): C 55.67, H 5.84, N 16.23; found: C 54.07, H 6.25, N 15.32.

*4-Methyl-9-[(4-methylphenylsulfonyl)hydrazono]-*trans-*1-*cisoid-*1,7-*trans-*7-2,4,6-triazatetracyclo[5.4.2.2^{8,11}.0^{2,6}]pentadecane-3,5-dione* (**22**). As for **21** with **20** (11.2 g, 42.7 mmol), $TsNHNH_2$ (8.5 g, 45.7 mmol), and 5 drops of conc. HCl soln. in THF (75 ml): 15.5 g (84%) of **22**. M.p. 286°. IR: 3430, 3180, 2950, 1738, 1675, 1475, 1420, 1400, 1338, 1320, 1169, 1025, 938, 740. Anal. calc. for $C_{20}H_{25}N_5O_4S$ (431.5): C 55.67, H 5.84, N 16.23; found: C 55.68, H 5.82, N 16.04.

*4-Methyl-*trans-*1-*cisoid-*1,7-*trans-*7-2,4,6-triazatetracyclo[5.4.2.2^{8,11}.0^{2,6}]pentadec-9-ene-3,5-dione* (**23**). A mixture of **22** (1.16 g, 2.8 mmol) in MeOH (10 ml) and 1M NaOMe/MeOH (3 ml) was stirred until the soln. had cleared up. After solvent evaporation, the semisolid residue was dried *in vacuo*, pulverized, suspended in diglyme (20 ml), and heated to 160° for 2 h. Solvent was distilled off *in vacuo* and the residue partitioned between CH_2Cl_2/H_2O. The org. layer was dried (Na_2SO_4) and concentrated to leave a solid which was subjected to FC (CH_2Cl_2/acetone 3:1, R_f 0.35): 287 mg (43%) of **23**. M.p. 151°. IR: 3035, 2940, 1752, 1690, 1470, 1458, 1395, 1300, 849, 760, 730. ^{1}H-NMR (250 MHz): 6.37 (*m*, H–C(9), H–C(10)); 4.77 (*m*, H–C(1), H–C(7)); 3.15 (*s*, CH_3N); 3.02 (*m*, H–C(8), H–C(11)); 2.03 (*m*, H_{syn}–C(14), H_{syn}–C(15)); 1.81 (*m*, H_{anti}–C(12), H_{anti}–C(13)); 1.69 (*m*, H_{syn}–C(12), H_{syn}–C(13)); 1.42 (*m*, H_{anti}–C(14), H_{anti}–C(15)). Anal. calc. for $C_{13}H_{17}N_3O_3$ (247.3): C 63.14, H 6.93, N 16.99; found: C 62.81, H 6.84, N 16.78.

cis-*1-*cisoid-*1,6-*cis-*6-3,4-Diazatricyclo[4.2.2.2^{2,5}]dodec-3-en-7-one* (**24**). Under N_2, **15** (2.8 g, 10.6 mmol) and NaOH (1.5 g, 37.5 mmol) in i-PrOH (50 ml) were refluxed for 3.5 h. After addition of H_2O (300 ml), the mixture was neutralized with 2N HCl, brought to pH ≈ 9 by addition of conc. NH_3, and extracted thoroughly with CH_2Cl_2 (TLC control of the aq. phase; detection of the resulting semicarbazide *7-oxo-*cis-*1-*cisoid-*1,6-*cis-*6-3,4-diazatricyclo[4.2.2.2^{2,5}]dodecane-4-(*N-methyl)carboxamide:* ^{1}H-NMR (250 MHz): 5.95 (*m*, 1 H); 5.18 (br. *s*, 1 H); 4.52 (*t*, 1 H); 3.73 (*t*, 1 H); 2.81 (*m*, 1 H); 2.74 (*d*, 3 H); 2.27 (*q*, 1 H); 2.17–1.32 (*m*, 10 H); with 5% $CuCl_2$ soln. in EtOH; R_f 0.3 (acetone)). The extract was dried (Na_2SO_4), concentrated to *ca.* 50 ml and stirred with act. MnO_2 (18 g, 0.2 mol, *Merck*) for 4.5 h at r.t. The MnO_2 cake was thoroughly washed with CH_2Cl_2, the solvent evaporated, und the crystalline residue sublimed at 80°/*ca.* 10^{-3} Torr: 1.4 g (74%) of **24**. M.p. 205° (pale yellow crystals; subl., dec.). UV (MeCN): 399 (75), 295 (sh, 26); $\varepsilon_{254} = 136$. UV (MeOH): 395 (62), 295 (sh, 32); $\varepsilon_{254} = 147$. IR: 2930, 1710, 1480, 1460, 1400, 1365, 1335, 1320, 1235, 1215, 1193, 1185, 1100. ^{1}H-NMR (400 MHz): 5.66 (*dd*, H–C(2)); 5.55 (*dd*, H–C(5)); 3.03 (*m*, H–C(6)); 2.78 (*m*, H–C(1)); 2.45 (*dt*, H_α–C(8)); 2.30 (*dt*, H_{syn}–C(10)); 2.23 (*m*, H_{syn}–C(9)); 2.13 (*m*, H_{syn}–C(11), H_{syn}–C(12)); 2.01 (*dd*, H_β–C(8)); 1.78 (*m*, H_{anti}–C(10)); 1.62 (*m*, H_{anti}–C(9)); *ca.* 1.47 (*m*, H_{anti}–C(11), H_{anti}–C(12)); $J(1,2) = 11$, $J(1,8\alpha) \approx 2$, $J(1,8\beta) \approx J(6,10a) \approx J(1,9a) \approx 5$, $J(2,11a) \approx 6$,

$J(5,6) = 12$, $J(5,12a) \approx 6.5$, $J(8,8) = 19.5$. ^{13}C-NMR (100 MHz): 211.41 (C(7)); 63.66 (J(C,H) = 147.6, C(2)); 62.48 (J(C,H) = 150, C(5)); 51.52 (J(C,H) = 138, C(6)); 40.37 (J(C,H) = 127, 134, C(8)); 32.66 (J(C,H) = 134, C(1)); 22.53 (J(C,H) = 135, C(9)); 21.05 (J(C,H) = 135, C(10)); 17.55, 15.39 (J(C,H) = 135, C(11), C(12)); J(C(2),C(5)) = 18.7. ^{15}N-NMR (44.6 MHz): 545.72 (N(3)); 535.66 (N(4)). Anal. calc. for $C_{10}H_{14}N_2O$ (178.2): C 67.39, H 7.92, N 15.72; found: C 66.98, H 8.08, N 15.62.

trans-*1*-cisoid-*1,6*-trans-*6-3,4-Diazatricyclo[4.2.2.2^{2,5}]dodec-3-en-7-one* (**25**). Under N_2, **20** (5.3 g, 10.6 mmol) and NaOH (1.5 g, 37.5 mmol) in *i*-PrOH (50 ml) were refluxed for 3.5 h. The cooled mixture was acidified with 2N HCl to pH ≈ 5 and stirred, after addition of a soln. of $CuCl_2$ (30 g, 0.2 mol) in H_2O (200 ml), for 3 h at r.t. Conc. NH_3 was added until a deep blue soln. persisted. The aq. phase was thoroughly extracted with CH_2Cl_2 and the extract washed with brine and dried (Na_2SO_4). Solvent evaporation left a brownish solid which was purified by filtration over silica gel (CH_2Cl_2/acetone 3:1, R_f 0.5) and sublimation at 80°/10^{-2} Torr: 2.4 g (67%) of **25** as slightly yellow crystals. M.p. *ca.* 200° (subl., dec.). UV (MeCN): 399 (50), 304 (78); $\varepsilon_{254} = 220$. UV (MeOH): 395 (45), 302 (77); $\varepsilon_{254} = 203$. IR: 2945, 2878, 1710, 1549, 1468, 1368, 1325, 1112, 820. ^{1}H-NMR (400 MHz): 5.72 (*m*, H–C(2)); 5.55 (*m*, H–C(5)); 3.10 (*m*, H–C(6)); 3.09 (*m*, H–C(1)); 2.77 (*dt*, H_α–C(8)); 2.20 (*dd*, H_β–C(8)); 2.13 (*m*, H_{syn}–C(10)); 2.05 (*m*, H_{syn}–C(9)); 1.82 (*m*, H_{syn}–C(11)); 1.71 (*m*, H_{syn}–C(12)); 1.58–1.48 (*m*, H_{anti}–C(9), H_{anti}–C(10)); *ca.* 1.41 (*m*, H_{anti}–C(11), H_{anti}–C(12)); $J(1,2) \approx J(5,6) \approx 12$, $J(1,8\beta) \approx J(6,10a) \approx 4.5$, $J(1,8\alpha) \approx J(5,12s) \approx 2.5$, $J(2,11a) \approx J(5,12a) \approx 6$, $J(8,8) = 19.5$. ^{13}C-NMR (100 MHz): 213.22 (C(7)); 62.76 (J(C,H) = 146, C(2)); 59.79 (J(C,H) = 150, C(5)); 52.82 (J(C,H) = 136, C(6)); 41.51 (J(C,H) = 128, C(8)); 34.59 (J(C,H) = 135, C(1)); 20.09 (J(C,H) = 133, C(9)); 18.29 (J(C,H) = 133, C(10)); 17.96 (J(C,H) = 133, C(12)); 17.22 (J(C,H) = 133, C(11)); J(C(2),C(5)) = 18.8. ^{15}N-NMR (44.6 MHz): 551.38 (N(4)*); 540.39 (N(3)*). Anal. calc. for $C_{10}H_{14}N_{20}$ (178.2): C 67.39, H 7.92, N 15.72; found: C 67.15, H 7.85, N 15.63.

