Synthesis and Reactions of Oligomethylene-Clamped 1*H*-Azepines and Benzene Imines. Their Valence Tautomeric Equilibrium and Nitrogen Stereochemistry[1)]

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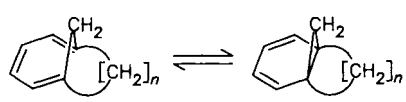
Syntheses of the clamped 1*H*-azepines and benzene imines, **6a**, **5b/6b**, and **5c**, and of some of their *N*-derivatives are described, and the positions of their valence tautomeric equilibria are examined. The *N*-methyl and *N*-chloro substituents favour the closed valence tautomer whereas the *N*-methoxycarbonyl group shifts the equilibrium towards the open isomer. The *N*-trimethylsilyl group also exerts a slight effect in the latter sense. Low temperature ^1H and ^{13}C NMR examination of **5b/6b** demonstrates that the free activation enthalpy of the valence tautomerization must be below 5 kcal/mol (21 kJ/mol), but that the nitrogen inversion can be frozen, with the *syn* isomer (i.e., H on N *syn* relative to the C=C double bonds) predominating. ^1H NMR shifts of the *N*-substituents and, for **14a**, preliminary X-ray data indicate that the *N*-substituents of the above benzene imines prefer *syn* orientation. **6a** rearranges on silica gel to give **33** which is silylated to yield **34**. Action of sodium methoxide on **14a** leads to **37** which is again chlorinated at nitrogen and treated with sodium methoxide to produce **40** and **41**. Plausible mechanisms for these transformations are proposed.

Synthese und Reaktionen von Oligomethylen-überbrückten 1*H*-Azepinen und Benzoliminen; Lage des Valenztautomerie-Gleichgewichtes und Stereochemie am Stickstoff[1)]

Die Synthese der überbrückten 1*H*-Azepine und Benzolimine **6a**, **5b/6b** und **5c** wird beschrieben und die Lage ihrer Valenztautomerie-Gleichgewichte untersucht. Der *N*-Methyl- und *N*-Chlor-Substituent verschieben das Gleichgewicht zugunsten der „geschlossenen", der *N*-Methoxycarbonyl- und (in geringerem Ausmaße) *N*-Trimethylsilyl-Substituent zugunsten der „offenen" Struktur. Eine Tieftemperatur-^1H- und -^{13}C-NMR-Untersuchung von **5b/6b** zeigt, daß die Freie Aktivierungsenthalpie der Valenztautomerisierung unter 5 kcal/mol (21 kJ/mol) liegen muß, daß jedoch die Inversion des Stickstoffs eingefroren werden kann, wobei das *syn*-Isomer (d. h. H am N *syn* relativ zu den C=C-Doppelbindungen) vorwiegt. Die ^1H-chemischen Verschiebungen der *N*-Substituenten und für **14a** eine grobe Röntgenstrukturanalyse zeigen, daß die *N*-Substituenten der Benzolimine die *syn*-Orientierung bevorzugen. **6a** lagert sich auf Kieselgel zu **33** um, das zu **34** silyliert wird. Einwirkung von Natriummethanolat auf **14a** ergibt **37**, welches bei erneuter *N*-Chlorierung und Behandlung mit Natriummethanolat in **40** und **41** übergeht. Plausible Mechanismen für diese Umwandlungen werden vorgestellt.

The cycloheptatriene/norcaradiene and oxepine/benzene oxide equilibria have been the subjects of a considerable number of preparative and theoretical investigations[2)]. Among the many compounds synthesized, the oligomethylene-clamped derivatives **1**/**2**[3)] and **3**/**4**[2a)] are of special interest. According to Bredt's rule, the bridgehead olefins **1** and **3** suffer from considerable strain which decreases with increasing clamp length *n* while the strain of their valence tautomers **2** and **4** shows little dependence on *n* as it is localized mainly in the three-membered ring. It has thus been possible to shift the equilibrium position from exclusively "open" representatives such as **1c** to exclusively "closed" ones such as **2a** and **4a**[4)]. 7-Substituted cycloheptatrienes/norcaradienes have been useful for an understanding of the factors which govern the equilibrium position. Briefly summarized, donor and acceptor substituents at C-7 favour the open and closed isomer, respectively, due to their interaction with the Walsh orbitals of the cyclopropane ring[5)].



