The Azo/Nitrene Route to *cis,cis*-Trialkyltriaziridines, 1

Synthesis of *syn*-Azo Azides of Defined Proximity

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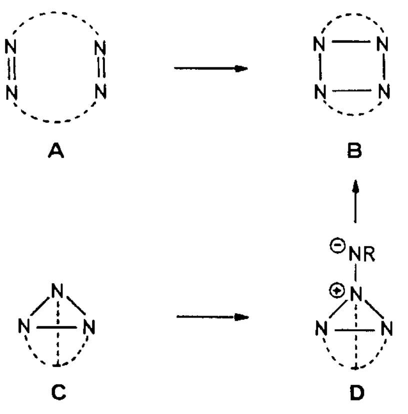
Bi- and polycyclic *syn*-azo azide substrates **H**, **5**, **14** and **I**, **15**–**18**, **36**, **41d**, respectively, of varying rigidity and proximity (with the potential nitrene nitrogen atom in the π plane of the azo function) are prepared in order to synthesize kinetically stabilized *cis,cis*-trialkyltriaziridines.

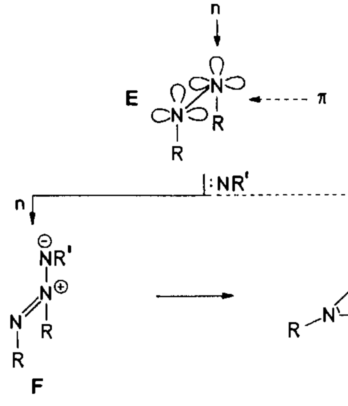
The application of light in organic synthesis is a longstanding topic in our research activities[1]. Specifically, intramolecular photocycloaddition reactions of the [2 + 2]-[2] and [6 + 6]-type[3] have been instrumental in the construction of a multitude of novel structures ranging from heteroquadricyclanes[4] and *cis*-tris-σ-homobenzenes[5] to dodecahedranes[6]. In contrast, all our efforts to bring about cycloadditions between two N=N units to obtain the still unknown N_4-ring compounds (**A**→**B**) had met with only very limited success: In a singular, structurally very special case an N=N/N=N(O) photometathesis reaction was originated[7]. The relatively poor quality of the N=N chromophores as π_2 components[7–9] and the lability of N_4 rings **B** define rather strict prerequisites for such transformations. In this context we became interested in triaziridines **C**, primarily in *cis,cis*-trisubstituted ones, since the addition of nitrenes (→**D**), followed by ring enlargement, could – principally in competition with fragmentation – open up an alternative pathway to tetrazetidines **B**.



The problems inherent in this project are intimately tied to the thermodynamic and kinetic properties of "high nitrogen compounds"[10]. Generally, because of their intrinsic bonding situation, compounds with saturated nitrogen chains or nitrogen rings are thermodynamically as well as kinetically labile. Stabilization may be provided by manipulations which lessen the n-electron repulsion and/or counteract the tendency to N–N dissoziation[11].

For the parent triaziridine (N_3H_3), the last and long-missing member in the sequence cyclopropane → aziridine → diaziridine, calculations on different levels of complexity[14,15] underline the lower enthalpy of formation of the *cis,trans* versus the *cis,cis* isomer, the propensity for electrocyclic ring opening into the azimine valence tautomer and postulate a barrier to N inversion comparable to that found in diaziridine[16]. Experimentally, the N_3H_3 ring was observed as first member of its class by Seff et al. as an Ag^+ complex embedded in a special Zeolithe cavity[17]. A series of derivatives with strongly electron-accepting and/or voluminous substituents were then prepared by Dreiding et al.[18] by intermolecular addition of stabilized (alkoxycarbonyl)nitrenes to dialkylazines (n addition) and photoinduced azimine electrocyclizations (**E**→ **F**→ **G**). In the absence of such stabilizing groups, competing reactions like nitrene elimination, (*E*)/(*Z*) isomerization, or triazene formation dominate. By the same route, ending up without exception in *cis,trans*-configurated triaziridines, Kaupp, Burger et al. could add some more examples[19].

Our approach to triaziridines is different insofar as the nitrene is added to the π plane of the N=N bond (**E**→**G**).



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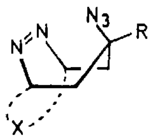
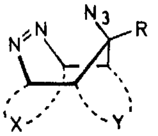
To this end, for reasons well documented in the course of analogous approaches to azaheterocyclic three-membered rings by nitrene (nitrenoid) addition to C = C bonds, a priori only intramolecular azo/nitrene additions were considered securing the *cis,cis* configuration in the resulting triaziridines. The azide function was the preferred nitrene source, since the conditions for the photochemical nitrene generation could be adjusted to the potential thermal lability of the triaziridine products. From our search for *syn*-azo azide substrates which would provide the stereoelectronic prerequisites with respect to proximity and orientation between the N = N/N – R (N_3R) functionalities on the side of the starting compound as well as the skeletal rigidity sufficient to prevent N – N-bond dissociation on the product side, skeletons of the general type **H**/**I** emerged as first choice: They feature the stereoelectronically optimal δ,ε orientation of the N = N bond relative to the azide function, potentially providing anchimeric assistance in the N_3-fragmentation step, and rigidity and proximity may be modified by variation of the X,Y skeletal bridges. Obviously, the preparative price for increasingly rigid and proximate alignment of the azo/azide functions are complications to be expected in the built-up of the very same substrates. Yet, this "azo/nitrene approach" has the advantage of being rather versatile and of providing the aspired *cis,cis*-substitution pattern in the N_3 rings, not accessible by the alternative approaches.



H



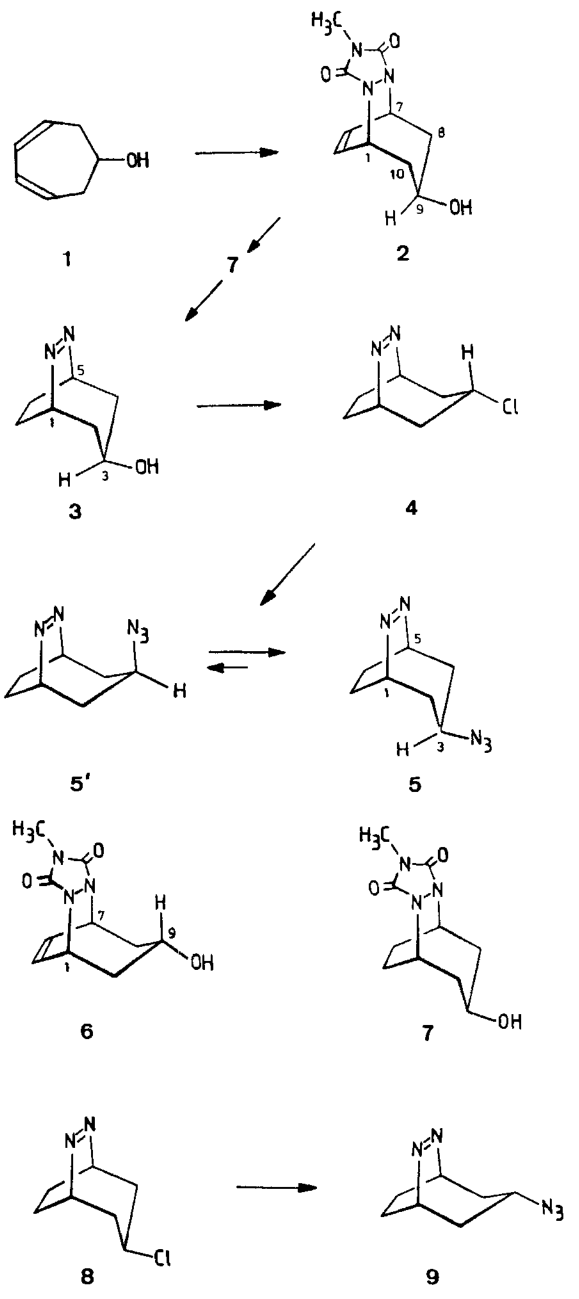
I

In this paper, we detail our efforts directed towards the construction of *syn*-azo azides of type **H**/**I** (R = H) and in the following paper[20] the conversion of these substrates into triaziridines.

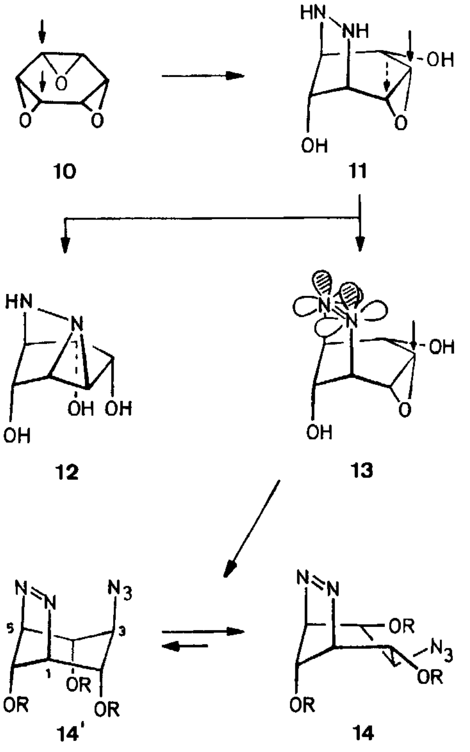
Bicyclic *syn*-Azo Azides of Type H (5, 14)

The synthesis of *syn*-azo azide **5**[21] starts from 3,5-cycloheptadienol (**1**) available in preparative quantities by reduction of tropone with $NaBH_4$[22]. It rapidly reacts with *N*-methyltriazoline-3,5-dione (MTAD) to give an 11:1 mixture of the epimeric cycloadducts **2** and **6**. The latter are separated by fractional crystallization from methanol (81% of **2**) and shown (^{1}H NMR) to preferentially exist as conformers with quasi-equatorial OH function (**2**: $\delta_{9\text{-H}} = 3.83$; $J_{8\alpha,9} = 10.0$; $J_{8\beta,9} = 6$ Hz; **6**: $\delta_{9\text{-H}} = 4.35$; $J_{8\alpha,9} = 6.5$, $J_{8\beta,9} = 9.5$ Hz). A *syn*-directing influence of the hydroxy group in **1** presumably contributes to the high side selectivity, similarly observed inter alia in the addition of singlet oxygen to **1**[23]. After catalytic hydrogenation (93% of **7**; $\delta_{9\text{-H}} = 4.23$), hydrolytic degradation of the urazole unit, and oxidation, the yellowish hygroscopic (3α)-alcohol **3** [86%; m.p. 97°C; $J_{2\alpha,3} = 11.5$; $J_{2\beta,3} \approx 6$ Hz; diazacycloheptene chair, λ_{max} (ε) = 391 nm (103; sh), 386 (106) (in CH_3CN)] is converted with triphenylphosphine/CCl_4[24] into the (3β)-chloride **4** (91%, m.p. 79–80°C; $J_{2\alpha,3} = 6$; $J_{2\beta,3} = 9$ Hz) with quasi-equatorial orientation of the Cl substituent. Treatment of **4** with sodium azide in DMF (80°C) yields – in a reaction complicated by the intervention of the (3α)-chloride **8** – the yellowish crystalline (1α,3β,5α)-azide **5** [m.p. 70°C, $\tilde{\nu}$ = 2085 cm^{-1} (N_3), 1558 (N = N)] featuring a UV/Vis spectrum [λ_{max} (ε) = 393 nm (77; sh), 388 (80; N = N), 288 (31; N_3) (in CH_3CN)][25] very similar to that of **3**. The ^{1}H-NMR spectrum manifests a clear preference for a diazacycloheptene chair with the N_3 function being quasi-equatorial ($J_{2\alpha,3} = 12$, $J_{2\beta,3} \approx 6$ Hz). For comparison, (3β)-azide **9** ($J_{1,2\beta} \approx 3.5$, $J_{2\alpha,3} = 6.5$ Hz) is analogously prepared from **3** (as mesylate) via (3α)-chloride **8**.