cis-*1*-cisoid-*1,6*-cis-*6-3,4-Diazatricyclo[4.2.2.2^{2,5}]dodeca-3,7-diene* (**1**) *and 6-(3'-Cyclohexenyl)-1,4,5,6-tetrahydro-1-methylpyridazine* (**26**). To a stirred suspension of **21** (4.8 g, 11.1 mmol) in THF (60 ml), under N_2 and cooled to 10°, $LiAlH_4$ (1.7 g, 45.0 mmol) was added in portions. When H_2 evolution had stopped, the mixture was stirred at 50–55° overnight. The residue, after cautious hydrolysis with H_2O (10 ml) and evaporation of solvent/H_2O, was suspended in CH_2Cl_2 and stirred at 0° with act. MnO_2 (35 g, 0.4 mol) for 4.5 h. Solids were separated by filtration and thoroughly washed with CH_2Cl_2. Solvent evaporation left a yellow oil which was subjected to FC (AcOEt): 843 mg (43%) of **26** (R_f 0.37; yellow oil; further purification by bulb-to-bulb distillation at 80°/10^{-2} Torr) and 415 mg (23%) of **1** (R_f 0.17; pale yellow crystals which sublimed at 60°/10^{-2} Torr).

26: IR (film): 3015, 2919, 2835, 2785, 1615, 1445, 1430, 1310, 935, 762. ^{1}H-NMR (400 MHz): 6.68 (*t*, H–C(3)); 5.67 (*m*, H–C(3'), H–C(4')); 2.87 (*s*, CH_3–N(1)); 2.53 (*m*, H–C(6)); 2.15–1.60 (*m*, 10 H); 1.39 (*m*, 1 H). ^{13}C-NMR (100 MHz): 137.55 (C(3)); 126.92, 126.60 (C(3'), C(4')); 62.20 (C(6)); 44.00 (CH_3); 35.36 (C(1')); 26.15 (C(2')); 26.10 (C(6')); 25.48 (C(5)); 22.91 (C(4)); 18.48 (C(5')). ^{15}N-NMR (44.6 MHz): 345.13 (N(2)); 114.31 (N(1)). MS: *i.a.* 178 (3), 97 (100), 96 (3).

1: M.p. *ca.* 155° (subl.; dec.: **1**→**28**). UV (MeCN): 392 (76); $\varepsilon_{254} = 236$. UV (MeOH): 383 (55), 245 (sh, 346). PES: 8.00, 9.05, 10.3 eV. IR: 3030, 2935, 1625, 1535, 1485, 1470, 1450, 1386, 1360, 1324, 1266, 1169, 821, 734. ^{1}H-NMR (400 MHz): 6.11 (*m*, H–C(7), H–C(8)); 5.43 (*m*, H–C(2), H–C(5)); 2.91 (*m*, H–C(1), H–C(6)); 2.15 (*m*, H_{syn}–C(9), H_{syn}–C(10)); 2.10 (*m*, H_{syn}–C(11), H_{syn}–C(12)); 1.45 (*m*, H_{anti}–C(11), H_{anti}–C(12)); 1.39 (*m*, H_{anti}–C(9), H_{anti}–C(10)); $J(1,2) \approx J(5,6) \approx 10.5$, $J(1,8) \approx J(6,7) \approx 6$, $J(1,7) \approx J(6,8) \approx 3$. ^{13}C-NMR (100 MHz): 134.92 (J(C,H) = 164, C(7), C(8)); 70.20 (J(C,H) = 148, C(2), C(5)); 37.03 (J(C,H) = 135, C(1), C(6)); 22.30 (J(C,H) = 130, C(9), C(10)); 16.98 (J(C,H) = 132, C(11), C(12)). ^{15}N-NMR (44.6 MHz): 525.97 (N(3), N(4)). Anal. calc. for $C_{10}H_{14}N_2$ (162.2): C 74.03, H 8.70, N 17.27; found: C 73.90, H 8.98, N 17.21.

trans-*1*-cisoid-*1,6*-trans-*6-3,4-Diazatricyclo[4.2.2.2^{2,5}]dodeca-3,7-diene* (**2**). To a stirred suspension of **22** (6.45 g, 17.8 mmol) in THF (80 ml), cooled to 10°, $LiAlH_4$ (1.8 g, 44.0 mmol) was added in portions under N_2. Following the procedure described for **1**, 732 mg (25%) of **2** were obtained as pale yellow crystals which were further purified by sublimation at 80°/10^{-3} Torr. M.p. 152° (subl.; dec.). R_f 0.36 (AcOEt). UV (MeCN): 419 (sh, 38), 411 (47); $\varepsilon_{254} = 171$. PES: 8.00, 9.25, 10.3 eV. IR: 3030, 2940, 2875, 1635, 1560, 1505, 1449, 1382, 1334, 840, 820, 750. ^{1}H-NMR (250 MHz): 6.24 (*m*, H–C(7), H–C(8)); 5.54 (*m*, H–C(2), H–C(5)); 3.14 (*m*, H–C(1), H–C(6)); 2.09, 1.97 (*m*, H_{syn}–C(9), H_{syn}–C(10), H_{syn}–C(11), H_{syn}–C(12)); 1.38–1.22 (*m*, H_{anti}–C(9), H_{anti}–C(10), H_{anti}–C(11), H_{anti}–C(12)); $J(1,2) \approx J(5,6) \approx 11$, $J(1,7) \approx J(6,8) \approx 5.5$, $J(1,8) \approx J(6,7) \approx 3$. Anal. calc. for $C_{10}H_{14}N_2$ (162.2): C 74.03, H 8.70, N 17.27; found: C 73.72, H 8.80, N 17.40.

3,4-Diazatricyclo[4.2.2.2^{2,5}]dodec-3-ene (**27**). Diene **2** (35 mg, 0.25 mmol) in MeOH (20 ml) was hydrogenated over 10% Pd/C (*ca.* 20 mg). After 1 h, the catalyst was removed, the solvent evaporated, and the residue dissolved in CH_2Cl_2 (20 ml) and stirred with MnO_2 (8 g) for 2 h. After filtration and solvent evaporation, the solid was sublimed at 80°/10^{-2} Torr: 24 mg (69%) of **27**. M.p. 209–210°. UV (MeCN): 401 (sh, 71), 396 (73); $\varepsilon_{254} = 303$.

^{1}H-NMR (250 MHz): 5.45 (*m*, 2 H); 2.56 (*m*, 2 H); 2.13–2.08 (*m*, 4 H); 1.88 (*m*, 2 H); 1.49 (*m*, 2 H); 1.36–1.22 (*m*, 4 H). Anal. calc. for $C_{10}H_{16}N_2$ (225.3): C 73.12, H 9.81, N 17.06; found: C 73.19, H 9.70, N 16.81.

cis-*2*-cis-*7-1,12-Diazatricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene* (**28**). At 105°, **1** (80 mg, 0.49 mmol) in N_2-purged toluene (10 ml) was stirred for 62 h. Solvent evaporation and FC (AcOEt) afforded 11 mg (14%) of **1** (R_f 0.2) and 27 mg (34%) of **28** (R_f 0.1) as a colorless oil which solidified after short-path distillation (80°/10^{-2} Torr). M.p. 28°. UV (MeCN): 251 (4550). IR (film): 3020, 2925, 2845, 1575, 1430, 1190, 1160, 1092, 1060, 870, 698. ^{1}H-NMR (250 MHz): 6.91 (br. *d*, H–C(11)); 6.12–5.98 (*m*, H–C(3), H–C(4)); 4.70 (br. *d*, H–C(2)); 4.30 (*m*, H–C(8)); 3.02 (*m*, H–C(7)); 2.20–1.42 (*m*, CH_2(5), CH_2(6), CH_2(9), CH_2(10)); J(7,2) ≈ J(7,8) ≈ J(6a,7) ≈ 7, J(10a,11) ≈ J(6b,7) ≈ 5, J(3,4) = 10.5. ^{13}C-NMR (62.8 MHz): 140.65 (J(C,H) = 181, C(11)); 130.94 (J(C,H) = 157, C(4)); 126.19 (J(C,H) = 161, C(3)); 66.53 (J(C,H) = 146, C(2)); 62.38 (J(C,H) = 149, C(8)); 31.38 (J(C,H) = 139, C(7)); 22.83 (J(C,H) = 127, C(10)); 21.61 (J(C,H) = 127, C(5)); 19.09 (J(C,H) = 127, C(9)); 16.71 (J(C,H) = 130, C(7)). Anal. calc. for $C_{10}H_{14}N_2$ (162.2): C 74.03, H 8.70, N 17.27; found: C 74.17, H 8.77, N 17.26.