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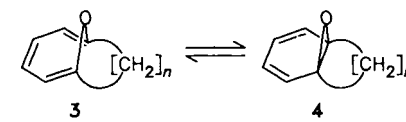

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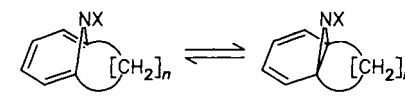

	X	
5	H	6
7	Me	8
9	$SiMe_3$	10
11	COOMe	12
13	Cl	14

a: $n = 3$; **b**: $n = 4$; **c**: $n = 5$

A large variety of 1*H*-azepine derivatives have been obtained through work on nitrene chemistry[6)]. Investigation of their valence tautomerism revealed that monocyclic 1*H*-azepines possess a low

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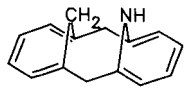
tendency to isomerize to the related benzene imines; even Diels-Alder adducts are derived from the former[7] in contrast to the behaviour of cycloheptatriene[8] and oxepine/benzene oxide[7a]. In only a few cases[9] minor amounts of the bicyclic isomers were detected by ^{1}H NMR or intercepted by addition of diazomethane. The parent compound[10] exists exclusively in the open form.



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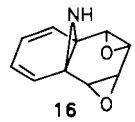

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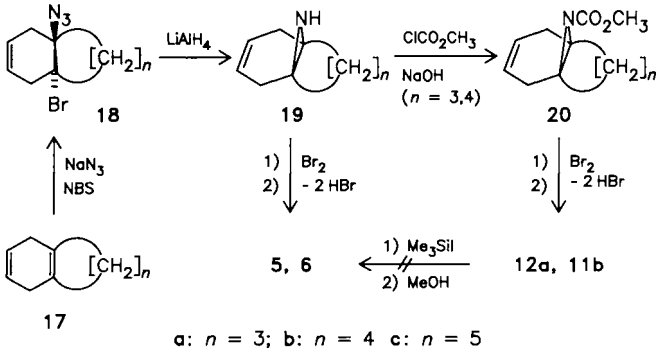
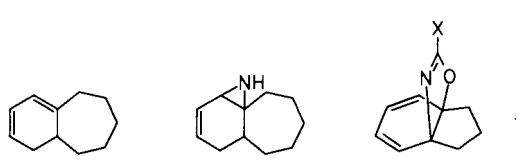
While the clamped urethanes **11b** and **12a**[11] are stable compounds as expected, it was not clear until recently whether 1*H*-azepines and benzene imines without *N*-substituents would be sufficiently stable to permit their isolation. 1*H*-Azepine[10] and some monocyclic derivatives[12] could be characterized only in dilute solutions, but the clamped derivatives **15**[13] and **16**[14] were isolated without difficulty. It was therefore anticipated that the synthesis of the unprotected clamped 1*H*-azepines and/or benzene imines **5/6 a–c** should feasible. Furthermore, these compounds might serve as intermediates for a variety of *N*-derivatives which might give an insight into the factors which determine the position of the azepine/benzene imine equilibrium.

Syntheses

Following ample precedent[2a,2c,3,11], our synthetic plan was based on the bromination/dehydrobromination of the dihydro precursors **19**, with or without use of a nitrogen protecting group. Compounds **19**, in turn, should be accessible from the dihydro aromatics **17** by aziridine annulation.



The cyclohexadienes **17a, b** were obtained from indane and tetralin in good purity and yield by a modification[15] of the reported[3] procedure (3 eq. Li, liq. NH_3/THF, reflux; protonation with ethanol). However, **17c** was invariably contaminated with an isomeric compound as well as overreduced hydrocarbons or starting material, under these and several other conditions. The isomer exhibits a UV maximum at 273 nm and may be tentatively assigned to structure **21** because the aziridine **22** could be isolated in low yield by repeated chromatography after the following step. As we were not able to separate this hydrocarbon mixture, it had to be used as such in the next step.