The synthetic route to azo azide **14a**[26] starts from *cis*-benzene trioxide (**10**) and is patterned after earlier applica-



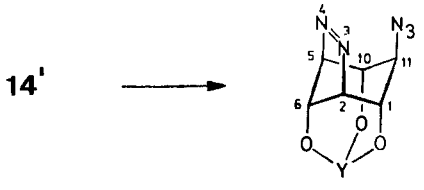
tions in the broader context of aminodeoxyinositols[27]. Under improved conditions (ca. 30% conversion of **10**), hydrazo diol **11a** is reproducibly obtained in up to 80% yield. In order to prevent in **11a** the deleterious intramolecular aziridine formation (→ **12**), epoxide opening by azide ion is postponed after oxidation to **13**. The *trans*-diaxial opening of the epoxide ring at C-3 in **13** via an all-axial transition state meets a rather unfavorable stereoelectronic situation. After intensive variations of the reaction conditions with no better than 40% of **14a** ⟨NaN_3, methanol/water, $ZnSO_4$, 80°C, 4 d; $(CH_3)_3SiN_3$, $Ti[OCH(CH_3)_2]_4$; N_3H/DMF⟩[28] the best result (60% of **14a**; m.p. 153°C) has been achieved at the cost of long reaction times in methanol/water in the presence of Al_2O_3 at 25°C (see Remarks). According to the vicinal H/H-coupling constants around the cyclohexane ring, triol **14a** [D_2O; $J_{1,2(4,5)} \approx 0$; $J_{2,3(3,4)} = 8.3$; $J_{5,8(8,1)} = 5.3$ Hz] and triacetate **14b** [$CDCl_3$; $J_{1,2(4,5)} \approx 0$; $J_{2,3(3,4)} = 7.0$ Hz] prefer flattened boat-like conformations for their cyclohexane unit with the smaller $J_{2,3(3,4)}$ value for **14b** probably indicating a higher equilibrium portion of a chair-like (**14'**) conformer (cf. Tables 1,2 in ref.[20]). The UV/Vis spectra (in CH_3CN) of **14a**/**14b** exhibit the n→π* maximum at λ (ε) = 349 nm (129)/346 (152) and the N_3 shoulder at λ (ε) = 296 nm (50)/290 (50).

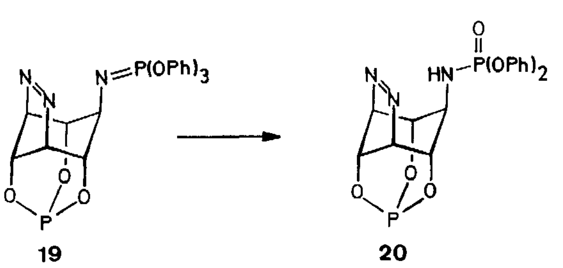


	a	b
R	H	Ac

Polycyclic *syn*-Azo Azides of Type I (15–18, 36, 41d)

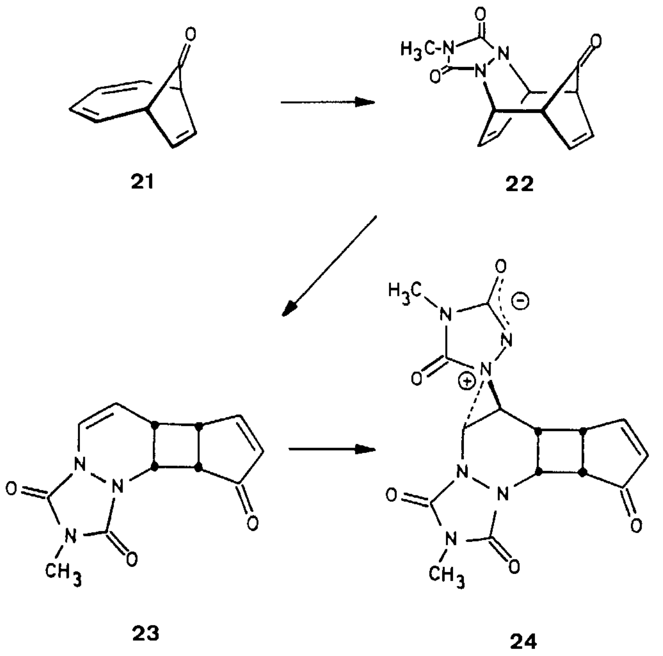
For the esterification of bicyclic triol **14a** to provide the rigid, all-axial trioxaadamantanoid *syn*-azo azides **15**–**18**, the literature offers ample analogies[29]. **14a** reacts under not yet optimized conditions with trimethyl orthoformate to give 72% of **15** (m.p. 174°C), with trimethyl orthoacetate to give 66% of **16** (m.p. 135°C). In the reactions with PCl_3 [$P(OC_6H_5)_3$] yielding up to 70% of **18** [m.p. 175°C (dec.)] and $POCl_3$ yielding up to 60% of **17** [m.p. 211°C (dec.)], competitive attack at the azido group becomes detractive [e.g. 25% of **20** via **19** with $P(OC_6H_5)_3$ at 60°C]. The ^1H- and ^{13}C-NMR spectra for **15**–**18** are in line with C_{2h} symmetries; the signals for 11-H with $J_{1,11(10,11)} \approx 3$ Hz, broadened by long-range coupling, manifest a slight flattening of the cyclohexane chairs in order to relieve the azo/azide interaction [$J_{1,2(5,10)} = J_{2,6(5,6)} = 5.3$ Hz, calculated dihedral angle H1–C1–C11–H11 = 67°[20]]. The P(V) and P(III) esters **17** and **18**[30] are distinguished by the $^3J_{H,P}$ coupling constants of ca. 19–21 and ca. 8 Hz, respectively. In the UV spectra of colorless **15**–**18** the n→π* maxima [λ = 358–361 nm (in CH_3CN)] are, with respect to those of **14a,b**, redshifted by 10–15 nm, the extinction coefficients [ε = 530–590 (in CH_3CN)] are four to five times larger; the weak N_3 shoulders at λ ≈ 290 nm are therefore not discernible. It can be speculated whether in these spectral peculiarities a through-space interaction between the N_2 and N_3 chromophores is expressed.

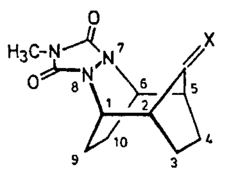




	15	16	17	18
Y	CH	CCH_3	PO	P

For the appreciation of the synthetic strategy ultimately applied to the case of *syn*-azo azide **36**[31], pertinent exploratory results must be cited: (i) Addition of MTAD to [4.2.1] ketone **21** occurred, as needed, exclusively from the *exo* face[32]; the [4+2] adduct **22**, however, was not stable at room temperature because of rapid Cope rearrangement to **23**, which by treatment with MTAD was finally converted into **24**; (ii) neither via ketone **25a** nor via oxime **25b** or *N*-tosylate **25c**, the amino (azide) function could be introduced under multiply varied sets of conditions ($NaCNBH_3$[33], Zn/AcOH, AlH_3[34], $NaBH_4/MoO_3$[35], $TiCl_3/LiAlH_4$[36]), undoubtedly due to the severe transannular compression built up with the addition to the C=X bond (**28**); (iii) similarly, azo ketone **26a** could not be converted into its oxime **26b**. Yet, with the azoxide **27a**, oxime formation under standard conditions was rapid and practically quantitative [**27b**, (*E*)/(*Z*) = 5:2] – for whatever reasons (tighter π cloud?). The deoxygenation of **27a** to **26a** can be brought about in the oxime acetate **27d** [(*E*):(*Z*) = 5:2] in refluxing triethyl phosphite; acetate **26d** is solvolyzed with ammonia to give **26b**.





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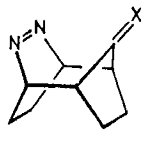

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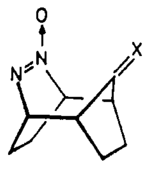

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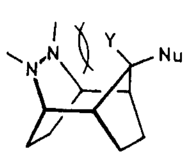

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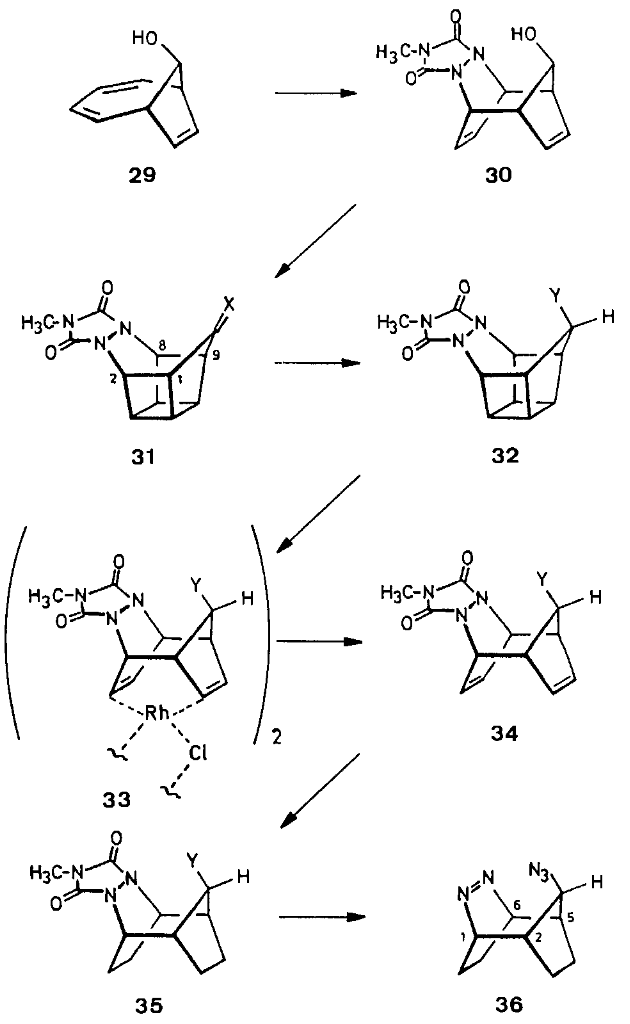
	a	b	c	d
X	O	NOH	NOTos(*p*)	NOAc

The compressional effects hampering additions to the sp^2 centers in tricyclo[4.2.2.1^{2,5}]nonane structures like **25** or **26** – according to model studies, or more exactly to MMX calculations[20] – should be significantly lowered in the hexacyclic structures derived from the latter by directly linking the two ethano bridges as in the hexacyclic ketone **31a**. The latter is available in a sequence of conventional high-yield steps by side-specific addition of MTAD to the carbinol **29** to give the kinetically sufficiently stable 1,5-diene adduct **30**, [2 + 2] cycloaddition (sensitized excitation) in the 1,5-cyclooctadiene part, and subsequent oxidation. As expected, oximation of ketone **31a** as well as reduction of oxime **31b** to amine **32a** proceed rapidly and with high selectivity. A criterion for the *syn* orientation of the amino group with respect to the N=N bond is once more the vicinal coupling constant $J_{11,12(12,13)}$ = 5.5 Hz (calculated interplanary angle ca. 150°). From **32a** *syn*-azide **32d** [$J_{11,12(12,13)}$ = 6 Hz] is obtained in 83% yield by diazo-group transfer from trifluoromethane sulfonic azide prepared in situ[37]. For inducing the thermodynamically favorable $2\sigma \rightarrow 2\pi$ isomerization of homocubane structures of type **32**, Rh(I) catalysts are well established[38]. Because of the need for thermal activation (heating to ca. 60°C) and the tendency of the resulting 1,5-dienes (like **34**) to undergo a Cope rearrangement, it has turned out indispensable to isolate the dienes **34** in a stabilized form, preferably as Rh(I) complexes **33**. Thus, stoichiometric amounts of the Rh(I) reagent are needed, with



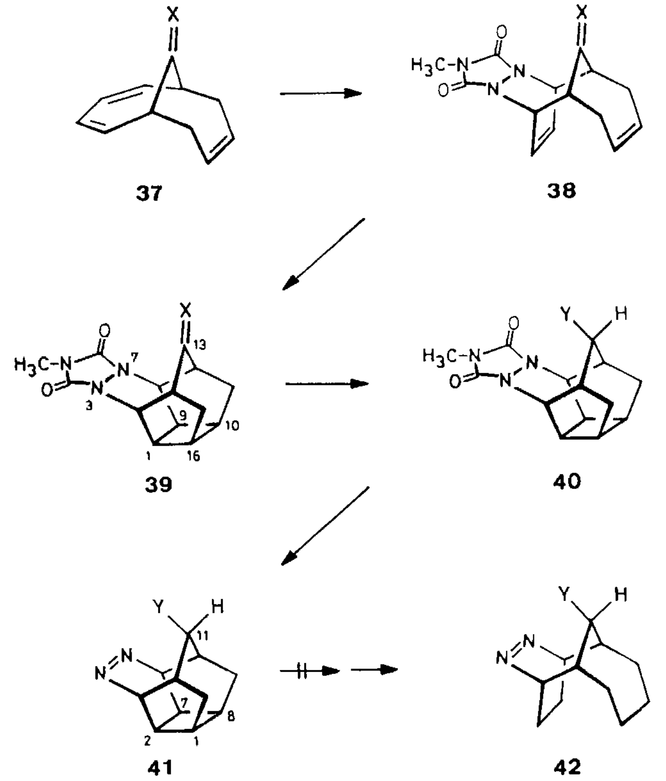
	a	b	c
X	O	NOH	NOAc

	a	b	c	d
Y	NH$_2$	NHAc	NHCOCF$_3$	N$_3$

the consequence that with both, the amine **32a** as well as the azide **32d**, the reaction rates become too low at tolerable temperatures because of complexation between catalyst and nitrogen functionalities.