9-syn-*Methoxybicyclo[4.2.1]nona-2,4-dien-7-one* (**11**). a) *Hydroboration of* **8b**. At 0° under N_2, the stirred soln. of **8b** [28] (26.3 g, 177 mmol) in THF (120 ml) was treated dropwise with 1M BH_3·THF (123 ml, 123 mmol) and stirred for 1.5 h. H_2O was added dropwise until gas evolution ceased, followed by addition of 3N NaOH (41 ml) and dropwise treatment with 35% H_2O_2 (17.1 g, 170.0 mmol) at < 35°. After 2 h stirring, the org. layer was separated and partitioned between CH_2Cl_2/H_2O. The combined aq. layers were saturated with NaCl and extracted thoroughly with CH_2Cl_2; the org. extracts were dried (Na_2SO_4) and evaporated; the waxy residue was subjected to FC (AcOEt/cyclohexane 3:1): 2.1 g (9%) of **8b** (R_f 0.56 (AcOEt)) and 22.6 g (77%) of *9*-syn-*methoxybicyclo[4.2.1]nona-2,4-dien-7*-exo-*ol* (R_f 0.31, AcOEt). M.p. 25–30° (Et_2O/hexane). IR: 3400, 3010, 2920, 2820, 1660, 1595, 1440, 1355, 1320, 1280, 1245, 1205, 1135, 1100, 1030, 1000, 880, 690. ^{1}H-NMR (250 MHz): 5.98–5.75 (*m*, H–C(2), H–C(3), H–C(4), H–C(5)); 4.37 (*t*, H–C(9)); 4.23 (*dd*, H–C(7)); 3.31 (*s*, CH_3O); 2.98 (*m*, H–C(6)); 2.81 (br. *t*, H–C(1)); 2.26 (*ddd*, H_{endo}–C(8)); 1.93 (*m*, H_{exo}–C(8), OH).

b) Swern *Oxidation*. A stirred soln. of oxalyl chloride (21.8 g, 0.16 mol) in CH_2Cl_2 (375 ml) at −70° was treated dropwise with DMSO (28.1 g, 0.36 mol) in CH_2Cl_2 (75 ml) maintaining the temp. < −60°. After an additional 2 min stirring, the *exo*-alcohol (13.5 g, 0.08 mol; see *a)*) in CH_2Cl_2 (80 ml) was added, and after additional 20 min, Et_3N (77 g, 0.76 mol) at < −20°. At r.t., the mixture was diluted with H_2O (400 ml) and thoroughly extracted with CH_2Cl_2. After evaporation the residue was partitioned between Et_2O/aq. K_2CO_3 soln., the org. layer dried (Na_2SO_4), the solvent evaporated, and the resulting yellow oil subjected to FC (AcOEt): 12.7 g (96%) of **11** (R_f 0.47). ^{1}H-NMR (250 MHz): 6.15–5.65 (series of *m*, H–C(2), H–C(3), H–C(4), H–C(5)); 4.20 (*t*, H–C(9)); 3.67 (*m*, H–C(6)); 3.34 (*s*, CH_3O); 3.14 (*m*, H–C(1)); 2.68–2.51 (*m*, H_{endo}–C(8), H_{exo}–C(8)).

2,4-Dinitrophenylhydrazone of **11**. M.p. 192°. IR: 3280, 3090, 3020, 2985, 2920, 2820, 1610, 1580, 1495, 1415, 1335, 1310, 1270, 1200, 1125, 710. ^{1}H-NMR (250 MHz): 9.09 (*d*, J = 2, 1 H); 8.27 (*dd*, J = 9, 2, 1 H); 7.82 (*d*, J = 9, 1 H); 6.13, 5.97 (2*m*, H–C(2), H–C(3), H–C(4), H–C(5)); 4.19 (*dd*, H–C(9)); 3.87 (*m*, H–C(6)); 3.38 (*s*, CH_3O); 3.09 (*m*, H–C(1)); 2.95–2.75 (*m*, CH_2(8)). Anal. calc. for $C_{16}H_{16}N_4O_5$ (344.3): C 55.81, H 4.68, N 16.27; found: C 55.78, H 4.55, N 16.30.

14-'syn'-*Methoxy-4-methyl-*cis-*1-*cisoid-*1,7-*cis-*7-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradec-12-ene-3,5,9-trione* (**30**). At r.t. **11** (12.7 g, 77 mmol) in CH_2Cl_2 (150 ml) was stirred with MTAD (10.4 g, 92 mmol) for 18 h. After solvent evaporation and filtration through a short pad of bas. Al_2O_3 (act. III) with AcOEt, the residue was recrystallized from i-PrOH: 18.9 g (88%) of **30**. M.p. 209° (subl.). R_f 0.25 (AcOEt). IR: 3060, 2980, 2940, 2805, 2740, 1770, 1740, 1700, 1460, 1385, 1270, 1240, 1140, 1025, 995, 950, 795, 755, 700, 615, 525. ^{1}H-NMR (250 MHz): 6.41, 6.25 (2*m*, H–C(12), H–C(13)); 5.14–5.05 (*m*, H–C(1), H–C(7)); 3.68 (*t*, H–C(14)); *ca.* 3.3 (*m*, H–C(11)); 3.25 (*s*, CH_3O); 3.16 (*m*, H–C(8)); 3.00 (*s*, CH_3); 2.84 (*d*, H_α–C(10)); 2.19 (*dd*, H_β–C(10)); J(1,11) = J(7,8) = 9, J(8,14) = J(11,14) = 4, J(10,10) = 18.5, J(10α,11) ≈ 0, J(10β,11) = 11. Anal. calc. for $C_{13}H_{15}N_3O_4$ (277.3): C 55.31, H 5.45, N 15.15; found: C 55.70, H 5.31, N 15.16.

14- 'syn'- *Methoxy-4-methyl-* cis-*1-*cisoid-*1,7-*cis-*7-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradecane-3,5,9-trione* (**31a**). Enetrione **30** (18.6 g, 67.0 mmol) was suspended in MeOH (150 ml) and hydrogenated over 10% Pd/C (*ca.* 200 mg). The catalyst was filtered off and thoroughly washed with CH_2Cl_2. Solvent evaporation gave 18.5 g (99%) of **31a**. M.p. 242° (from i-PrOH). R_f 0.14 (AcOEt). IR: 2980, 2940, 2820, 1700, 1680, 1450, 1390, 1295, 1225, 1140, 1105, 1000, 745. ^{1}H-NMR (250 MHz): 4.80–4.68 (*m*, H–C(1), H–C(7)); 3.72 (*t*, H–C(14)); 3.46 (*s*, CH_3O); 3.21–3.09 (*m*, H–C(8), H–C(11)); 3.07 (*s*, CH_3); 2.63–2.45 (*m*, H_{syn}–C(12), H_{syn}–C(13)); 2.57 (*d*, H_α–C(10)); 2.22 H_β–C(10)); 1.98–1.80 (*m*, H_{anti}–C(12), H_{anti}–C(13)). Anal. calc. for $C_{13}H_{17}N_3O_4$ (279.3): C 55.91, H 6.16, N 15.05; found: C 55.51, H 5.98, N 15.05.

14-'syn'-*Methoxy-4-methyl-9-(tosylhydrazono)-*cis-*1-*cisoid-*1,7-*cis-*7-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]-tetradecane-3,5-dione* (**31b**). For 16 h, **31a** (18.0 g, 64.0 mmol) and $TsNHNH_2$ (13.2 g, 71.0 mmol) in THF (150 ml)

were heated to reflux, after addition of 10 drops of conc. HCl. The precipitate was collected by suction filtration, unreacted starting material removed by washing with cold CH_2Cl_2, and the solid recrystallized from MeOH: 18.3 g (64%; not optimized) of **31b**. M.p. 270° (dec.). IR: 3100, 2980, 2940, 2740, 1740, 1680, 1460, 1340, 1295, 1160, 1125, 1000, 720, 550. ^{1}H-NMR (250 MHz, main isomer): 7.79 (*d*, 2 H_o); 7.30 (*d*, 2 H_m); 4.69–4.57 (*m*, H–C(1), H–C(7)); 3.52 (*t*, H–C(14)); 3.40 (*s*, CH_3O); *ca.* 3.35 (*m*, H–C(8)); 2.96 (*m*, H–C(11)); 2.91 (*s*, CH_3); 2.51 (*m*, H_α–C(10)); 2.14 (*dd*, H_β–C(10)); 2.02–1.74 (*m*, CH_2(12), CH_2(13)). Anal. calc. for $C_{20}H_{25}N_5O_5S$ (225.3): C 53.68, H 5.63, N 15.96; found: C 52.54, H 6.03, N 14.92.

11-'syn'-*Methoxy*-cis-*1*-cisoid-*1,6*-cis-*6-7,8-diazatricyclo[4.2.2.1^{2,5}]undeca-3,7-diene* (**3**). Following the procedure described for **1**, **31b** (3.6 g, 8.0 mmol) in THF (35 ml) was reduced by $LiAlH_4$ (1.3 g, 34.0 mmol) and oxidized subsequently with act. MnO_2 (20.0 g, 0.23 mmol) in CH_2Cl_2 (30 ml). FC (AcOEt/cyclohexane 5:1, R_f 0.27) afforded a yellow oil which solidified after short-path distillation at 60°/10^{-2} Torr: 205 mg (12%; not optimized) of **3** as a waxy solid. M.p. 32°. UV (MeCN): 396 (113), 388 (sh, 91), 242 (sh, 903). IR (film): 3050, 2930, 1540, 1450, 1390, 1350, 1330, 1285, 1230, 1210, 1125, 1100, 1010, 890, 770, 740, 705. ^{1}H-NMR (250 MHz): 5.98 (*m*, H–C(3), H–C(4)); 5.24 (*m*, H–C(1), H–C(6)); 3.40 (*t*, H–C(11)); 3.35 (*s*, CH_3O); 2.69 (*m*, H–C(2), H–C(5)); 2.40 (br. *d*, H_{syn}–C(9), H_{syn}–C(10)); 1.41 (*m*, H_{anti}–C(9), H_{anti}–C(10)). ^{1}H-NMR (250 MHz, (D_6)benzene): 5.75 (*m*, H–C(3), H–C(4)); 5.05 (*m*, H–C(1), H–C(6)); 3.03 (*t*, H–C(11)); 2.81 (*s*, CH_3O); 2.25–2.17 (*m*, H–C(2), H–C(5), H_{syn}–C(9), H_{syn}–C(10)); 1.24 (*m*, H_{anti}–C(9), H_{anti}–C(10)). ^{13}C-NMR (20 MHz): 136.05 (C(3), C(4)); 87.92 (C(11)); 70.98 (C(1), C(6)); 57.28 (CH_3O); 42.32 (C(2), C(5)); 19.15 (C(9), C(10)). MS: *i.a.* 178 (5, M^+), 117 (100).