In line with this argumentation, the ring opening is straightforward in the case of the acetamide **32b** and trifluoroacetamide **32c**, the preparation of which poses no difficulties (81% and 87%, respectively) in spite of the *syn* configuration at C-12. Upon heating with [RhNorCl]$_2$ (Nor = norbornadiene) at 60°C, the colorless Rh(I) complexes, tentatively formulated as **33b, c**, are formed very slowly (in days) and can be isolated in yields higher than 80%, with the Cope isomers of **34** running up to 10% and 5%, respectively; to achieve a nearly quantitative yield of **33c** repeated exchange of the solvent is mandatory. According to a protocol by Eaton[39], the complexes **33b, c** can be hydrogenated with NaBH$_4$ in methanol to yield **35b, c** without prior isolation of the dienes **34b, c**. It is of interest in this context, that the isomerizations of **32** to **34** cannot be effected by one-electron oxidation with tris(4-bromophenyl)ammoniumyl hexachloroantimonate[40]. Diazo-group transfer from **35b, c** to **35d**, under the conditions applied to **32a**, has failed again for steric reasons. It is only after deprotonation of the amine function that this transfer occurs sufficiently rapid, though not without side reactions. The major additional component (ca. 10%) is probably a methylsemicarbazide arising from the reduction of the urazole ring. Because of the azide function the urazole → azo conversion **35d** → **36** has to be performed hydrolytically; with NaOH even in boiling 2-propanol the reaction is unusually sluggish; workup after ca. 50% conversion turns out neccessary to avoid a major loss of material; the semicarbazide salt is cleanly separated with the aqueous phase and selectively transformed into **36** by a standard procedure. The yellowish crystalline azo azide **36** (86% based on converted **35d**) melts without decomposition at 98–99°C; the *syn* orientation shows up in $J_{2,11(5,11)}$ = 4 Hz (interplanary angle 57°[20]). In the UV spectrum as judged by the n→π* and N$_3$ absorptions [λ_{max} (ε) = 395 nm (89), 388 (78; sh), 285 (42; sh) (in CH$_3$CN)] no marked proximity effects between the *syn*-azo/azide groups are documented.

Access to the *syn*-azo azides **41d** and **42d** has been sought by making use of the procedures successfully applied to **36**[41]. From the bicyclo[4.4.1]undeca-2,4,8-trien-11-one (**37a**), efficiently prepared according to literature procedures[42], as well as from its oxime **37b**, the intermediates **38a** and **b** are obtained by *exo*-specific MTAD addition (71 and 95%, respectively). In line with a π/π-transannular distance of ca. 2.95 Å and a π/π-interorbital angle (ω) of ca. 164° (MMX)[20] in these bridged 1,6-cyclodecadiene units, acetone-sensitized excitation provides high yields (88 and 85%, respectively) of the cages **39a** and **b**. After selective reduction of oxime **39b** to the *syn-endo*-amine **40a** [86%; m. p. 218°C; $J_{12,13(13,14)}$ = 3 Hz], diazo-group transfer to give *syn*-azide **40d** (51%, not optimized; m.p. 242°C), and saponification of the urazole ring (71%) the *syn*-azo azide **41d** is isolated as pale yellowish crystals, melting at 125°C without decomposition. The elucidation of the structure is based on ^{1}H-NMR [$J_{10,11(11,12)}$ = 2.5 Hz; interplanary angle 68°[20]], ^{13}C-NMR, and mass spectra. In the UV-absorption curve with the longest wavelenght maxima at λ(ε) = 397 nm (168; sh) and 391 (175), the N$_3$ shoulder is not recognized. For the pentacyclic parent hydrocarbon skeleton of the cages **39/40** a strain energy much lower (50.0/53.1 kcal/mol) than for the hexacyclic tetradecane skeleton underlying **31/32** is calculated (88.5/92.0 kcal/mol, MMX). It is therefore not too great a surprise, that in none of the derivatives **40/41** 2σ→2π isomerization has been brought about thermally or catalytically, what ultimately prohibits access to the *syn*-azo azide **42**.



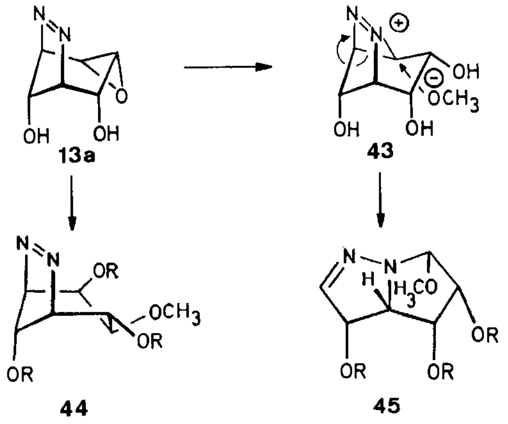
	a	b	c	d
X	O	NOH	NOAc	NH

	a	b	c	d
Y	NH$_2$	NHAc	NHCOCF$_3$	N$_3$

Remarks

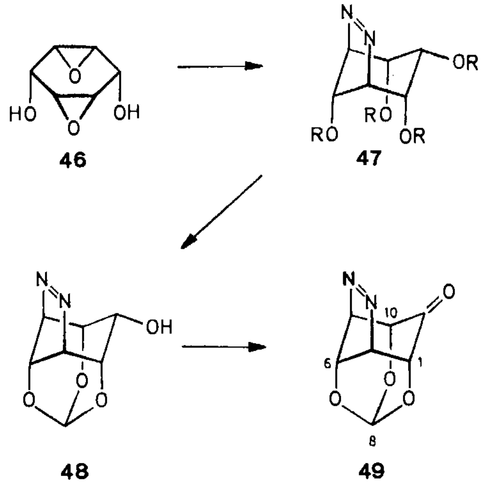
A hint as to the potential complexity of C-4 substitution reactions of **13** and to the nature of potential competition processes comes from the reaction with hydroxide ion in the presence of Al$_2$O$_3$ as catalyst. After stirring a solution of **13a** and KOH in methanol/water to complete the conversion (7 d), two monomeric components are extracted from the crude reaction mixture: 64% of **45a** and 5% of what is considered as **44a**. The oily and highly acid-sensitive triol **45a** is additionally characterized as crystalline triacetate **45b**. NOE experiments confirm the all-*cis* orientation of the four substituents. Tight steric limitations to the *endo* addition of the nucleophile to the 1,2-diazetidinium intermediate **43** might explain the observation that in ethanol/water this reaction channel is not available (→ mainly oligomers).

Azo ketone **49** is an intermediate in an alternative synthesis of *syn*-azo azide **15a** and a component in the photolysis mixture of



	a	b
R	H	Ac

$15a$[20]; it has independently been synthesized according to an established route[27]: Addition of hydrazine to the all-*cis*-diepoxydiol **46** and oxidation to the *myo*-azotetrol **47a** (56%, not optimized), esterification in analogy to **14a**→**15** [89% of **48**, $J_{1,2(5,10)} \approx 6.0$; $J_{2,6(5,6)} = 5.3$ Hz], and Swern oxidation [81%; colorless crystals; λ_{max} (ε) = 359 nm (230) (in CH_3CN); $J_{1,2(5,10)} = 4.5$; $J_{2,6(5,6)} = 5.5$ Hz].



	a	b
R	H	Ac

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Experimental*)

Melting points (m.p.): Bock Monoscop M. – Anal. TLC: Merck silica-gel plates with F_{254} indicator. – Flash chromatography: 0.04–0.06 mm silica gel, Macherey-Nagel. – Anal. GC: Varian 3700, glass capillary column 25 m, OV 17, FID; integrator Varian CDS 111. – ^1H NMR: Bruker WM 250, WM 400; ^{13}C NMR: Bruker WP 80, WM 250, WM 400. Chemical shifts relative to TMS (δ = 0) and coupling constants in Hz; if not specified differently the 250-MHz spectra are given; assignments indicated with * can be interchanged; *a* and *s* denote *anti* and *syn* positions. – IR: Perkin-Elmer 457, Philips PU 9706. – UV: Perkin-Elmer Lambda 15. – MS: Finnigan MAT 44S.

(1α,7α,9α)- and (1α,7α,9β)-9-Hydroxy-4-methyl-2,4,6-triazatricyclo[5.3.2.0^{2,6}]dodec-11-ene-3,5-dione (**2** and **6**): A stirred solution of 8.8 g (78.5 mmol) of **1**[27] in 60 ml of CH_2Cl_2 at 0°C was treated dropwise with a solution of 9.0 g (79.6 mmol) of MTAD in 30 ml of CH_2Cl_2 until a pink color persisted. After filtration with ethyl acetate through a short pad of aluminum oxide (basic, activity III), the residue, consisting of **2**/**6** in an 11:1 ratio, was recrystallized from methanol to give 14.3 g (81%) of **2**, m.p. 125–126°C, and after repeated recrystallization of the mother liquor 1.1 g (6%) of **6**.

2: IR (KBr): $\tilde{\nu}$ = 1749 cm^{-1}, 1680, 1465. – ^1H NMR ($CDCl_3$): δ = 6.26 (m, 11-, 12-H), 4.91 (m, 1-, 7-H), 3.83 (m, 9-H), 3.04 (s, CH_3), 2.42 (dt, 8β-, 10β-H), 2.34 (d, OH), 1.84 (dd, 8α-, 10α-H); $J_{1,10\beta(7,8\beta)} = J_{8\beta,9(9,10\beta)} = J_{9,OH} = 6$; $J_{1,10\alpha(7,8\alpha)} = 1.5$; $J_{8\alpha,9(9,10\alpha)} = 10.0$; $J_{8\alpha,8\beta} = 15.0$.

$C_{10}H_{13}N_3O_3$ (223.3) Calcd. C 53.80 H 5.87 N 18.82
Found C 53.56 H 5.79 N 18.86

6: IR (KBr): $\tilde{\nu}$ = 3485 cm^{-1}, 2960, 1752, 1685, 1465, 1392, 1241, 1053, 1015, 860, 760, 740. – ^1H NMR ($CDCl_3$): δ = 6.39 (m, 11-, 12-H), 4.90 (m, 1-, 7-H), 4.35 (m, 9-H), 3.06 (s, CH_3), 2.67 (s, OH), 2.50 (dt, 8α-, 10α-H), 1.69 (dd, 8β-, 10β-H); $J_{1,10\alpha(7,8\alpha)} = J_{8\alpha,9(10\alpha,9)} = 6.5$; $J_{1,10\beta(7,8\beta)} = 1.0$; $J_{8\beta,9(9,10\beta)} = 9.5$; $J_{8\alpha,8\beta} = 12.5$.

(1α,3α,5α)-6,7-Diazabicyclo[3.2.2]non-6-en-3-ol (**3**): A stirred suspension of 9.5 g (42.2 mmol) of **2** and 7.0 g (75.0 mmol) of sodium hydroxide in 70 ml of 2-propanol was heated to reflux under nitrogen for 4 h. The cooled mixture was acidified with 2 N HCl until pH ≈ 5 and stirred with a solution of 40.0 g (0.29 mol) of $CuCl_2$ in 200 ml of water at room temp. for 4 h. For decomplexation concd. NH_3 was added, and the deep blue solution was extracted continuously (5 d) with CH_2Cl_2. After evaporation of the solvent from the extracts a semisolid residue was obtained that was subjected to flash chromatography on silica gel (R_f = 0.16; ethyl acetate) to give 5.1 g (86%) of **3**; after sublimation at 80°C/10^{-2} Torr pale yellow, hygroscopic crystals, m.p. 97°C (subl.). – IR (KBr): $\tilde{\nu}$ = 1650 cm^{-1}, 1550, 1450. – UV (CH_3CN): λ_{max} (ε) = 391 nm (sh, 103), 386 (106); ε_{254} = 20, ε_{230} = 200. – ^1H NMR ($CDCl_3$): δ = 5.11 (m, 1-, 5-H), 4.14 (m, 3-H), 2.80 (d, OH), 2.04 (m, 2β-, 4β-H), 1.83–1.57 (m, 4H, 8-, 9-H), 1.29 (dd, 2α-, 4α-H); $J_{1,2\beta(4\beta,5)} \approx J_{2\beta,3(3,4\beta)} \approx J_{3,OH} \approx 6.0$; $J_{2\alpha,3(3,4\alpha)} \approx 11.5$; $J_{2\alpha,2\beta} = 14.0$.

$C_7H_{12}N_2O$ (140.2) Calcd. C 59.97 H 8.63 N 19.98
Found C 59.77 H 8.57 N 19.82

(1α,3β,5α)-3-Chloro-6,7-diazabicyclo[3.2.2]non-6-ene (**4**): 0.8 g (5.7 mmol) of **3** and 1.7 g (6.4 mmol) of triphenylphosphine in 25 ml of CCl_4 were heated to reflux for 20 h. After solvent evaporation, the residue was subjected to flash chromatography on silica gel (R_f = 0.37; ethyl acetate) and the crude product purified from traces of triphenylphosphine oxide by sublimation at 60°C/10^{-2} Torr to give 0.8 g (91%) of **4** as colorless crystals, m.p. 79–80°C (subl.). – IR (KBr): $\tilde{\nu}$ = 1531 cm^{-1}, 1462, 1445. – ^1H NMR ($CDCl_3$): δ = 5.27 (m, 1-, 5-H), 3.52 (m, 3-H), 2.52 (dt, 2α-, 4α-H), 1.96 (m, 8*s*-, 9*s*-H), 1.85 (ddd, 2β-, 4β-H), 1.67 (m, 8*a*-, 9*a*-H); $J_{1,2\alpha(4\alpha,5)} = J_{2\alpha,3(3,4\alpha)} = 6.0$; $J_{1,2\beta(4\beta,5)} = 1.5$; $J_{2\beta,3(3,4\beta)} = 9.0$; $J_{2\alpha,2\beta(4\alpha,4\beta)} = 14.0$.

$C_7H_{11}ClN_2$ (158.6) Calcd. C 53.00 H 6.99 N 17.65 Cl 22.35
Found C 53.18 H 6.98 N 17.70 Cl 22.75

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*) When applying the α/β notation for the stereochemical descriptors, we treat the hydrogen atom at the bridgehead as "preferred substituent". This is in accord with our former papers, but does not comply with the rules given in *Chem. Abstr.* These rules also require that all stereogenic centers are denoted; for the sake of clarity, however, those centers for which there are no alternatives for logic or geometric reasons will not be denoted in this paper.

(1α,3α,5α)-3-Azido-6,7-diazabicyclo[3.2.2]non-6-ene (**5**): 810 mg (5.1 mmol) of **4** and 520 mg (8.0 mmol) of NaN_3 in 15 ml of DMF were heated to 80°C for 18 h. The solvent was distilled off in vacuo and the residue partitioned between water and ethyl acetate. The dried (Na_2SO_4) organic extracts were concentrated, and the residue was subjected to flash chromatography on silica gel with ethyl acetate. The crude product [770 mg (91%); R_f = 0.4] contained ca. 10% of (3α)-chloride **8** and (3β)-azide **9**. By repeated recrystallization from ether at −20°C 240 mg (28%, unoptimized) of pure **5** was obtained as slightly yellow crystals, m. p. 70°C. – IR (KBr): $\tilde{\nu}$ = 2085 cm^{-1}, 1558, 1428. – UV (CH_3CN): λ_{max} (ε) = 393 nm (77; sh), 388 (79), 288 (31); ε_{254} = 22; ε_{230} = 387. – ^1H NMR ($CDCl_3$): δ = 5.18 (m, 1-, 5-H), 3.80 (m, 3-H), 2.04 (m, 2β-, 4β-H), 1.83–1.63 (m, 8*s*/*a*-, 9*s*/*a*-H), 1.43 (t, 2α-, 4α-H); $J_{1,2\beta(4\beta,5)} \approx J_{2\beta,3(3,4\beta)} \approx 6$; $J_{1,2\alpha(4\alpha,5)} < 1$; $J_{2\alpha,3(3,4\alpha)} = 12$; $J_{2\alpha,2\beta} = 14$.

$C_7H_{11}N_5$ (165.2) Calcd. C 50.89 H 6.71 N 42.39
Found C 50.81 H 6.57 N 42.87

9: ^1H NMR ($CDCl_3$): δ = 5.18 (m, 1-, 5-H), 3.40 (m, 3-H), 2.12 (dt, 2α-, 4α-H), 1.98 (m, 8*s*-, 9*s*-H), 1.70 (ddd, 2β-, 4β-H), 1.65 (m, 8*a*-, 9*a*-H); $J_{1,2\alpha(4\alpha,5)} = J_{2\alpha,3(3,4\alpha)} = 5.0$, $J_{1,2\beta(4\beta,5)} = 3.5$, $J_{2\beta,3(3,4\beta)} = 6.5$, $J_{2\alpha,2\beta(4\alpha,4\beta)} = 15.0$.

(1α,7α,9α)-9-Hydroxy-4-methyl-2,4,6-triazatricyclo[5.3.2.0^{2,6}]dodecane-3,5-dione (**7**): 14.1 g (63.2 mmol) of **2** in 70 ml of methanol was hydrogenated after addition of ca. 100 mg of 10% Pd/C. The catalyst was removed by suction filtration and, after solvent evaporation, the residue recrystallized from ethyl acetate/ether to give 13.3 g (93%) of **7**, m. p. 144–147°C. – IR (KBr): $\tilde{\nu}$ = 1755 cm^{-1}, 1675, 1465. – ^1H NMR ($CDCl_3$): δ = 4.56 (m, 1-, 7-H), 4.23 (m, 9-H), 3.09 (s, CH_3), 2.41 (dt, 8β-, 10β-H), 2.25 (d, OH), 2.10–1.88 (m, 4H, 11-, 12-H), 1.78 (dd, 8α-, 10α-H); $J_{1,10\beta(7,8\beta)} \approx J_{8\beta,9(9,10\beta)} \approx J_{9,OH} \approx 6.0$; $J_{8\alpha,9(9,10\alpha)} \approx 10.5$.

$C_{10}H_{15}N_3O_3$ (225.3) Calcd. C 53.32 H 6.71 N 18.65
Found C 53.07 H 6.64 N 18.73

(1α,2β,3α,4β,5α)-3-Azido-6,7-diazabicyclo[3.2.1]oct-6-ene-2,4-syn-8-triol (**14a**): To a vigorously stirred suspension of 42.0 g of alumina (neutral, Woelm Super I) and 11.5 g (0.18 mmol) of NaN_3 in 30 ml of water at room temp. a solution of 6.7 g (43.0 mmol) of **13**[27] in 170 ml of methanol was added and the mixture stirred for 3 d. 200 ml of methanol was added and, after stirring for 4 h, the mixture filtered and the filter cake washed with 200 ml of methanol. After concentration of the filtrate in vacuo, the residue was dissolved in water and continuously extracted with ethyl acetate. After solvent evaporation, the residue was recrystallized from methanol to yield 4.38 g (51%) of **14a** as colorless crystals, m. p. 153°C. The mother liquor contained additional **14a** which could be isolated as triacetate **14b** after acetylation (total yield of **14a** ca. 60%). – IR (KBr): $\tilde{\nu}$ = 2140 cm^{-1} (N_3), 1510, 1350. – UV (CH_3CN): λ_{max} (ε) = 349 nm (129), 296 (50); ε_{220} = 1580. – ^1H NMR (D_2O): δ = 4.71 (d, 1-, 5-H), 4.55 (t, 8-H), 4.44 (t, 3-H), 3.47 (d, 2-, 4-H); $J_{1,2(4,5)} < 0.5$; $J_{2,3(3,4)} = 8.3$; $J_{5,8(8,1)} = 5.3$. – MS [CI (methane), 170 eV]: *m*/*z* (%) = 200 (100) [M^+ + 1], 182 (34), 171 (8), 157 (58), 139 (74).

$C_6H_9N_5O_3$ (199.2) Calcd. C 36.18 H 4.55 N 35.16
Found C 36.19 H 4.48 N 34.96

(1α,2β,3α,4β,5α)-3-Azido-6,7-diazabicyclo[3.2.1]oct-6-ene-2,4-syn-8-triyl Triacetate (**14b**): Colorless crystals, m. p. 119°C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 2100 cm^{-1}, 1740, 1380. – UV (CH_3CN): λ_{max} (ε) = 346 nm (152), 290 (50; sh); ε_{254} = 25, ε_{220} = 1470. – ^1H NMR ($CDCl_3$): δ = 5.00 ("s", 1-, 5-H), 4.97 ("s", 8-H), 4.74 (d, 2-, 4-H), 4.32 (t, 3-H), 2.23 (s, OCH_3), 2.15 (s, 2 OCH_3); $J_{1,2(4,5)} < 0.5$, $J_{2,3(3,4)} = 7.0$; (C_6D_6): δ = 4.89 (d, 2-, 4-H), 4.75 (d, 1-, 5-H), 4.45 (t, 8-H), 4.31 (t, 3-H), 1.61 (s, 2 OCH_3), 1.59 (s, OCH_3); $J_{1,2(4,5)} < 0.5$; $J_{1,8(5,8)} = 5.3$; $J_{2,3(3,4)} = 7.0$.

$C_{12}H_{15}N_5O_6$ (325.3) Calcd. C 44.31 H 4.65 N 21.53
Found C 44.02 H 4.61 N 21.44

(1α,11α)-11-Azido-7,9,12-trioxa-3,4-diazatetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodec-3-ene (**15**): A stirred solution of 1.10 g (5.5 mmol) of **14a** in 120 ml of dry acetonitrile was treated with 117 mg of concd. H_2SO_4 and 2.33 g (22.0 mmol) of trimethyl orthoformate and heated to 40°C for 3 d (TLC). After solvent evaporation, the residue was partitioned between water and CH_2Cl_2 and the organic extract washed with $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated in vacuo to yield 0.84 g (72%) of **15** as colorless crystals, m. p. 174°C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 2100 cm^{-1} (N_3), 1390. – UV (CH_3CN): λ_{max} (ε) = 361 nm (530), 352 (380; sh); ε_{254} = 400, ε_{220} = 1780. – ^1H NMR ($CDCl_3$): δ = 5.69 (s, 8-H), 5.30 (m, 2-, 5-H), 4.59 (m, 1-, 10-H), 4.30 (m, 11-H), 4.19 (m, 6-H); $J_{1,2(5,10)} = J_{2,6(5,6)} = 5.3$; $J_{1,11(10,11)} = 3.0$. – MS [CI (isobutane), 170 eV]: *m*/*z* (%) = 210 (100) [M^+ + 1].

$C_7H_7N_5O_3$ (209.2) Calcd. C 40.19 H 3.37 N 33.48
Found C 40.33 H 3.38 N 33.09

(1α,11α)-11-Azido-8-methyl-7,9,12-trioxa-3,4-diazatetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodec-3-ene (**16**): A solution of 1.5 g (7.5 mmol) of **14a**, 2.9 g (24.0 mmol) of trimethyl orthoacetate and 50 mg of 4-methylphenylsulfonic acid in 15 ml of acetonitrile was stirred at 80°C for 3 d (TLC). After solvent evaporation, the residue was partitioned between water and CH_2Cl_2 and the organic extract washed with $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated in vacuo to give 1.1 g (66%) of **16** as colorless crystals, m. p. 135°C (ethyl acetate; activated carbon). – IR (KBr): $\tilde{\nu}$ = 2100 cm^{-1}, 1400, 1380. – UV (CH_3CN): λ_{max} (ε) = 360 nm (580), 331 (400; sh); ε_{254} = 320, ε_{220} = 1900. – ^1H NMR ($CDCl_3$): δ = 5.20 (m, 2-, 5-H), 4.55 (m, 1-, 10-H), 4.31–4.22 (m, 6-, 11-H), 1.51 (s, 3H); $J_{1,2(5,10)} \approx J_{2,6(5,6)} \approx 5.3$ Hz. – ^{13}C NMR ($CDCl_3$): δ = 108.4 (C-8), 73.5 (C-11), 70.6 (C-1, -10), 66.2 (C-2, -5), 59.6 (C-6), 23.9 (CH_3).