5-Methoxy-cis-*2*-cis-*6-1,11-diazatricyclo[5.4.0.0^{2,6}]undeca-3,10-diene* (**32**). For 3 d, **3** (80 mg, 0.45 mmol) in refluxing *p*-xylene (15 ml) was stirred under N_2. After solvent evaporation, the residue was subjected to FC. With AcOEt, **3**, (12 mg, 15%; R_f 0.26) was eluated, with acetone, **32** (41 mg, 52%; R_f 0.08, AcOEt). Short-path distillation (60°/10^{-2} Torr) gave 34 mg (42%) of **32**, colorless oil. IR (film): 3050, 2970, 2920, 2810, 1580, 1442, 1428, 1378, 1358, 1190, 1168, 1120, 1107, 928, 850, 735. ^{1}H-NMR (400 MHz): 6.93 (*dd*, 4 H); 6.12 (*dd*, H–C(4)); 6.07 (*dt*, H–C(3)); 5.02 (*dd*, H–C(2)); 4.70 (str. *d*, H–C(5)); 4.25 (*q*, H–C(7)); 3.42 (*q*, H–C(6)); 3.33 (*s*, CH_3O); 2.08 (*dq*, H_a–C(9)); 1.82 (*m*, CH_2(8)); 1.69 (*m*, H_b–C(9)); $J(2,6) = 6$, $J(2,3) = 2$, $J(9b,10) = 2$, $J(9a,10) = 6$, $J(9,9) = 16$, $J(7,8) = 8$, $J(6,7) \approx J(5,6) \approx 7$, $J(4,5) \approx 1.5$, $J(3,5) = 2$, $J(3,4) = 6$. ^{13}C-NMR (100 MHz): 142.37 (C(10)); 137.19 (C(3)); 133.56 (C(4)); 86.89 (C(5)); 74.24 (C(2)); 65.41 (C(7)); 57.64 (CH_3O); 36.98 (C(6)); 20.97 (C(9)); 18.24 (C(8)). MS: *i.a.* 179 (13, $M^+ + 1$), 178 (100, M^+), 96 (83), 83 (88), 81 (79), 80 (79), 80 (76).

Photolyses of **1**. a) *Photolysis at 77 K.* A glassy soln. of **1** in EPA at 77 K was exposed to light of $\lambda = 365$ nm. After 1.5 h, no changes in the UV spectrum were observed, except for a base-line shift. After thawing, the UV of **1** remained unchanged.

At 77 K in EPA glass, on 254-nm irradiation, strong absorptions at 272, 260, 251, and 242 nm emerged, while the weak maximum at 386 nm, due to **1**, did not disappear. On thawing to −100°, no changes were observed; at r.t., 2 additional bands appeared at 414 and 340 nm.

b) *Photolysis ($\lambda > 280$ nm) at −60°.* A soln. of **1** (92 mg, 0.57 mmol) in N_2-purged Et_2O (250 ml) was irradiated at −60° for 6.5 h (*Pyrex; Hanau TQ 150*). ^{1}H-NMR control after solvent evaporation at −20° showed no products; TLC: besides **1**, only high-molecular-weight material (R_f 0). After filtration through silica gel (AcOEt), 74 mg (80%) of **1** were recovered.

c) *254-nm Photolysis.* In a quartz NMR tube, a soln. of **1** (18 mg, 0.11 mmol) in CD_3OD (0.5 ml) was irradiated at r.t. with light of $\lambda = 254$ nm (*Rayonet* photoreactor). ^{1}H-NMR monitoring: **34** and other olefins (after 1 h, *ca.* 20% conversion) whose concentration did not increase on prolonged irradiation; TLC: growing decomposition. From the photolysis mixture, the olefins codistilled with CD_3OD at *ca.* 80°; the residue contained **1** and high-molecular-weight material. After filtration through SiO_2 (AcOEt), 11 mg (61%) of **1** were recovered.

cis-*3,6-Diethenylcyclohexene* (**34**). ^{1}H-NMR (250 MHz, CD_3OD): 5.78 (*ddd*, H–C(1′), H–C(1″)); 5.63 (*d*, H–C(1), H–C(2)); 5.04–4.96 (*m*, CH_2(2′), CH_2(2″)); 2.76 (*m*, H_β–C(3), H_β–C(6)); 1.8–1.4 (*m*, CH_2(4), CH_2(5)); additional olef. signals complicated further analysis. UV (CH_3CN/CD_3OD): 266, 256, 247, 237; though the UV was measured with a soln. practically free of other olef./arom. components (^{1}H-NMR), it cannot be excluded, that these – for structure **34** unexpectedly long-wave length – absorptions are (partially) due to another photoproduct.

d) *Benzophenone-Sensitized Photolysis.* In a quartz NMR tube, **1** (7.7 mg, 0.047 mmol) and benzophenone (5 mg) in (D_6)benzene (0.5 ml) were irradiated with light of $\lambda = 300$ nm for 6.5 h (conversion *ca.* 60%; from the ^{1}H-NMR, the portion of **34** was estimated to *ca.* 30%). After codistillation of solvent and **34** at *ca.* 100°, the residue contained **1** and decomposition products.

34: ^{1}H-NMR (250 MHz, $C_6D_6/CDCl_3$ 3:1): 5.73 (*ddd*, H–C(1′), H–C(1″)); 5.65 (*m*, H–C(1), H–C(2)); 5.05–4.95 (*m*, CH_2(2′), CH_2(2″)); 2.66 (*m*, H_β–C(3), H_β–C(6)); 1.65–1.40 (*m*, CH_2(4), CH_2(5)); $J(1,6) \approx 1.5$, $J(3,1') \approx 6.5$, $J(1',2'a) \approx 10.5$, $J(1',2'b) \approx 17$.

Photolyses of **3**. a) *UV-Monitored Irradiation.* A $1.9 \cdot 10^{-3}$ M soln. of **3** in CH_3CN was irradiated with *Pyrex*-filtered light of $\lambda > 280$ nm at r.t. and monitored in 1-min intervals. The absorption of **3** at 396 nm rapidly disappeared (70% conversion after 8 min); isosbestic points were observed only at low conversion. TLC: olef. product (R_f 0.67, AcOEt).

b) *NMR-Monitored Irradiations.* In a quartz NMR tube, a degassed soln. of **3** (10 mg, 60 μmol) in CD_3OD (0.5 ml) was irradiated with *Pyrex*-filtered light of $\lambda > 280$ nm at r.t. After 10 min, conversion was *ca.* 90%; according to ^{1}H-NMR and GC, 2 olefins were present, **35** and presumably **36**, in a *ca.* 10:1 ratio. The mixture **35**/**36** codistilled with the solvent.

After 10 min, the 254-nm irradiation of **3** (7 mg, 39 μmol) in CD_3CN (0.5 ml) gave according to ^{1}H-NMR, a 12:7:1 mixture **35**/**3**/**36**.

^{1}H-NMR control of acetone-sensitized photolysis ($\lambda = 300$ nm, quartz) of **3** (6 mg, 34 μmol) in (D_6)acetone (0.5 ml) revealed, after 55 min, mainly **35**/**3** (3:1) and only traces of **36**. Compound **35** codistilled with the solvent. r-*3*,c-*5*-*Diethenyl*-c-*4*-*methoxy*-*1*-*cyclopentene* (**35**). UV (MeCN): 245 (sh). ^{1}H-NMR (250 MHz, (D_6)acetone): 5.86 (*ddd*, H–C(1′),H–C(1″)); 5.70 (*m*, H–C(1),H–C(2)); 5.04 (str. *d*, H_b–C(2′),H_b–C(2″)); 4.96 (str. *d*, H_a–C(2′), H_a–C(2″)); 4.05 (*t*, H_β–C(4)); 3.36 (str. *t*, H_β–C(3), H_β–C(5)); 3.28 (*s*, CH_3O); $J(3,4) \approx J(3,1') \approx 7.5$, $J(1',2'a) \approx 10.5$, $J(1',2'b) \approx 17$. CI-MS (isobutane): 151 (100, $M+1$). EI-MS: *i.a.* 149 (2, $M-1$), 147 (3), 117 (51), 109 (44), 91 (87), 79 (61), 77 (53), 72 (12), 41 (93), 39 (100).