$C_8H_9N_5O_3$ (223.2) Calcd. C 43.05 H 4.06 N 31.38
Found C 42.75 H 3.98 N 31.23

(1α,11α)-11-Azido-7,9,12-trioxa-3,4-diaza-8-phosphatetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodec-3-ene-8-one (**17**): A stirred suspension of 100 mg (0.5 mmol) of **14a** in 2 ml of dry acetonitrile was treated dropwise with a solution of 92 mg (0.6 mmol) of phosphoryl chloride and 303 mg (3.0 mmol) of triethylamine in 2 ml of acetonitrile at room temp. After 1 h, the solvent was removed in vacuo and the residue partitioned between water and CH_2Cl_2. The organic extract was dried ($MgSO_4$) and concentrated in vacuo. After crystallization (ethyl acetate; activated carbon), 73 mg (60%) of **17** as colorless crystals, m. p. 211°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2120 cm^{-1} (N_3), 1370. – UV (CH_3CN): λ_{max} (ε) = 358 nm (590), 335 (400; sh), 228 (1115); ε_{254} = 200. – ^1H NMR ([D_6]acetone): δ = 5.60 (m, 2-, 5-H), 5.32 (m, 1-, 10-H), 5.14 (m, 6-H), 4.80 (m, 11-H); $J_{1,2(5,10)} \approx J_{2,6(5,6)} \approx 5.3$; $J_{1,11(10,11)} \approx 3.0$; $J_{6,P} = 21.0$; $J_{1,P(10,P)} = 19.2$

$C_6H_6N_5O_4P$ (243.1) Calcd. C 29.64 H 2.48 N 28.80
Found C 29.88 H 2.38 N 28.63

(1α,11α)-11-Azido-7,9,12-trioxa-3,4-diaza-8-phosphatetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodec-3-ene (**18**): To a stirred solution of 1.00 g (5.02 mmol) of **14a** in 60 ml of dry acetonitrile were added 1.56 g (5.02 mmol) of triphenyl phosphite and 16 drops of triethylamine. After 4 h at room temp., the solvent was removed in vacuo and the residue partitioned between water and CH_2Cl_2. The organic extract was dried ($MgSO_4$) and concentrated in vacuo. From the solution of the oily residue in ethyl acetate 0.80 g (70%) of **18** crystallized, m. p. 175°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2100 cm^{-1} (N_3), 1380. – UV

(CH_3CN): λ_{max} (ε) = 360 nm (570), 354 (390; sh); ε_{254} = 324, ε_{220} = 1366. — ^1H NMR ($CDCl_3$): δ = 5.42 (m, 2-, 5-H), 4.61 (m, 1-, 10-H), 4.35 (m, 11-H), 3.98 (m, 6-H); $J_{1,2(5,10)} \approx J_{2,6(5,6)} \approx 5.3$; $J_{1,11(10,11)} \approx 3.0$; $J_{1,P(10,P)} \approx J_{6,P} \approx 8.0$. — ^{13}C NMR ($CDCl_3$): δ = 72.8 (d, $J_{C,P}$ = 7.4, C-1, -10), 67.2 (C-11), 66.1 (C-2, -5), 61.0 (d, $J_{C,P}$ = 6.0, C-6).

$C_6H_6N_5O_3P$ (227.1)	Calcd.	C 31.72	H 2.66	N 30.84
	Found	C 31.70	H 2.61	N 30.59

Diphenyl (1α,11α)-7,9,12-Trioxa-3,4-diaza-8-phosphatetracyclo-[6.3.1.0^{2,6}.0^{5,10}]dodec-3-en-11-ylaminophosphonate (**20**): To a stirred solution of 50 mg (0.25 mmol) of **14a** in 1 ml of dry acetonitrile 84 mg (0.27 mmol) of triphenyl phosphite and 1 drop of triethylamine were added. After 30 min at 60°C, the solvent was removed in vacuo and the residue subjected to chromatography on silica gel [cyclohexane/ethyl acetate (2:1)] to yield 33 mg (58%) of **18** (R_f = 0.58) and 27 mg (25%) of **20** (R_f = 0.30). — **20**: Colorless needles, m.p. 118°C (ethyl acetate). — IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1}, 1480. — ^1H NMR ($CDCl_3$): δ = 7.35 (m, 4 aromatic H), 7.23 (m, 6 aromatic H), 5.42 (dd, 2-, 5-H), 4.30 (m, 1-, 10-H), 4.10 (dd, 11-H), 3.93 (m, 6-H), 3.07 (dd, NH); $J_{1,2(5,10)} \approx J_{2,6(6,5)} = 5.3$; $J_{NH,P} \approx J_{11\text{-}H,P} \approx J_{11\text{-}H,NH} \approx 12.0$. — MS (EI, 70 eV): m/z (%) = 433 (14) [M$^+$], 405 (22), 376 (14), 325 (32), 233 (10), 94 (54), 77 (100).

$C_{18}H_{17}N_3O_6P_2$ (433.3)	Calcd.	C 49.90	H 3.95	N 9.70
	Found	C 49.15	H 3.87	N 9.62

5-Methyl-3,5,7-triazahexacyclo[7.5.0.0^{2,13}.0^{3,7}.0^{8,11}.0^{10,14}]tetradecane-4,6,12-trione (**31a**): 18.2 g (73.60 mmol) of **30**[9] and 75.0 g (0.86 mmol) of manganese dioxide in 40 ml of CH_2Cl_2 were stirred at room temp. for 3.5 h. After suction filtration and thorough extraction of the filter cake with boiling CH_2Cl_2, the solvent was evaporated and the residue crystallized from 2-propanol to give 15.4 g (85%) of **31a** as colorless crystals, m.p. 210°C. — IR (KBr): $\tilde{\nu}$ = 1745 cm^{-1}, 1688, 1460. — ^1H NMR ($CDCl_3$): δ = 5.31 (m, 2-, 8-H), 3.71–3.60 (m, 11-, 13-, 10*-, 14*-H), 3.46 (m, 1*-, 9*-H), 3.07 (s, CH_3).

$C_{12}H_{11}N_3O_3$ (245.3)	Calcd.	C 58.77	H 4.52	N 17.13
	Found	C 58.60	H 4.33	N 17.18

12-(Hydroxyimino)-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 (**31b**): 23.2 g (93.8 mmol) of **31a** suspended in 40 ml of methanol was stirred with 25.0 g (0.36 mol) of hydroxylamine hydrochloride, 25.0 g (0.24 mol) of Na_2CO_3 and 2 ml of water at room temp. for ca. 12 h and at 50°C for 6 h. After solvent evaporation in vacuo, the solid residue was thoroughly extracted with boiling CH_2Cl_2. After concentration of the extract and crystallization of the residue from methanol, 22.0 g (90%) of **31b** was obtained as colorless powder, m.p. 232°C (subl., dec.). — IR (KBr): $\tilde{\nu}$ = ca. 1742 cm^{-1}, 1670, 1455, 1400. — ^1H NMR ($CDCl_3$): δ = 8.12 (br., 1H), 5.30 (m, 2H), 4.66 (m, 1H), 4.01 (m, 1H), 3.46 (m, 2H), 3.35 (m, 2H), 3.07 (s, CH_3).

$C_{12}H_{12}N_4O_3$ (260.3)	Calcd.	C 55.38	H 4.64	N 21.53
	Found	C 55.24	H 4.70	N 21.53

endo-12-Amino-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 (**32a**): A stirred suspension of 7.8 g (30.0 mmol) of **31b** and 4.7 g (32.5 mmol) of MoO_3 in 20 ml of methanol was treated with 4.8 g (127 mmol) of $NaBH_4$ in portions (strongly exothermic reaction). After 2.5 h, the dark brown suspension was partitioned between water and CH_2Cl_2; muddy inorganic material, obscuring the separation of the layers, was removed by centrifugation. The organic layers were dried (Na_2SO_4), the solvent was evaporated, and the residue crystallized from methanol to yield 6.2 g (84%) of **32a** as colorless crystals, m.p. 181°C (subl.). — IR (KBr): = 1748 cm^{-1}, 1680, 1465. — ^1H NMR ($CDCl_3$): δ = 5.07 (m, 2H), 3.74 (t, J = 5.5, 1H), 3.36 (m, 4H), ca. 3.09 (m, 2H), 3.07 (s, 3H), 1.62 (br., 2H).

$C_{12}H_{14}N_4O_2$ (246.3)	Calcd.	C 58.53	H 5.73	N 22.75
	Found	C 58.00	H 5.67	N 22.46

endo-12-(Acetylamino)-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 (**32b**): A solution of 520 mg (2.1 mmol) of **32a** in 10 ml of CH_2Cl_2 and 5 ml of triethylamine was treated with 5 ml of acetic anhydride at room temp. for 22 h. 50 ml of water was added and, after stirring for 1 h, the mixture extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4) and concentrated in vacuo. The residue was filtered with ethyl acetate and acetone (R_f = 0.32) through a short pad of silica gel. After crystallization from methanol, 490 mg (81%) of **32b** was obtained, m.p. 219–220°C. — IR (KBr): $\tilde{\nu}$ = 1748 cm^{-1}, 1690, 1660, 1520, 1465. — ^1H NMR ($CDCl_3$): δ = 6.15 (br. d, NH), 5.19 (m, 2-, 8-H), 4.65 (q, 12-H), 3.65 (m, 11-, 13-H), 3.30 (m, 10*-, 14*-H), ca. 3.12 (m, 1*-, 9*-H), 3.12 (s, CH_3), 1.94 (s, $COCH_3$).

$C_{14}H_{16}N_4O_3$ (288.3)	Calcd.	C 58.32	H 5.59	N 19.43
	Found	C 58.12	H 5.55	N 19.31

5-Methyl-endo-12-(trifluoroacetylamino)-3,5,7-triazahexacyclo[7.5.0.0^{2,13}.0^{3,7}.0^{8,11}.0^{10,14}]tetradecane-4,6-dione (**32c**): A stirred solution of 12.4 g (50.3 mmol) of **32a** and 15.0 g (148 mmol) of triethylamine in 75 ml of CH_2Cl_2 at 0°C was treated dropwise with a solution of 12.0 g (57.0 mmol) of trifluoroacetic anhydride in 30 ml of CH_2Cl_2. After stirring at 0°C for 2 h, 200 ml of water was added and the mixture thoroughly extracted with CH_2Cl_2. The organic extract was washed with brine, dried (Na_2SO_4), and concentrated in vacuo, the solid residue crystallized from methanol. The concentrated mother liquor was filtered with acetone through a short pad of silica gel (R_f = 0.46) and, after solvent evaporation, the residue crystallized from methanol. In toto 15.1 g (87%) of **32c** was obtained as colorless crystals, m.p. 256°C. — IR (KBr): $\tilde{\nu}$ = 1755 cm^{-1}, 1718, 1685, 1540, 1464. — ^1H NMR ($CDCl_3$): δ = 7.11 (m, NH), 5.23 (m, 2-, 8-H), 4.60 (q, 12-H), 3.78 (m, 11-, 13-H), 3.35 (m, 10*-, 14*-H), 3.21 (m, 1*-, 9*-H), 3.10 (s, CH_3).

$C_{14}H_{13}F_3N_4O_3$ (342.3)	Calcd.	C 49.13	H 3.83	N 16.37
	Found	C 49.13	H 3.71	N 16.58

endo-12-Azido-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 (**32d**): An intensively stirred, ice-cooled mixture of 1.80 g (27.7 mmol) of NaN_3 in 5 ml of water and 5 ml of CH_2Cl_2 was treated dropwise with 820 mg (2.9 mmol) of trifluoromethanesulfonic anhydride (by syringe). After 1 h, the organic layer was transferred into a solution of 515 mg (2.1 mmol) of **32a** in 15 ml of CH_2Cl_2. 253 mg (2.5 mmol) of lutidine was added and the mixture stirred at room temp. for 48 h. Excess sulfonyl azide was destroyed by stirring with 25 ml of concd. NH_3 for 2 h. After extraction with CH_2Cl_2, drying (Na_2SO_4) of the extract, and solvent evaporation, the residue was subjected to flash chromatography on silica gel (R_f = 0.25; ethyl acetate) to give 467 mg (83%) of **32d** as colorless crystals, m.p. 170–171°C (subl.). — IR (KBr): $\tilde{\nu}$ = 2105 cm^{-1}, 1745, 1689, 1459. — ^1H NMR ($CDCl_3$): δ = 5.17 (m, 2-, 8-H), 4.28 (t, J = 6, 12-H), 3.57 (m, 11-, 13-H), 3.43 (m, 10-, 14-H), 3.16 (m, 1-, 9-H), 3.13 (s, CH_3).

$C_{12}H_{12}N_6O_2$ (272.3)	Calcd.	C 52.94	H 4.44	N 30.87
	Found	C 52.44	H 4.44	N 30.28

Di-μ-Chlorobis{[(1α,7α,8β,11β)-syn-14-acetamido-4-methyl-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradeca-9,12-diene-3,5-dione]rhodium(I)} (**33b**): A solution of 54 mg (0.188 mmol) of **32b** in 5 ml of $CHCl_3$ was treated with 48 mg (0.104 mmol) of $[RhNorCl]_2$ and stirred at 60°C for 20 h (N_2). After concentration of the mixture in vacuo, the raw material (^1H NMR: ca. 83% of **33b**) was used without further purification. — ^{1}H NMR (CDCl$_3$): δ = 6.73 (br. d, 2H), 5.54 (m, 4H), 4.97 (m, 4H), 4.28 (m, 4H), 4.20 (m, dt, 2H), 3.18 (m, 4H), 3.01 (s, 6H), 1.82 (s, 6H).

Di-μ-Chlorobis{[(1α,7α,8β,11β)-4-methyl-syn-14-(trifluoroacetamido)-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradeca-9,12-diene-3,5-dione]rhodium(I)} (**33c**): 720 mg (2.10 mmol) of **32c** in 5 ml of CHCl$_3$ was stirred with 495 mg (1.07 mmol) of [RhNorCl]$_2$ at 60°C for 3 d (N$_2$). **33c** was precipitated with ether, removed by centrifugation and recrystallized from CH$_2$Cl$_2$/ether to yield 860 mg (85%) of colorless crystals, m.p. > 300°C (dec.). — IR (KBr; br. bands): ṽ = ca. 1750–1650 cm^{-1}, 1460, 1395. — ^{1}H NMR (CDCl$_3$): δ = 7.74 (br. d, 2H), 5.63 (m, 4H), 5.02 (m, 4H), 4.37 (m, 4H), 4.16 (dt, 2H), 3.35 (m, 4H), 3.06 (s, 6H, CH$_3$).

$C_{28}H_{26}Cl_2F_6N_8O_6Rh_2$ (961.3)
Calcd. C 34.99 H 2.73 Cl 7.38 N 11.66
Found C 34.93 H 2.82 Cl 7.22 N 11.38

(1α,7α,8β,11β)-4-Methyl-syn-14-(trifluoroacetamido)-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradecane-3,5-dione (**35c**): To a stirred suspension of 3.75 g (3.9 mmol) of **33c** in 50 ml of methanol was added 1.50 g (39.0 mmol) of NaBH$_4$ in portions during 2 h (strongly exothermic reaction). The mixture was partitioned between water and CH$_2$Cl$_2$ and insoluble inorganic material removed by centrifugation. The organic extract was dried (Na$_2$SO$_4$) and concentrated in vacuo to leave a residue that was subjected to flash chromatography on silica gel (R_f = 0.16; ethyl acetate) to yield 2.10 g (78%) of **35c** as colorless crystals, m.p. 239°C (subl.) (methanol). — IR (KBr): ṽ = 1755 cm^{-1}, 1710, 1680, 1549, 1465. — ^{1}H NMR (CDCl$_3$): δ = 7.63 (br. d, NH), 4.68 (br. d, J ≈ 9.0, 1-, 7-H), 4.20 (dt, J ≈ 4.5, 14-H), 3.13 (s, 4-CH$_3$), 2.95 (m, 8-, 11-H), 2.16 (m, 2H), 1.99–1.79 (m, 4H), 1.72 (m, 2H).

$C_{14}H_{17}F_3N_4O_3$ (346.3) Calcd. C 48.55 H 4.95 N 16.18
Found C 48.34 H 4.85 N 16.06

[1α,7α,8β,11β)-syn-14-Amino-4-methyl-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradecane-3,5-dione (**35a**): A suspension of 4.20 g (12.1 mmol) of **35c** in 25 ml of methanol was stirred with 120 ml of concd. NH$_3$ at room temp. for 1 d. The reaction mixture was thoroughly extracted with CH$_2$Cl$_2$ and the extract dried (Na$_2$SO$_4$) and concentrated. After recrystallization of the residue from methanol; 2.62 g (86%) of **35a** was obtained as colorless crystals, m.p. 184°C. — IR (KBr): ṽ = 1755 cm^{-1}, 1680, 1463, 1441. — ^{1}H NMR (CDCl$_3$): δ = 4.64 (br. d, 1-, 7-H), 3.30 (t, 14-H), 3.05 (s, CH$_3$), 2.62 (m, 8-, 11-H), 2.21 (m, 2H), 1.90–1.63 (series of m, 8H).

$C_{12}H_{18}N_4O_2$ (250.3) Calcd. C 57.58 H 7.25 N 22.38
Found C 57.17 H 6.98 N 22.18

(1α,7α,8β,11β)-syn-14-Acetamido-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradecane-3,5-dione (**35b**): To a stirred suspension of **33b** [from 54 mg (0.188 mmol) of **32b**] in methanol 50 mg (1.320 mmol) of NaBH$_4$ was added. After 2.5 h, water was added and the mixture extracted with CH$_2$Cl$_2$. The dried organic extracts were concentrated in vacuo, and the solid residue was filtered with ethyl acetate and acetone (R_f = 0.23) through a short pad of silica gel; 42 mg (76%) of **35b**, m.p. 219–221°C. — ^{1}H NMR (CDCl$_3$): δ = 6.61 (br. d, NH), 4.65 (m, 1-, 7-H), 4.27 (dt, 14-H), 3.14 (s, CH$_3$), 2.82 (m, 8-, 11-H), 2.17–1.65 (series of m, 8H, 9-, 10-, 12-, 13-H), 1.93 (s, COCH$_3$).

$C_{14}H_{20}N_4O_3$ (293.3) Calcd. C 57.52 H 6.89 N 19.16
Found C 56.95 H 6.55 N 18.98

(1α,7α,8β,11β)-syn-14-Azido-4-methyl-2,4,6-triazatetracyclo[5.4.2.1^{8,11}.0^{2,6}]tetradecane-3,5-dione (**35d**): An ice-cooled, intensively stirred mixture of 15.0 g (0.24 mol) of NaN$_3$ in 5 ml of CH$_2$Cl$_2$/5 ml of water was treated dropwise with 8.20 g [5.00 ml (29.0 mmol)] of trifluoromethanesulfonic anhydride. After 1.5 h, the layers were separated, and the organic phase was dried (Na$_2$SO$_4$) and transferred dropwise to a stirred suspension of 1.68 g (6.70 mmol) of **35a** and 1.10 g (36.0 mmol) of NaH (80% paraffin dispersion) in 35 ml of THF. After 4 h at room temp., the mixture was stirred with 60 ml of concd. NH$_3$ to destroy excess trifluoromethanesulfonyl azide. After extraction with CH$_2$Cl$_2$, drying (Na$_2$SO$_4$) of the extract, and solvent evaporation, the residue was subjected to flash chromatography on silica gel. Impurities were eluted with ethyl acetate, **35d** was eluted with acetone (R_f = 0.39). Crude **35d** [1.52 g (82%)] was crystallized from methanol to give 1.33 g (72%) of colorless crystals, m.p. 254°C (subl., dec.). — IR (KBr): ṽ = 2100 cm^{-1}, 1740, 1685, 1455, 1402. — ^{1}H NMR (CDCl$_3$): δ = 4.69 (br. d, 1-, 7-H), 3.71 (t, 14-H), 3.12 (s, CH$_3$), 2.87 (m, 8-, 11-H), 2.24 (m, 2H), 2.02–1.84 (m, 4H), 1.73 (m, 2H); $J_{1,11(7,8)} \approx 8$, $J_{8,14(11,14)} \approx 4$.

$C_{12}H_{16}N_6O_2$ (276.3) Calcd. C 52.17 H 5.84 N 30.25
Found C 51.97 H 5.74 N 30.42

(1α,2β,5β,6α)-syn-11-Azido-7,8-diazatricyclo[4.2.2.1^{2,5}]undec-7-ene (**36**): A stirred suspension of 1.12 g (4.10 mmol) of **35d** and 11.2 g (0.20 mol) of NaOH in 75 ml of 2-propanol was heated to reflux for 4.5 h (N$_2$). The mixture was diluted with 200 ml of water, and by extraction with CH$_2$Cl$_2$ 0.49 g (44%) of **35d** was recovered. The aqueous phase was acidified with 2 N HCl until pH ≈ 5 and stirred with 30.0 g (0.22 mol) CuCl$_2$ at room temp. for 4 h. After decomplexation with concd. NH$_3$, extraction with CH$_2$Cl$_2$, drying (Na$_2$SO$_4$) of the extract and solvent evaporation, the residue was subjected to flash chromatography on silica gel [R_f = 0.36; ethyl acetate/methanol (20:1)] to give 0.40 g (35%; i.e. 86% based on conversion) of **36** as pale yellow crystals, m.p. 98–99°C (ether). — IR (KBr): ṽ = 2080 cm^{-1}, 1520, 1475, 1442. — UV (CH$_3$CN): λ_{max} (ε) = 395 nm (89), 388 (78; sh), 285 (42; sh); ε_{254} = 125. — ^{1}H NMR (CDCl$_3$): δ = 5.28 (m, 1-, 6-H), 3.45 (t, 11-H), 2.73 (m, 2-, 5-H), 2.00–1.86 (m, 3β-, 4β-, 9s-H), 1.64 (m, 3α, 4α-H), 1.24 (m, 9*a*-, 10*a*-H); $J_{2,11(5,11)} \approx 4$. — MS (EI, 70 eV): *m/z* (%) = 191 (4) [M$^+$], 134 (9), 120 (7), 54 (100).

$C_9H_{13}N_5$ (191.2) Calcd. C 56.52 H 6.85 N 36.62
Found C 57.33 H 6.81 N 35.43

Bicyclo[4.4.1]undeca-2,4,8-trien-11-one Oxime (**37b**): To a solution of 5.5 g (34.9 mmol) of **37a**$^{42)}$ in 50 ml of methanol/water (1:1) were added 8.6 g (123 mmol) of hydroxylamine hydrochloride and 9.4 g (88.3 mmol) of Na$_2$CO$_3$. The mixture was stirred at 0°C for 2 h, then diluted with water, and extracted with ethyl acetate; the extract was dried (Na$_2$SO$_4$) and concentrated in vacuo to yield 4.6 g (77%) of colorless crystals, m.p. 122°C (petroleum ether). — IR (KBr): ṽ = 1447 cm^{-1}. — ^{1}H NMR (CDCl$_3$): δ = 8.59 (br., OH), 5.77 (m, 2-, 3-, 4-, 5-, 8-, 9-H), 4.62 (m, 1-H)*, 3.53 (m, 6-H)*, 2.6–2.3 (m, 7-, 7′-, 10-, 10′-H).

$C_{11}H_{13}NO$ (175.2) Calcd. C 75.39 H 7.46 N 7.99
Found C 75.19 H 7.32 N 7.85

(1α,2β,7β,8α)-11-Methyl-9,11,13-triazatetracyclo[6.5.2.1^{2,7}.0^{9,13}]hexadeca-4,14-diene-10,12,16-trione (**38a**): A solution of 1.41 g (12.5 mmol) of MTAD in 10 ml of CH$_2$Cl$_2$ was added at 0°C to a solution of 2.00 g (12.5 mmol) of **37a** in 10 ml of CH$_2$Cl$_2$. After stirring at room temp. for 3 h, the solution was concentrated in vacuo. Chromatography of the residue on silica gel (R_f = 0.44; ethyl acetate, column 35 × 2 cm) gave 2.42 g (71%) of **38a** as colorless crystals, m.p. > 260°C (methanol). — IR (KBr): ṽ = 1762 cm^{-1}, 1702, 1447. — UV (CH$_3$CN): λ_{max} (ε) = 245 nm (3870), 196 (4980). — ^{1}H NMR (CDCl$_3$): δ = 6.43 (m$_c$, 14-, 15-H), 5.39 (m$_c$,

4-, 5-H), 4.97 (m_c, 1-, 8-H), 3.50 (2-, 7-H), 3.04 (s, CH_3), 2.48 (dd, 3-, 6-H), 2.17 (structured d, 3′-, 6′-H); $J_{3,3'(6,6')}$ = 14.

$C_{14}H_{15}N_3O_3$ (273.2) Calcd. C 61.52 H 5.53 N 15.37
Found C 61.28 H 5.43 N 15.14

(1α,2β,7β,8α)-16-(Hydroxyimino)-11-methyl-9,11,13-triazatetracyclo[6.5.2.1$^{2.7}$.0$^{9.13}$]hexadeca-4,14-diene-10,12-dione (**38b**): To a solution of 4.62 g (26.4 mmol) of **37b** in 30 ml of CH_2Cl_2 was added dropwise a solution of 3.28 g (29.0 mmol) of MTAD in 50 ml of CH_2Cl_2 at 0°C. After 30 min, **38b** was separated by filtration and washed with acetone to yield 7.20 g (95%) of colorless crystals, m. p. 278°C (acetone). – IR (KBr): $\tilde{\nu}$ = 1681 cm^{-1}, 1463. – UV (CH_3CN): λ_{max} (ε) = 246 nm (2850), 229 (2400). – ^1H NMR ([D_6]DMSO): δ = 10.76 (br., OH), 6.41 (m_c, 14-, 15-H), 5.24 (br. s, 4-, 5-H), 4.96 (m_c, 1-, 8-H), 4.22 (m, 2-H)*, 3.26 (m, 7-H)*, 2.90 (s, CH_3), 2.28 (m, 3-, 3′-, 6-, 6′-H).