cis-*1*-cisoid-*1,6*-cis-*6*-*3,4*-*Diazatricyclo*[*4.2.2.2*^{2,5}]*dodeca*-*3,7*-*diene 3*-*Oxide* (**37**). To a stirred soln. of **1** (930 mg, 5.74 mmol) in CH_2Cl_2 (35 ml) cooled to 0°, 85% *m*-chloroperbenzoic acid (1.14 g, 5.74 mmol) was added in small portions within 2 h. After stirring for another 2 h at 0°, the heterogeneous mixture was dissolved in CH_2Cl_2 (*ca.* 70 ml) and extracted with $NaHCO_3$ soln. The org. layer was dried (Na_2SO_4) and evaporated, the solid residue recrystallized from MeOH: 955 mg (93%) of **37**. M.p. 212° (subl.; dec.). UV (MeCN): 237 (3520). PES: 9.1, 9.3, 10.05, 10.8 eV. IR: 3030, 2940, 1499, 1371, 1342, 1292, 725. ^{1}H-NMR (400 MHz): 6.31 (*t*, H–C(8)); 6.19 (*t*, H–C(7)); 4.89 (*dd*, H–C(2)); 4.68 (*dd*, H–C(5)); 3.08 (*m*, H–C(6)); 3.04 (*m*, H–C(1)); 2.47 (*m*, H_{syn}–C(11)); 2.21 (*m*, H_{syn}–C(12)); *ca.* 2.12 (*m*, H_{syn}–C(9), H_{syn}–C(10)); *ca.* 2.09 (*m*, H_{anti}–C(11)); 1.75 (*m*, H_{anti}–C(12)); 1.55–1.43 (*m*, H_{anti}–C(9), H_{anti}–C(10)); $J(1,2) \approx J(5,6) \approx 11$, $J(1,9anti) \approx J(6,10anti) \approx 4$, $J(2,11anti) \approx J(5,12anti) \approx 6$, $J(2,11syn) \approx J(5,12syn) \approx 1$, $J(7,8) = 8$. ^{13}C-NMR (100 MHz): 134.09 (J(C,H) = 166, C(8)); 132.79 (J(C,H) = 166, C(7)); 81.44 (J(C,H) = 151, C(2)); 59.27 (J(C,H) = 148, C(5)); 36.30 (J(C,H) = 136, C(6)); 35.45 (J(C,H) = 136, C(1)); 22.92 (J(C,H) = 130, C(9)*); 21.98 (J(C,H) = 133, C(11)); 21.12 (J(C,H) = 130, C(10)*); 17.86 (J(C,H) = 133, C(12)). ^{15}N-NMR (44.6 MHz, $CDCl_3$): 355.56, *ca.* 356 (low intensity). Anal. calc. for $C_{10}H_{14}N_2O$ (178.2): C 67.39, H 7.92, N 15.72; found: C 67.23, H 8.02, N 15.47.

Photolyses of **37**. a) *UV-Monitored 254-nm Irradiation.* A 10^{-4} M soln. of **37** in MeCN was irradiated with light of $\lambda = 254$ nm through quartz. UV monitoring (1-min intervals) showed no isosbestic points; finger-like absorptions emerged at 266, 256, and 246 nm (indication of **34**?), which disappeared upon further irradiation. During the whole irradiation period, the weak maximum at *ca.* 383 nm (indicative of **42**) increased.

In EPA soln. at 77 K, on 254-nm photolysis, **37** showed the very same behavior as **1** with finger-like absorptions occurring at 271.5, 260.5, 250.5, and 241 nm.

b) *Preparative 254-nm Photolysis.* A soln. of **37** (140 mg, 0.79 mmol) in N_2-purged MeOH (10 ml) was photolysed with light of $\lambda = 254$ nm (quartz; *Rayonet* photoreactor) at r.t. for 17 h. After solvent evaporation, the residue was subjected to FC (Et_2O). The 1st fraction (R_f 0.25) consisted of 14 mg (*ca.* 10%) of an unseparable mixture (mainly **42**, **45**, and an unidentified MeOH adduct), the 2nd of 36 mg (26%) of **41a**/**41b** (R_f 0.20). With AcOEt, 17 mg (9%) of **37** were eluated.

trans-*1*-cisoid-*1,8*-trans-*8*-*9,10*-*Diazatricyclo*[*6.2.2.0*^{2,7}]*dodeca*-*5,9*-*diene 9*-*Oxide* (**41a**) *and* trans-*1*-cisoid-*1,8*-trans-*8*-*9,10*-*Diazatricyclo*[*6.2.2.0*^{2,7}]*dodeca*-*3,9*-*diene 9*-*Oxide* (**41b**). M.p. 75° (1:1 mixture from Et_2O). UV (MeCN): 233 (7200). IR: 3020, 1935, 1860, 1490, 1381, 1325, 1279, 1250, 1225, 1089, 980, 950, 930, 725, 709. ^{1}H-NMR (250 MHz): 6.24–6.09 (*m*, H–C(5) of **41a**, H–C(4) of **41b**); 5.58, 5.51 (*dt*, H–C(6) of **41a**, H–C(3) of **41b**); 4.49–4.42 (*m*, H–C(8) of **41a** and **41b**); 4.36 (br. *s*, H–C(1) of **41a** and **41b**); 2.57, 2.37 (*m*, H–C(2) of **41a**, H–C(7) of **41b**); 2.37, *ca.* 2.2 (*m*, H–C(7) of **41a**, H–C(2) of **41b**); 2.29–1.25 (*m*, 8 H of **41a** and **41b**); $J(2,7) \approx J(6,5;$ **41a**$) \approx J(3,4;$ **41b**$) \approx 10$, $J(7,8) \approx J(1,2) \approx 3.5$. ^{1}H-NMR (400 MHz, $CDCl_3/C_6H_6$): 5.93, 5.90 (*m*, H–C(5) of **41a**, H–C(4) of **41b**); 5.30, 5.20 (*dt*, H–C(6) of **41a**, H–C(3) of **41b**); 4.21 (*m*, H–C(8) of **41a** and **41b**); 4.01, 4.06 (*m*, H–C(1) of **41a** and **41b**); 2.31, 2.11 (*m*, H–C(7) of **41a**, H–C(2) of **41b**); 2.0–1.9 (*m*, H–C(2) of **41a**, H–C(7) of **41b**); 1.95–0.85 (*m*, 8 H of **41a** and **41b**). ^{13}C-NMR (100.6 MHz): 133.03, 131.89 (C(5) of **41a**, C(4) of **41b**); 126.05, 124.41 (C(6) of **41a**, C(3) of **41b**); 75.50, 74.57 (C(8) of **41a** and **41b**); 61.93, 61.56 (C(1) of **41a** and **41b**); 35.02, 34.57 (C(2) of **41a**, C(7) of **41b**); 31.97, 31.70 (C(7) of **41a**, C(2) of **41b**); 23.83, 23.20, 23.15, 22.52, 21.00, 19.41, 18.44, 17.82. MS: *i.a.* 178 (17), 106 (48), 99 (78), 91 (100). Anal. calc. for $C_{10}H_{14}N_2O$ (178.2): C 67.39, H 7.92, N 15.72; found: C 67.10, H 7.85, N 15.75.

Fraction 1 (**42**/**45**/MeOH adduct) in MeOH (10 ml) was stirred at r.t. with 2,4-dinitrophenylhydrazine (20 mg, 0.12 mmol) in MeOH (10 ml) for 20 h. FC (AcOEt/cyclohexane 4:1) afforded 7 mg (3% rel. to **37**) of hydrazone **46**.

*3-(*cis-*7,8-Diazabicyclo[4.3.0]nona-4,8-dien-9-yl)propanal* (**45**). ^{1}H-NMR (400 MHz; mixture with **42**/MeOH adduct): 9.85 (*s*, CHO); *ca.* 6.10 (*m*, H–C(4)); 5.83 (*ddt*, H–C(5)); 4.77 (*dd*, H–C(6)); 3.14 (*ddd*, H–C(1)); 2.92 (*t*, CH_2CH_2CHO); 2.59 (*m*, CH_2CH_2CHO); *ca.* 2.00–1.50 (CH_2(2), CH_2(3)); J(1,6) = 9.5. ^{13}C-NMR (100 MHz): 200.39 (CHO); 160.65 (C(9)); 132.30 (C(4)); 123.42 (C(5)); 75.78 (C(6)); 46.58 (C(1)); 39.60 (CH_2CH_2CHO); 22.10, 21.20 (C(2), C(3)); 19.58 (CH_2CH_2CHO).

2,4-Dinitrophenylhydrazone **46**. M.p. 147°. IR: 3250, 3100, 2920, 1615, 1585, 1515, 1420, 1330, 1220, 1138, 1072, 910, 874, 830, 740. ^{1}H-NMR (250 MHz): 11.04 (*s*, NH); 9.13 (*d*, J = 3, arom. H–C(3)); 8.31 (*dd*, J = 10, 3, arom. H–C(5)); 7.92 (*d*, J = 10, arom. H–C(6)); 7.70 (*t*, CH_2CH_2CH=N); 6.11 (*m*, H–C(4)); 5.88 (*m*, H–C(5)); 4.80 (*dd*, H–C(6)); 3.19 (*ddd*, H–C(1)); 2.85 (*m*, CH_2CH_2CH=N); 2.65 (*m*, CH_2CH_2CH=N); 2.05–1.55 (*m*, NH(7), CH_2(2), CH_2(3)); J(1,2a) = J(1,6) = 9, J(1,2b) = 4.5, J(4,5) = 10.5.

Irradiated under the conditions described above, **41a**/**41b** (15 mg, 84 μmol) in MeOH (10 ml) afforded, after filtration through a short SiO_2 pad with AcOEt, 9 mg (66%) of **42** (R_f 0.54) as a colorless oil; **34** or **45** were not observed.

trans-*1*-cisoid-*1,8*-trans-*8-9,10-Diazatricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene* (**42**). UV (MeCN): 383. ^{1}H-NMR (250 MHz): 6.10 (*m*, H–C(4)); 5.52 (*dt*, H–C(3)); 5.01 (*m*, H–C(1), H–C(8)); 2.17 (*m*, H–C(2)); 1.93 (*m*, H–C(7)); 1.89–0.95 (*m*, 8 H); J(2,7) ≈ J(3,4) ≈ 10.

7,8-Bis(trifluoromethyl)bicyclo[4.2.1]nona-2,4,7-triene (**6**) [54]. a) [$_\pi$2 + $_\sigma$2] cycloaddition in **47**: The soln. of **47** (1.0 g, 3.9 mmol) in MeCN (300 ml) was irradiated for 30 h at −15° with polychromatic light *(Hanau TQ 150)* through quartz (conversion > 80%). After solvent evaporation and filtration through a silica-gel pad with Et_2O, 930 mg (93%) of **48**/**47** were obtained in a 9:1 ratio.

b) The soln. of **48**/**47** (1.64 g, 6.07 mmol) and 3-methyl-benzothiazol-2-selone (1.44 g, 6.32 mmol) in CH_2Cl_2 (20 ml) was treated with CF_3COOH (0.79 g, 6.31 mmol) for 30 min at r.t., then for 4 h at 40°. Solids were filtered off, and the residue was chromatographed on silica gel with pentane (R_f 0.9): 935 mg (61%) of **6** as a colorless oil. Spectral data: as reported.

*4-Methyl-9,10-bis(trifluoromethyl)-*trans-*1*-cisoid-*1,7*-trans-*7-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradeca-9,12-diene-3,5-dione* (**49**). The soln. of **6** (935 mg, 3.68 mmol) and MTAD (520 mg, 4.60 mmol) in $CHCl_3$ (15 ml) was heated to 55° for 15 min and filtered with AcOEt over a short pad of bas. Al_2O_3 (act. III). Solvent evaporation and recrystallization from CH_2Cl_2/hexane afforded 1.32 g (94%) of **49**. M.p. 156°. IR: 2960, 2100, 1770, 1700, 1460, 1400, 1360, 1320, 1295, 1250, 1235, 1215, 1188, 1150, 1050, 990, 810, 755, 715. ^{1}H-NMR (250 MHz): 6.17 (*m*, H–C(12), H–C(13)); 5.18 (*m*, H–C(1), H–C(7)); 3.56 (*dd*, H–C(8), H–C(11)); 3.07 (*s*, CH_3); 2.83 (br. *d*, H_{syn}–C(14)); 2.30 (*dt*, H_{anti}–C(14)); J(1,11) = J(7,8) = 9, J(1,2) = J(7,13) = 4.5, J(1,13) = J(7,12) = 3, J(11,14*anti*) = J(8,14*anti*) = 4.5, J(14,14) = 12. Anal. calc. for $C_{14}H_{11}F_6N_3O_2$ (367.3): C 45.79, H 3.02, N 11.44; found: C 45.79, H 2.91, N 11.44.

5-Methyl-10,14-bis(trifluoromethyl)-3,5,7-triazahexacyclo[7.5.0.0^{2,13}.0^{3,7}.0^{8,11}.0^{10,14}]tetradecane-4,6-dione (**50**). At r.t. **49** (1.5 g, 4.08 mmol) in acetone (150 ml) was irradiated through *Pyrex* for 5 h with light of λ > 280 nm *(Hanau TQ 80)*. After solvent evaporation, filtration over a short silica-gel pad with AcOEt, and recrystallization from CH_2Cl_2/hexane, 1.2 g (80%) of **50** were obtained. M.p. 251–252°. IR: 3000, 1765, 1690, 1470, 1370, 1320, 1240, 1120, 1010, 955, 840, 800, 740, 680, 635. ^{1}H-NMR (250 MHz): 5.25 (*m*, H–C(2), H–C(8)); 3.94 (*m*, H–C(11), H–C(13)); 3.62 (*m*, H–C(1), H–C(9)); 3.11 (*s*, CH_3); 2.24 (*dt*, H_β–C(12)); 2.18 (br. *d*, H_α–C(12)); J(1,2) = J(8,9) = 7, J(1,8) = J(2,9) = 3, J(2,13) = J(8,11) = 9, J(11,12β) = J(12β,13) = 5.5, J(12,12) = 14. ^{13}C-NMR (100 MHz): 148.99 (C(4), C(6)); 123.91 (J(C,F) = 257.7, 2 CF_3); 53.60 (C(10), C(14)); 50.71 (C(11), C(13)*); 44.38 (C(2), C(8)*); 33.57 (C(1), C(9)); 30.68 (C(12)); 25.40 (CH_3). Anal. calc. for $C_{14}H_{11}F_6N_3O_2$ (367.3): C 45.79, H 3.02, N 11.44; found: C 45.33, H 2.63, N 11.23.

*4-Methyl-10,11-bis(trifluoromethyl)-*cis-*1*-cisoid-*1,9*-cis-*9-2,4,6-triazatetracyclo[7.5.0.0^{2,6}.0^{10,14}]tetradeca-7,11-diene-3,5-dione* (**51**). For 16 h, **49** (90 mg, 0.25 mmol) in toluene (15 ml) was heated to 100°. Solvent evaporation and recrystallization from CH_2Cl_2/hexane afforded 72 mg (80%) of **51**. M.p. 154°. IR: 3080, 1771, 1696, 1460, 1400, 1362, 1270, 1190, 1160, 735. ^{1}H-NMR (400 MHz): 7.01 (*dd*, H–C(7)); 6.74 (br. *s*, H–C(12)); 5.10 (*m*, H–C(8)); 4.94 (*t*, H–C(1)); 3.83 (*m*, H–C(9)); 3.61 (*m*, H–C(14)); 3.14 (*s*, CH_3); 2.71 (*m*, H_β–C(13)); 2.48 (*dq*, H_α–C(13)); J(1,9) = J(1,14) = 9, J(7,8) = 8.5, J(7,9) = 1.5, J(8,9) = 5, J(9,14) = 2, J(13β,14) = 10, J(13α,14) = 3, J(13,13 = 19.5, J(12,13β) ≈ J(12,13α) ≈ J(13β, CF_3–C(10)) ≈ J(13α, CF_3–C(10)) ≈ 3. ^{13}C-NMR (100 MHz): 149.31 (C(5)); 147.24 (C(3)); 146.97 (J(C,F) = 5, C(12)); 128.45 (J(C,F) = 35, C(11)); 125.70 (J(C,F) = 278, CF_3–C(11)); 121.10 (J(C,F) = 271, CF_3–C(10)); 118.94 (C(7)); 100.94 (C(8)); 59.87 (J(C,F) = 30, C(10)); 46.00 (C(1)); 42.52 (C(14)); 36.01 (C(9)); 31.98 (C(13)); 25.33 (CH_3). Anal. calc. for $C_{14}H_{11}F_6N_3O_2$ (367.3): C 45.79, H 3.02, N 11.44; found: C 45.64, H 2.80, N 11.37.

2,3-Bis(trifluoromethyl)-8,9-diazapentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{4,10}]undec-8-ene (**52**). Under N_2, a stirred suspension of **50** (340 mg, 0.93 mmol) and NaOH (1.4 g, 35 mmol) in i-PrOH (25 ml) was heated to reflux for 3 h. The dark mixture was cooled down in an ice bath, acidified with 2N HCl to pH *ca.* 5, and stirred, after treatment with a soln. of $CuCl_2$ (15 g) in H_2O (100 ml), at r.t. for 3 h. Conc. NH_3 soln. was added, and the deep blue soln. was extracted thoroughly with CH_2Cl_2. The combined extracts were washed with brine, dried (Na_2SO_4), and evaporated. After FC (Et_2O/petroleum ether 4:1, R_f 0.3) and sublimation at $\leq 40°/10^{-2}$ Torr, 80 mg (31%) of **52** were obtained. Pale yellow crystals which gradually decomposed at *ca.* > 70°, no m.p. IR: 2980, 1535, 1370, 1330, 1300, 1271, 1245, 1232, 1165, 1045, 1010, 975. ^{1}H-NMR (250 MHz): 6.03 (*m*, H–C(7), H–C(10)); 3.60 (*dd*, H–C(4), H–C(6)); 2.92 (*m*, H–C(1), H–C(11)); 1.81 (*dt*, H_β–C(5)); 1.38 (*d*, H_α–C(5)); $J(10,11) = J(1,7) = 5$, $J(7,11) = J(1,10) = 3$, $J(4,10) = J(6,7) = 10$, $J(4,5\beta) = J(5\beta,6) = 5.5$, $J(4,5\alpha) = J(5\alpha,6) \approx 0$, $J(5,5) = 14$. ^{13}C-NMR (20 MHz): 123.85 (J(C,F) = 276, 2 CF_3); 56.24 (C(7), C(10)); 46.55 (C(4), C(6)); 30.17 (C(5)); 24.74 (C(1), C(11)); the low intensity signals of C(2), C(3) were not recorded (*ca.* 55 ppm). Anal. calc. for $C_{11}H_8F_6N_2$ (282.2): C 46.82, H 2.86, N 9.93; found: C 46.63, H 2.39, N 9.94.