$C_{14}H_{16}N_4O_3$ (288.3) Calcd. C 58.32 H 5.59 N 19.43
Found C 58.33 H 5.49 N 19.12

(1α,2β,7β,8α)-16-(Acetoxyimino)-11-methyl-9,11,13-triazatetracyclo[6.5.2.1$^{2.7}$.0$^{9.13}$]hexadeca-4,14-diene-10,12-dione (**38c**): A mixture of 100 mg (0.35 mmol) of **38b**, 3 ml of CH_2Cl_2, 6 ml of pyridine, and 3 ml of acetic anhydride was stirred at room temp. for 1.5 h (the opaque suspension had turned into a clear solution). The solution was concentrated in vacuo and the residue dissolved in CH_2Cl_2/H_2O. The organic phase was washed with $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated in vacuo to yield 95 mg (83%) of colorless crystals, m. p. 216°C (methanol). – IR (KBr): $\tilde{\nu}$ = 1760 cm^{-1}, 1701, 1455. – UV (CH_3CN): λ_{max} (ε) = 245 nm (3300), 204 (5570). – ^1H NMR ($CDCl_3$): δ = 6.39 (m_c, 14-, 15-H), 5.35 (m_c, 4-, 5-H), 5.01 (m, 1-H)*, 4.94 (m, 8-H)*, 4.37 (dd, 2-H)**, 3.68 (dd, 7-H)**, 3.05 (s, CH_3), 2.56 (m, 3-, 6-H), 2.24 (m, 3′-, 6′-H), 2.20 (s, CH_3); $J_{3,3'}$ = $J_{6,6'}$ = 14.

$C_{16}H_{18}N_4O_4$ (330.4) Calcd. C 58.17 H 5.49 N 16.96
Found C 58.03 H 5.43 N 16.59

5-Methyl-3,5,7-triazahexacyclo[7.7.0.0^{2,14}.0^{3,7}.0^{8,12}.0^{10,16}]hexadecane-4,6,13-trione (**39a**): A solution of 160 mg (0.58 mmol) of **38a** in 100 ml of dry acetone (purged with N_2) was irradiated for 40 min (high-pressure mercury lamp Hanau TQ 150, Solidex filter). After concentration of the solution in vacuo, 140 mg (88%) of **39a** is obtained as colorless crystals, m. p. 175°C (methanol). – IR (KBr): $\tilde{\nu}$ = 1759 cm^{-1}, 1691, 1471. – ^1H NMR ($CDCl_3$): δ = 4.80 (m_c, 2-, 8-H), 3.38 (m_c, 12-, 14-H), 3.15 (m, 1-, 9-, 10-, 16-H), 3.05 (s, NCH_3), 2.03 (d, 11-, 15-H), 1.95 (m, 11′-, 15′-H).

$C_{14}H_{15}N_3O_3$ (273.2) Calcd. C 61.52 H 5.53 N 15.37
Found C 61.28 H 5.43 N 15.14

13-(Hydroxyimino)-5-methyl-3,5,7-triazahexacyclo[7.7.0.0^{2,14}.0^{3,7}.0^{8,12}.0^{10,16}]hexadecane-4,6-dione (**39b**): A solution of 1.06 g (3.7 mmol) of **38b** in 300 ml of dry acetone (purged with N_2) was irradiated for 60 min (high-pressure mercury lamp Hanau TQ 150, Solidex filter). After concentration of the solution in vacuo, 0.87 g (85%) of **39b** was obtained as colorless crystals, m. p. >260°C (methanol). – IR (KBr): $\tilde{\nu}$ = 1755 cm^{-1}, 1675, 1470. – ^1H NMR ($CDCl_3$): δ = 8.11 (br. s, OH), 4.80 (m, 2-, 8-H), 4.64 (m, 12-H)*, 3.46 (m_c, 14-H)*, 3.06 ("s", CH_3, 1-, 9-, 10-, 16-H), 1.91 (br. s, 11-, 15-H), 1.82 (d, 11′-, 15′-H); $J_{11,11'(15,15')}$ = 14.

$C_{14}H_{16}N_4O_3$ (288.3) Calcd. C 58.41 H 5.59 N 19.43
Found C 58.28 H 5.47 N 19.38

13-(Acetoxyimino)-5-methyl-3,5,7-triazahexacyclo[7.7.0.0^{2,14}.0^{3,7}.0^{8,12}.0^{10,16}]hexadecane-4,6-dione (**39c**): A solution of 110 mg (0.33 mmol) of **38c** in 100 ml of dry acetone (purged with N_2) was irradiated for 20 min (high-pressure mercury lamp Hanau TQ 150, Solidex filter). After concentration of the solution in vacuo, 89 mg (81%) of **39c** was obtained as colorless crystals, m. p. 254°C (methanol). – IR (KBr): $\tilde{\nu}$ = 1773 cm^{-1}, 1749, 1679, 1462. – ^1H NMR ($CDCl_3$): δ = 4.83 (m_c, 2-, 8-H), 4.50 (m_c, 12-H)*, 3.71 (m_c, 14-H)*, 3.08 (br. s, 1-, 9-, 10-, 16-H), 3.03 (s, NCH_3), 2.21 (s, CH_3), 1.97 (m, 11-, 15-H), 1.85 (d, 11′-, 15′-H); $J_{11,11'(15,15')}$ = 14.

$C_{16}H_{18}N_4O_4$ (330.4) Calcd. C 58.17 H 5.49 N 16.96
Found C 58.03 H 5.43 N 16.59

endo-11-Amino-5-methyl-3,5,7-triazahexacyclo[7.7.0.0^{2,14}.0^{3,7}.0^{8,12}.0^{10,16}]hexadecane-4,6-dione (**40a**): To a mixture of 2.0 g (6.90 mmol) of **39b**, 150 ml of methanol, and 3.3 g (13.9 mmol) of $NiCl_2 \cdot 6H_2O$ was added at 0°C in portions 2.62 g (69.4 mmol) of $NaBH_4$. The mixture was stirred at room temp. for 1.5 h, hydrolyzed with 100 ml of water, filtered through a short pad of silica gel, the filtrate extracted with CH_2Cl_2, and the organic layer dried (Na_2SO_4) and concentrated in vacuo to yield 1.63 g (86%) of colorless needles, m. p. 218°C [CCl_4/CH_2Cl_2 (1:1)]. – IR (KBr): $\tilde{\nu}$ = 1748 cm^{-1}, 1679, 1464. – ^1H NMR ($CDCl_3$): δ = 4.68 (m_c, 2-, 8-H), 3.29 (t, 13-H), 3.06 (s, CH_3), 3.03 (m, 1-, 9-H), 2.88 (12-, 14-H), 2.57 (m, 10-, 16-H), 1.79 (m, 11-, 11′-, 15-, 15′-H), 1.30 (br. s, NH_2); $J_{12,13(13,14)}$ = 3.

$C_{14}H_{18}N_4O_2$ (274.3) Calcd. C 61.29 H 6.61 N 20.42
Found C 61.04 H 6.43 N 20.19

endo-13-(Trifluoroacetamido)-5-methyl-3,5,7-triazahexacyclo[7.7.0.0^{2,14}.0^{3,7}.0^{8,12}.0^{10,16}]hexadecane-4,6-dione (**40c**): To a solution of 1.00 g (3.65 mmol) of **40a**, 1.10 g (11.0 mmol) of triethylamine and 15 ml of CH_2Cl_2 was added dropwise at 0°C a solution of 0.84 g (4.02 mmol) of trifluoroacetic anhydride in 10 ml of CH_2Cl_2. After 2 h at 0°C, 20 ml of water was added and the mixture stirred for 20 min. The aqueous phase was extracted with CH_2Cl_2, the organic phase washed with brine, dried (Na_2SO_4), and concentrated in vacuo to yield 0.92 g (68%) of colorless needles, m. p. 258°C (methanol). – IR (KBr): $\tilde{\nu}$ = 1756 cm^{-1}, 1708, 1684, 1468. – ^1H NMR ($CDCl_3$): δ = 7.00 (br., NH), 4.79 (m_c, 2-, 8-H), 4.28 (br. s, 13-H), 3.13 (s, CH_3), 2.94 (m, 1-, 9-, 10-, 12-, 14-, 16-H), 1.92 (br. s, 11-, 11′-, 15-, 15′-H).

$C_{16}H_{17}F_3N_4O_3$ (370.4) Calcd. C 51.89 H 4.63 N 15.13
Found C 51.91 H 4.65 N 15.03

endo-13-Azido-5-methyl-3,5,7-triazahexacyclo[7.7.0.0^{2,14}.0^{3,7}.0^{8,12}.0^{10,16}]hexadecane-4,6-dione (**40d**): To a mixture of 4.6 g (71.2 mmol) of NaN_3 and 80 ml of CH_2Cl_2/H_2O (1:1) was added at 0°C 1.4 ml (6.56 mmol) of trifluoromethanesulfonic anhydride, and the mixture was stirred for 1 h at the same temp. The organic phase was added by syringe to a solution of 1.5 g (5.50 mmol) of **40a** and 0.47 ml (0.56 mmol) of lutidine in 20 ml of CH_2Cl_2. The mixture was stirred at room temp. for 2.5 h and after the addition of 25 ml of concd. NH_3 for further 30 min. Then it was thoroughly extracted with CH_2Cl_2 and the extract was dried (Na_2SO_4) and concentrated in vacuo. Chromatography of the residue on SiO_2 (R_f = 0.25; ethyl acetate, column 30 × 2 cm) yielded 0.84 g (51%, not optimized) of colorless crystals, m. p. 242°C (CCl_4). – IR (KBr): $\tilde{\nu}$ = 2094 cm^{-1}, 1750, 1685, 1461. – ^1H NMR ($CDCl_3$): δ = 4.74 (m_c, 2-, 8-H), 3.79 (t, 13-H), 3.14 (s, CH_3), 3.06 (m, 1-, 9-H), 2.95 (m, 10-, 16-, 12-, 14-H), 1.84 (11-, 15-H), 1.76 (d, 11′-, 15′-H); $J_{11,11'(15,15')}$ = 14; $J_{12,13(13,14)}$ = 2.8. – MS [CI (isobutane), 170 eV]: m/z (%) = 301 (19)[M^+ + 1], 300 (100) [M^+], 273 (36), 166 (33).

$C_{14}H_{16}N_6O_2$ (300.3) Calcd. C 55.99 H 5.37 H 27.98
Found C 55.67 H 5.37 N 27.98

4,5-Diazapentacyclo[6.5.0.0^{2,7}.0^{3,12}.0^{6,10}]tridec-4-en-endo-11-ylamine (**41a**): A suspension of 0.30 g (1.09 mmol) of **40a**, 0.88 g (21.9 mmol) of NaOH, and 10 ml of dry 2-propanol was heated at reflux (N_2) for 4.5 h. After cooling and addition of 20 ml of water, dild. HCl was added until pH ≈ 6, then 2.90 g (21.9 mmol) of $CuCl_2$, and the mixture was stirred at room temp. for 3 h. After decomplexation with concd. NH_3, the solution was extracted with CH_2Cl_2 and the extract was dried (Na_2SO_4) and concentrated in vacuo. Chromatography on silica gel [R_f = 0.49; $CHCl_3$/MeOH (4:1)/1% triethylamine, column 25 × 1 cm] gave 0.15 g (74%) of colorless crystals, m.p. 209°C (CCl_4). – IR (KBr): $\tilde{v}$ = 1448 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 5.62 (m_c, 3-, 6-H), 3.08 (m_c, 1-, 8-H), 2.73 (m_c, 10-, 12-H), 2.65 (t, 11-H), 2.56 (m_c, 2-, 7-H), 2.16 (br. s, 1 NH_2), 1.73 (m, 9-, 13-H), 1.55 (d, 9'-, 13'-H); $J_{10,11(11,12)}$ = 3.5; $J_{9,9'(13,13')}$ = 14.

$C_{11}H_{15}N_3$ (189.3) Calcd. C 69.81 H 7.99 N 22.20
Found C 69.63 H 7.85 N 22.17

endo-11-Azido-4,5-diazapentacyclo[6.5.0.0^{2,7}.0^{3,12}.0^{6,10}]tridec-4-ene (**41d**): A suspension of 0.60 g (2.00 mmol) of **40b**, 15 ml of dry 2-propanol and 1.60 g (40.0 mmol) of NaOH was heated to reflux (N_2) for 4 h. After cooling to room temp., it was diluted with 10 ml of water, acidified with 40% HCl and stirred for 2.5 h with 6.72 g (50.0 mmol) of $CuCl_2$. After decomplexation with concd. NH_3, the mixture was extracted with CH_2Cl_2 and the organic phase was dried (Na_2SO_4) and concentrated in vacuo. After filtration through silica gel (R_f = 0.41; ethyl acetate, column 5 × 1 cm), 0.31 g (71%) of **41d** was obtained as pale yellow crystals, m.p. 125°C (ether). – IR (KBr): $\tilde{v}$ = 2088 cm^{-1}, 1453. – UV (CH_3CN): λ_{max} (ε) = 397 nm (168; sh), 391 (175), 228 (1570). – ^1H NMR ($CDCl_3$): δ = 5.55 (m_c, 3-, 6-H), 3.47 (t, 11-H), 3.11 (m_c, 1-, 8-H), 2.86 (10-, 12-H), 2.59 (2-, 7-H), 1.87 (m, 9-, 13-H), 1.58 (d, 9'-, 13'-H); $J_{9,9'(13,13')}$ = 14; $J_{10,11(11,12)}$ = 2.5. – ^{13}C NMR ($CDCl_3$): δ = 69.0 (C-3, -6), 64.1 (C-11), 42.9 (C-10, -12), 40.2 (C-1, -8), 35.1 (C-2, -7), 31.0 (C-9, -13).