*3',4'-Dihydro-4',7-dimethyl-3',6,8,12-tetraoxospiro[*cis-*1*-cisoid-*1,10*-cis-*10-5,7,9-triaza-3-azoniapentacyclo-[8.5.0.0^{2,4}.0^{5,9}.0^{11,15}]pentadec-13-ene-3,2'-2'*H-*1',2',4'-triazolium]-5'-olate* (**55**). At r.t., **7** [28] (264 mg, 2.0 mmol) in acetone (10 ml) was stirred with MTAD (456 mg, 4.0 mmol). After a short period, a colorless precipitate appeared which was collected after 2.5 h by centrifugation. After repeated washing with Et_2O and drying *in vacuo*, 472 mg (96%) of **55** were obtained as a hardly soluble powder. ^{1}H-NMR (400 MHz, (D_6)DMSO): 7.80 (*dd*, H–C(14)); 6.50 (*d*, H–C(13)); 5.98 (*d*, H–C(4)); 5.24 (br. *d*, H–C(10)); 5.20 (br. *d*, H–C(2)); 3.77 (br. *d*, H–C(1)); *ca.* 3.6 (H–C(15)); *ca.* 3.3 (H–C(11)); *ca.* 2.9 (2 CH_3); $J(2,4) = 8$, $J(1,2) = 0$. ^{13}C-NMR (100 MHz, (D_6)DMSO): 206.84 (C(12)); 162.06 (C(14)); 161.06, 153.81 (C(3'), C(5')); 153.23, 151.79 (C(6), C(8)); 139.74 (C(13)); 67.70 (J(C,H) = 175, C(4)); 60.32 (J(C,H) = 160, C(2)); 46.56 (C(10)); 46.18 (C(11)); 38.77 (C(15)); 36.46 (C(1)); 25.96, 24.87 (2 CH_3N).

Following the same procedure, **55** was obtained when **54** (see below) and MTAD were mixed in a 1:1 ratio. In (D_6)DMSO (traces of H_2O), **55** was transformed in a few h into **56a**.

*7β-Hydroxy-4-methyl-8β-(4'-methyl-3',5'-dioxo-1',2',4'-triazolidin-1'-yl)-*cis-*1*-cisoid-*1,9*-cis-*9-2,4,6-triazatetracyclo[7.5.0.0^{2,6}.0^{10,14}]tetradec-11-ene-3,5,13-trione* (**56a**). When **55** (90 mg, 0.25 mmol) in H_2O (5 ml) was heated, **56a** crystallized on cooling: 92 mg (98%). M.p. 305–310° (dec.). IR: 3600–3000, 1750, 1690, 1466, 1395, 1305, 1250, 1020, 762. ^{1}H-NMR (250 MHz, (D_6)DMSO): 10.08 (br., H–C(2')); 7.73 (*dd*, H–C(11)); 7.15 (br., OH); 6.61 (*d*, H–C(12)); 5.41 (*d*, H–C(7)); 5.05 (*t*, H–C(1)); 4.08 (*dd*, H–C(8)); 3.97 (*q*, H–C(9)); 3.58 (*m*, H–C(10)); 3.20 (*dd*, H–C(14)); 2.91 (*s*, 2 CH_3); $J(1,9) \approx J(1,14) \approx 9.5$, $J(7,8) = 3.5$, $J(8,9) = 8.5$, $J(10,14) = 5$, $J(11,12) = 5.5$. ^{13}C-NMR (100 MHz, (D_6)DMSO): 205.9 (C(13)); 165.07 (C(11)); 154.37, 154.08, 153.03, 150.40 (C(3), C(4), C(3'), C(5')); 139.62 (C(12)); 74.85 (C(7)); 54.31 (C(8)); 47.11 (C(14)); 43.16 (C(1)); 39.53 (C(10)); 32.94 (C(9)); 24.77, 24.70 (2 CH_3N).

*4-Methyl-8β-(4'-methyl-3',5'-dioxo-1',2',4'-triazolidin-1'-yl)-3,5,13-trioxo-*cis-*1*-cisoid-*1,9*-cis-*9-2,4,6-triazatetracyclo[7.5.0.0^{2,6}.0^{10,14}]tetradec-11-en-7β-yl Acetate* (**56c**). At *ca.* 70°, **55** (105 mg, 0.3 mmol) was dissolved in abs. AcOH. After addition of AcOEt, **56c** crystallized on cooling (in the presence of H_2O, **56c** was transformed gradually into **56a**): 90 mg (72%) of **56c**. M.p. *ca.* 305° (dec.). IR: 3120, 1770, 1750, 1710, 1685, 1460, 1385, 1340, 1300, 1280, 1262, 1218, 1050, 1015, 770. ^{1}H-NMR (400 MHz, (D_6)DMSO): 10.4 (br., H–C(2')); 7.85 (*dd*, H–C(11)); 6.68 (*d*, H–C(12)); 6.51 (*d*, H–C(7)); 5.15 (*t*, H–C(1)); 4.28 (*dd*, H–C(8)); 3.78 (br. *q*, H–C(9)); 3.67 (*m*, H–C(10)); 3.28 (*m*, H–C(14)); 2.93 (*s*, CH_3); 2.90 (*s*, CH_3); 1.96 (*s*, CH_3O); $J(1,9) \approx J(1,14) \approx J(8,9) \approx J(9,10) \approx 9$, $J(7,8) = 3.5$, $J(10,11) = 3$, $J(10,14) = 5$, $J(11,12) = 5.5$. ^{13}C-NMR (100 MHz, (D_6)DMSO): 205.79 (C(13)); 168.76 (CH_3CO); 164.02 (J(C,H) = 169, (C(11)); 154.43, 154.25, 150.93, 150.47 (C(3), C(5), C(3'), C(5')); 140.33 (J(C,H) = 173, C(12)); 71.77 (J(C,H) = 169, C(7)); 52.47 (J(C,H) = 140, C(8)); 46.98 (J(C,H) = 148, C(14)); 43.58 (J(C,H) = 160, C(1)); 39.53 (J(C,H) ≈ 150, C(10)); 33.31 (J(C,H) = 150, C(9)); 24.86, 24.76 (J(C,H) = 142, 2 CH_3); 20.29 (J(C,H) = 130, CH_3O).

14-'syn'-*Hydroxy-4-methyl-*trans-*1*-cisoid-*1,7*-trans-*7-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradeca-9,12-diene-3,5-dione* (**57**). A soln. of **8a** (15.1 mg, 113.0 mmol) and MTAD (15.0 g, 133.0 mmol) in acetone (35 ml) was stirred 6 h at r.t. and 2 h at 50°. After filtration through a short pad of Al_2O_3 (act. III, CH_2Cl_2/acetone 3:1) and solvent evaporation, the residue was recrystallized from AcOEt (the mother liquor contained **57**, **8a**, and **58** (*ca.* 5%)): 21.5 g (77%) of **57**. M.p. 126–127°. IR: 3330, 3050, 2930, 1735, 1670, 1462, 1395, 1310, 1246, 1200, 1100, 1085, 773, 734. ^{1}H-NMR (250 MHz): 6.10 (*m*, H–C(9), H–C(10), H–C(11), H–C(12)); 5.03 (*m*, H–C(1), H–C(7)); 4.40–4.28 (*m*, H–C(14), OH); 3.03 (*s*, CH_3); *ca.* 3.00 (*m*, H–C(8), H–C(11)). Anal. calc. for $C_{12}H_{13}N_3O_3$ (247.3): C 58.30, H 5.30, N 16.99; found: C 58.20, H 5.20, N 16.95.

*4-Methyl-*cis-*1*-cisoid-*1,9*-cis-*9-2,4,6-triazatetracyclo[7.5.0.0^{2,6}.0^{10,14}]tetradeca-7,11-diene-3,5,13-trione* (**54**). At r.t., **57** (80 mg, 0.32 mmol) was stirred with act. MnO_2 (11.5 g, 162.0 mmol) in CH_2Cl_2 (20 ml) for 4 h. After

filtration, chromatography on silica gel (AcOEt) and recrystallization from EtOH gave 65 mg (82%) of **54**. M.p. 210°. IR: 3090, 3050, 2980, 1760, 1700, 1640, 1565, 1470, 1455, 1400, 1350, 1330, 1305, 1275, 1235, 1215, 1160, 1075, 1015, 960, 825, 800, 770, 745, 705. ^{1}H-NMR (250 MHz): 7.58 (*dd*, H–C(11)); 6.86 (*d*, H–C(7)); 6.44 (*d*, H–C(12)); 5.10 (*t*, H–C(1)); 5.04 (*dd*, H–C(8)); 3.71 (*m*, H–C(9)); 3.55 (*m*, H–C(10)); 3.39 (*dd*, H–C(14)); 3.12 (*s*, CH_3); $J(1,9) = J(1,14) = 9$, $J(7,8) = 8.5$, $J(11,12) = 6$. Anal. calc. for $C_{12}H_{11}N_3O_3$ (245.3): C 58.77, H 4.52, N 17.13; found: C 58.41, H 4.16, N 17.08.