$C_{11}H_{13}N_5$ (215.3) Calcd. C 61.38 H 6.09 N 32.53
Found C 61.32 H 6.11 N 32.60

(4α,5β,6α,7α,8α)-8-Methoxy-1,2-diazabicyclo[3.3.0]oct-2-ene-4,6,7-triol (**45a**): To a vigorously stirred suspension of 5 g of aluminum oxide (neutral, Woelm Super I) and 400 mg (10.0 mmol) of NaOH in 5 ml of water a solution of 500 mg (3.20 mmol) of **13a** in 25 ml of methanol was added and the mixture stirred at room temp. for 7 d (TLC). 250 ml of methanol was added and, after stirring for 3 h, the mixture filtered, the filter cake washed with methanol, and the solution concentrated in vacuo. The residue was dissolved in 150 ml of water and continuously extracted with ethyl acetate (3 d). Evaporation of the solvent from the extracts in vacuo yielded 385 mg (64%) of **45a** as a yellow oil. – ^1H NMR (CD_3OD): δ = 6.78 (d, 3-H), 5.21 (dd, 4-H), 4.84 (d, 8-H), 4.28 (dd, 6-H), 4.21 (dd, 5-H), 4.12 (dd, 7-H), 3.55 (s, OCH_3); $J_{3,4}$ = 1.0; $J_{4,5}$ = 9.0; $J_{5,6}$ = 4.0; $J_{6,7}$ = 2.0; $J_{7,8}$ = 4.5. – ^{13}C NMR (CD_3OD): δ = 148.4 (d, C-3), 98.5 (d, C-8), 79.3 (q, OCH_3), 77.5 (d, C-7), 77.2 (d, C-6), 67.3 (d, C-4), 56.6 (d, C-5).

(4α,5β,6α,7α,8α)-8-Methoxy-1,2-diazabicyclo[3.3.0]oct-2-ene-4,6,7-triyl Triacetate (**45b**): To a solution of 97 mg (0.52 mmol) of **45a** in 10 ml of pyridine/acetic anhydride (1:1) 5 mg of 4-(dimethylamino)pyridine was added. After 24 h at room temp., the solution was concentrated in vacuo and the residue filtered through a short pad of aluminum oxide (Woelm 200 B III) [cyclohexane/ethyl acetate (1:1)] to yield 132 mg (81%) of colorless crystals, m.p. 66°C (ethyl acetate). – IR (KBr): $\tilde{v}$ = 1741 cm^{-1}, 1631, 1462. – ^1H NMR ($CDCl_3$): δ = 6.79 (d, 3-H), 5.83 (dd, 4-H), 5.42 (dd, 6-H), 5.20 (dd, 7-H), 4.98 (d, 8-H), 4.47 (dd, 5-H), 3.51 (s, OCH_3), 2.10 (s, $COCH_3$), 2.03 (s, $COCH_3$), 1.99 (s, $COCH_3$); $J_{3,4}$ = 1.0; $J_{4,5}$ = 9.5; $J_{5,6}$ = 4.5; $J_{6,7}$ = 4.0; $J_{7,8}$ = 4.5; NOE experiments revealed an effect of OCH_3 on 8-H. – ^{13}C NMR ($CDCl_3$): δ = 169.9 (CO), 169.5 (CO), 169.0 (CO), 142.2 (C-3), 94.0 (C-8), 75.8 (C-4), 74.4 (C-6), 74.1 (C-7), 64.0 (C-5), 56.3 (OCH_3), 20.8 (CH_3), 20.6 (CH_3), 20.5 (CH_3); $J_{C-3,H}$ = 193.5; $J_{C-4,H}$ = 157.0; $J_{C-5,H}$ = 153.0; $J_{C-6,H}$ = 160.0; $J_{C-7,H}$ = 157.0; $J_{C-8,H}$ = 160.0; $J_{CH_3,H}$ = 143.0. – MS (EI, 70 eV): m/z (%) = 314 (4) [M^+], 255 (36), 43 (100).

$C_{13}H_{18}N_2O_7$ (314.3) Calcd. C 49.68 H 5.77 N 8.91
Found C 49.12 H 5.69 N 8.79

(1α,2β,3α,4β)-3-Methoxy-6,7-diazabicyclo[3.2.1]oct-6-ene-2,4,syn-8-triyl Triacetate (**44b**): Besides **45b** <5% **44b** could be detected. – ^1H NMR ($CDCl_3$): δ = 4.96 (dd, 1-, 5-H), 4.90 (t, 8-H), 4.81 (dd, 2-, 4-H), 3.96 (t, 3-H), 3.29 (s, OCH_3), 2.16 (s, CCH_3), 2.10 (s, 2 CCH_3); $J_{2,3(3,4)}$ = 5.5; $J_{1,2(4,5)}$ = 1.0; $J_{1,8(5,8)}$ = 5.0.

(1α,2β,3β,4β,5α)-6,7-Diazabicyclo[3.2.1]oct-6-ene-2,3,4,syn-8-tetrol (**47a**): A solution of 2.0 g (13.9 mmol) of **46**[27] in 90 ml 0.46 M aqueous hydrazine (41.4 mmol) was refluxed for 24 h (N_2). After concentration of the solution in vacuo, the residue was dissolved in 30 ml of water and treated with 9.0 g (41.7 mmol) of freshly precipitated HgO. After stirring at room temp. for 4 h, it was filtered and concentrated in vacuo and the residue filtered through a pad of silica gel with ethyl acetate/methanol (2:1). Recrystallization from methanol yielded 1.36 g (56%) of colorless crystals, m.p. 143°C (dec.). – IR (KBr): $\tilde{v}$ = 1420 cm^{-1}. – ^1H NMR (D_2O): δ = 5.10 (dd, 1-, 5-H), 4.35 (t, 3-H), 4.28 (dd, 2-, 4-H), 3.37 (t, 8-H); $J_{1,2(4,5)} \approx J_{5,8(8,1)}$ = 4.9.

$C_6H_{10}N_2O_4$ (174.2) Calcd. C 41.38 H 5.79 N 16.08
Found C 41.70 H 5.74 N 15.76

(1α,2β,3β,4β,5α)-6,7-Diazabicyclo[3.2.1]oct-6-ene-2,3,4,syn-8-tetryl Tetraacetate (**47b**): 100 mg (0.57 mmol) of **47a** was acetylated; after filtration through a pad of silica gel [cyclohexene/ethyl acetate (1:1)], 154 mg (79%) of **47b** was obtained as colorless crystals, m.p. 162°C. – IR (KBr): $\tilde{v}$ = 1740 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 5.52 (dd, J = 5.7, J = 6.0, 2H), 5.44 (dd, J = 5.3, J = 5.7, 2H), 4.76 (t, J = 6.0, 1H), 4.70 (t, J = 5.3, 1H), 2.15 (s, OCH_3), 2.01 (s, 2 OCH_3), 1.99 (s, OCH_3).

$C_{14}H_{18}N_2O_8$ (342.3) Calcd. C 49.12 H 5.30 N 8.18
Found C 48.93 H 5.27 N 8.15

(1α,11β)-7,9,12-Trioxa-3,4-diazatetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodec-3-en-11-ol (**48**): To a stirred solution of 92 mg (0.53 mmol) of **47a** in 1 ml of absolute acetonitrile 250 mg (1.69 mmol) of trimethyl orthoformate and 5 mg of anhydrous *p*-toluenesulfonic acid were added. After 2 h at room temp., 10 ml of water was added, the mixture extracted with 50 ml of CH_2Cl_2, and the organic phase dried ($MgSO_4$) and concentrated in vacuo to yield 87 mg (89%) of colorless crystals, m.p. 228°C (dec.). – IR (KBr): $\tilde{v}$ = 1434 cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 349 nm (262); ε_{220} = 1002. – ^1H NMR ($CDCl_3$): δ = 5.57 (s, 8-H), 5.50 (dd, 2-, 5-H), 4.38 (d, 1-, 10-H), 4.21 (t, 6-H), 3.07 (br. s, 11-H), 1.58 (br. s, 1H, OH); $J_{1,2(5,10)} \approx$ 6.0; $J_{2,6(5,6)} \approx$ 5.3.

$C_7H_8N_2O_4$ (184.2) Calcd. C 45.65 H 4.38 N 15.22
Found C 45.60 H 4.25 N 15.23

7,9,12-Trioxa-3,4-diazatetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodec-3-en-11-one (**49**): To a solution of 1.06 ml (15.2 mmol) of dimethyl sulfoxide in 3.6 ml of CH_2Cl_2, cooled to –70°C (N_2), a solution of 1.30 g (10.0 mmol) of oxalyl chloride in 16.5 ml of CH_2Cl_2 was slowly added. After stirring the solution for 10 min and warming up to –20°C, a solution of 0.50 g (2.71 mmol) of **48** in 13.5 ml of dimethyl sulfoxide and 13.5 ml of CH_2Cl_2 was slowly added. After stirring for 1.5 h, the solution was treated with 7 ml of triethylamine and 5 min later with 150 ml of water. The mixture was extracted with 500 ml of CH_2Cl_2 and the extract dried ($MgSO_4$) and concentrated in vacuo. The residue was filtered through a pad of silica gel [CH_2Cl_2/methanol (10:1)] to yield 0.40 g (81%) of **49** (R_f = 0.76) as colorless crystals, m.p. 148°C (dec.) (methanol). – IR (KBr): =

1743 cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 359 nm (230), 311 (140; sh), 304 (150); ε_{220} = 2200. – ^{1}H NMR ($CDCl_3$): δ = 5.73 (s, 8-H), 5.55 (dd, 2-, 5-H), 4.70 (d, 1-, 10-H), 4.46 (t, 6-H); $J_{1,2(5,10)}$ = 4.5; $J_{2,6(5,6)}$ = 5.5.

$C_7H_6N_2O_4$ (182.1) Calcd. C 46.16 H 3.32 N 15.38
Found C 46.21 H 3.29 N 15.34

CAS Registry Numbers

1: 1121-63-7 / **2**: 131251-20-2 / **3**: 131251-21-3 / **4**: 131251-22-4 / **5**: 115492-56-3 / **6**: 131346-87-7 / **7**: 131251-23-5 / **8**: 131346-88-8 / **9**: 131346-89-9 / **13a**: 131346-90-2 / **14a**: 108291-93-6 / **14b**: 108291-94-7 / **15**: 108291-95-8 / **16**: 108291-96-9 / **17**: 108291-97-0 / **18**: 108291-98-1 / **19**: 131251-24-6 / **20**: 131251-25-7 / **30**: 115492-63-2 / **31a**: 115492-64-3 / **31b**: 115492-53-0 / **32a**: 131251-26-8 / **32b**: 131251-27-9 / **32c**: 115492-65-4 / **32d**: 131251-28-0 / **33b**: 131273-55-7 / **33c**: 131273-56-8 / **35a**: 115516-62-6 / **35b**: 131251-29-1 / **35c**: 115492-70-1 / **35d**: 115492-67-6 / **36**: 115516-61-5 / **37a**: 36628-74-7 / **37b**: 131251-30-4 / **38a**: 131251-31-5 / **38b**: 131251-32-6 / **38c**: 131273-57-9 / **39a**: 131251-33-7 / **39b**: 131273-58-0 / **39c**: 131251-34-8 / **40a**: 131251-35-9 / **40c**: 131273-59-1 / **40d**: 131251-36-0 / **41a**: 131179-36-7 / **41d**: 131179-31-2 / **44b**: 131273-60-4 / **45a**: 131251-37-1 / **45b**: 131251-131251-38-2 / **46**: 50474-02-7 / **47a**: 131251-39-3 / **47b**: 131251-40-6 / **48**: 131251-41-7 / **49**: 108292-10-0

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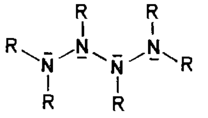
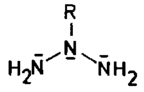


K



L

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