*13-Hydroxy-4-methyl-*cis-*1-*cisoid-*1,9-*cis-*9-2,4,6-triazatetracyclo[7.5.0.0^{2,6}.0^{10,14}]tetradeca-7,11-diene-3,5-dione* (**58**). At 106°, **57** (56 mg, 0.23 mmol) in N_2-purged toluene (20 ml) was stirred for 5 h. Solvent evaporation, FC (CH_2Cl_2/acetone 3:1), and recrystallization from MeOH yielded 42 mg (75%) of **58**. IR: 3420, 3090, 3050, 2950, 1750, 1700, 1645, 1470, 1420, 1395, 1350, 1329, 1305, 1260, 1193, 1012, 740. ^{1}H-NMR (250 MHz): 6.93 (*d*, H–C(7)); 5.81, 5.69 (*AB*, H–C(11), H–C(12)); 5.23 (*m*, H–C(13)); 5.03 (*dd*, H–C(8)); 4.87 (*m*, H–C(1)); 3.53 (*m*, H–C(9)); 3.38–3.24 (*m*, H–C(10), H–C(14)); 3.08 (*s*, CH_3); 2.12 (*d*, OH); $J(1,9) \approx J(1,14) \approx 9$, $J(7,8) = 8.5$, $J(8,9) = 5$, $J(11,12) = 5.5$. Anal. calc. for $C_{12}H_{13}N_3O_3$ (247.3): C 58.30, H 5.30, N 16.99; found: C 58.27, H 5.27, N 16.95.

*12-*endo-*Hydroxy-5-methyl-3,5,7-triazahexacyclo[7.5.0.0^{2,13}.0^{3,7}.0^{8,11}.0^{10,14}]tetradecane-4,6-dione* (**59**). At r.t., **57** (22.3 g, 90.0 mmol) was irradiated in acetone (2000 ml) with light of $\lambda = 300$ nm (*Rayonet* photoreactor; 10 200-ml quartz tubes) for 15 h (conversion > 95%). During photolysis, **59** crystallized partially. The soln. was concentrated to *ca.* 50 ml, the crystals collected by filtration, and the mother liquor subjected to FC (CH_2Cl_2/acetone 3:1; R_f 0.36): 19.1 g (86%) of **59**. M.p. *ca.* 200° (dec.). IR: 3390, 3000, 2870, 1745, 1675, 1460, 1395, 1348, 1290, 1140, 1062, 1015, 890, 805, 775, 642. ^{1}H-NMR (250 MHz): 5.13 (*m*, H–C(2), H–C(8)); 4.59 (*q*, H–C(12)); 3.41 (*m*, H–C(11), H–C(13), H–C(10)*, H–C(14)*); 3.09 (*m*, H–C(1)*, H–C(9)*); 3.07 (*s*, CH_3); 2.86 (*d*, OH). Anal. calc. for $C_{12}H_{13}N_3O_3$ (247.3): C 58.29, H 5.30, N 16.99; found: C 58.20, H 5.37, N 16.80.

*4-Methyl-*trans-*1-*cisoid-*1,7-*trans-*7-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradec-12-ene-3,5,14-trione* (**60**). At r.t., **9** [29] (2.68 g, 20.0 mmol) was stirred with MTAD (2.5 g, 22.1 mmol) in CH_2Cl_2 (20 ml) for 20 h. Filtration through a short Al_2O_3 pad (bas., act. III; R_f 0.3 (AcOEt)) and recrystallization from i-PrOH afforded 4.48 g (91%) of **60**. M.p. 168°. UV (MeCN): 247 (3557). IR: 3060, 2960, 1750, 1710, 1460, 1380, 1220, 1150, 1035, 990, 940, 910, 868, 790, 750. ^{1}H-NMR (250 MHz): 6.54 (*m*, H–C(12), H–C(13)); 5.18 (*m*, H–C(1), H–C(7)); 3.09 (*m*, H–C(8), H–C(11)); 3.00 (*s*, CH_3); 1.85–1.64 (*m*, H–C(9), H–C(10)). Anal. calc. for $C_{12}H_{13}N_3O_3$ (247.3): C 58.29, H 5.30, N 16.99; found: C 57.91, H 5.16, N 16.97.

4-Methyl-14-'syn'-*[(trimethylsilyl)oxy]-*cis-*1-*cisoid-*1,7-*cis-*7-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradec-12-ene-3,5-dione* (**61**). a) The stirred soln. of **9** (3.3 g, 24.6 mmol) in MeOH (25 ml) was treated dropwise at 0° with a soln. of $NaBH_4$ (0.5 g, 13.2 mmol) in 2N NaOH (6 ml). After stirring for an additional h, the mixture was partitioned between H_2O/Et_2O. The org. extracts were dried and evaporated. Recrystallization from CH_2Cl_2/hexane afforded 2.8 g (84%) of *bicyclo[4.2.1]nona-2,4-dien-9-*syn-*ol*. ^{1}H-NMR (90 MHz): 6.04–5.66 (*m*, 4 H); 4.48 (*t*, 1 H); 2.74 (*m*, 2 H); 2.1–1.85 (*m*, 5 H).

b) At 0°, bicyclo[4.2.1]nona-2,4-dien-9-*syn*-ol (2.60 g, 19.0 mmol) and Et_3N (2.0 g, 19.8 mmol) in Et_2O (20 ml) were treated dropwise with Me_3SiCl (2.2 g, 20.2 mmol) and stirred for 18 h. After filtration through a *Celite* pad with Et_2O and distillation, 2.9 g (73%) of *9-*syn-*[(trimethylsilyl)oxy]bicyclo[4.2.1]nona-2,4-diene* (**10**) were obtained as a colorless oil. B.p. 54°/3·10^{-1} Torr. ^{1}H-NMR (90 MHz): 5.93–5.47 (*m*, 4 H); 4.46 (*t*, 1 H); 2.59 (*m*, 2 H); 1.96–1.82 (*m*, 4 H); 0.1 (*s*, 9 H).

c) At r.t., **10** (1.30 g, 6.2 mmol) in CH_2Cl_2 (20 ml) was stirred with MTAD (980 mg, 8.6 mmol) for 20 h. After solvent evaporation, ^{1}H-NMR control revealed **61** and **62** in a 6:1 ratio: 1.23 g (62%) of **61** were obtained by FC (elution with AcOEt) and recrystallized from Et_2O. M.p. 185–186° (subl.). IR: 2950, 1760, 1700, 1462, 1392, 1345, 1296, 1248, 1228, 1208, 1182, 1119, 1043, 1026, 983, 900, 882, 840, 810, 768, 750, 690. ^{1}H-NMR (250 MHz): 6.18 (*m*, H–C(12), H–C(13)); 4.84 (*m*, H–C(1), H–C(7)); 3.74 (*t*, $J = 3.5$, H–C(14)); 3.03 (*s*, CH_3); 2.55 (*m*, H–C(8), H–C(11)); 1.91 (*m*, H_α–C(9), H_α–C(10)); 1.60 (*m*, H_β–C(9), H_β–C(10)); 0.07 (*s*, Me_3Si). Anal. calc. for $C_{15}H_{23}N_3O_3Si$ (321.4): C 56.04, H 7.21, N 13.07; found: C 55.99, H 7.27, N 13.49.

14-'syn'-*Hydroxy-4-methyl-*cis-*1-*cisoid-*1,7-*cis-*7-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradec-12-ene-3,5-dione* (**62**). For 15 min, **61** (1.1 g, 3.4 mmol) in CH_2Cl_2 (20 ml) was stirred intensively with conc. HCl soln. (20 ml). The org. layer was separated, washed with brine, and dried (Na_2SO_4). Solvent evaporation left 630 mg (74%) of **62** as colorless crystals. M.p. 228–229° (subl.). IR: 3600–3100, 2960, 1742, 1680, 1458, 1386, 1224, 1165, 1089, 1025, 890, 800, 750. ^{1}H-NMR (250 MHz): 6.55 (*m*, H–C(12), H–C(13)); 4.94 (*m*, H–C(1), H–C(7)); 3.75 (*dt*, H–C(14)); 3.03 (*s*, CH_3); 2.7 (*m*, H–C(4), H–C(8); *d*, OH); 1.94 (*m*, H_α–C(9), H_α–C(10)); 1.65 (*m*, H_β–C(9), H_β–C(10)); $J(1,11) = J(7,8) = 8$, $J(8,14) = J(11,14) = 3.5$, $J(14,OH) = 10$. Anal. calc. for $C_{12}H_{15}N_3O_3$ (249.3): C 57.82, H 6.01, N 16.70; found: C 57.08, H 6.06, N 16.86.

4-Methyl-cis-*1*-cisoid-*1,7*-cis-*7-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradec-12-ene-3,5,14-trione* (**63**). At r.t., **62** (605 mg, 2.4 mmol) in CH_2Cl_2 (3 ml) was stirred with act. MnO_2 (15 g) for 6 h. After filtration, solvent evaporation, and recrystallization from i-PrOH, 492 mg (83%) of **63** as colorless crystals were obtained. M.p. 265–267° (subl.). R_f 0.35 (AcOEt). IR: 2965, 2922, 1745, 1704, 1685, 1455, 1389, 1290, 1262, 1238, 1218, 1150, 1028, 975, 812, 786, 755. ^{1}H-NMR (250 MHz): 6.46 (*m*, H–C(11), H–C(12)); 5.02 (*m*, H–C(1), H–C(7)); 3.07 (*s*, CH_3); 2.70 (*m*, H–C(8), H–C(11)); 2.24 (*m*, H_α–C(9), H_α–C(10)); 1.90 (*m*, H_β–C(9), H_β–C(10)). Anal. calc. for $C_{12}H_{13}N_3O_3$ (247.3): C 58.29, H 5.30, N 16.99; found: C 57.99, H 5.31, N 16.69.

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