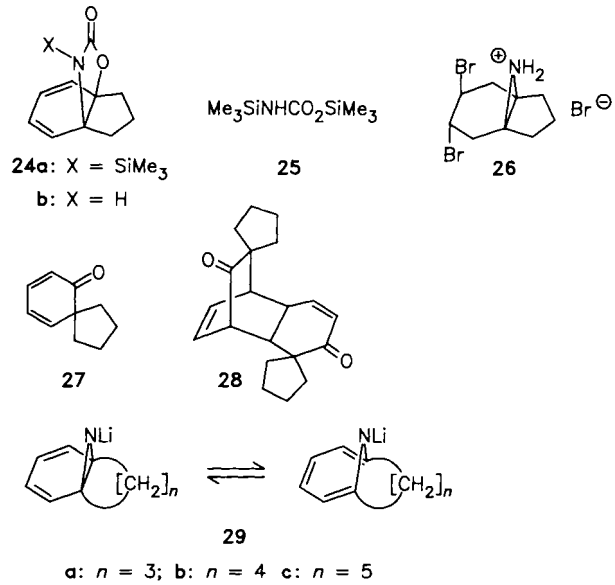


21 22 23a: X = OMe
b: X = OSiMe$_3$

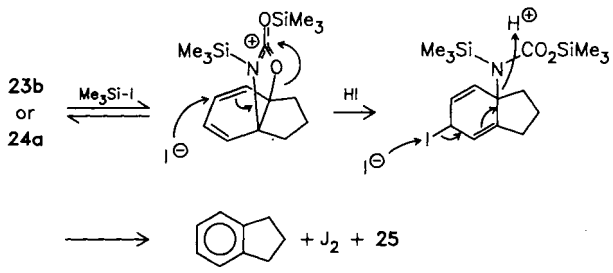
Aziridine annulation was performed by the Krief procedure[16] which had already proven superior to other methods in the synthesis of iminoannulenes[13,17]. The crude azides **18** are in all cases contaminated with rearomatized hydrocarbons which are apparently derived from **18** or the intermediate bromonium ions by elimination reactions induced by the basic azide anion. Only **18b** could easily be isolated in pure form by crystallization from methanol; it was therefore more convenient to subject the crude azides immediately to $LiAlH_4$ reduction. In this way the aziridines **19a, b** were isolated in pure form after acid extraction and distillation in 54 and 46–49% yield from **17a, b**. **19c**, however, was too sensitive for acid extraction. While the hydrocarbon contaminants could be removed by column chromatography, the separation of isomeric aziridines and those derived from overreduced material failed. Again, final purification had to be delayed to a later step.

With the aziridines **19a, b** in hand, our synthetic scheme could be linked to the work of Paquette et al.[11] by methoxycarbonylation ($ClCOOCH_3$, aq. NaOH, ether, 0°C). Bromination/dehydrobromination to give **11b** and **12a** was then achieved by a slight modification of the published procedure in 42 and 39% overall yields from **19a, b** omitting the GC purification in the case of **12a**. We found instead that the highly crystalline **12a** was conveniently purified by recrystallization from hexane. The melting point and spectral data differ considerably from those found by Paquette et al. We conclude that the data published by these authors belong to the rearrangement product **23a** formed from **12a** under a variety of conditions. Apparently **12a** is sensitive to heat or surface catalysis exerted by the GC column[18]; on a preparative scale, a more convenient procedure is to stir its solution in CCl_4 with catalytic amount of acid until the ^{1}H NMR spectrum indicates the completion of the rearrangement. It should be noted that the nitrogen of *N*-acyl aziridines has been shown to be pyramidal[19] and that, if the freezing of a dynamic process is observed, it will be that of nitrogen inversion which leaves intact the plane of symmetry of **12a**, and not that of rotation about the N–C bond which would destroy it. The ^{13}C NMR spectrum of **12a** exhibits accordingly 7 signals at room temperature and also at −60°C. Furthermore, the C=O stretching frequency of **12a** (1715 cm^{-1}) lies in the normal range for urethane carbonyls[20] in contrast to the C=N stretch of **23a** (1667 cm^{-1}; ref.[11]: 1665 cm^{-1}).

Both urethanes **11b** and **12a** gave disappointing results on attempted cleavage with iodotrimethylsilane[10,21]. While **11b** was slowly aromatized, **12a** underwent instantaneously a more complex degradation yielding, besides a rearranged silyl derivative **23b** or **24a**, minor and irreproducible amounts of indane, iodine, and the bis(trimethylsilyl) derivative of carbamic acid, **25**[22]. Replacement of the reagent by the less reactive bromotrimethylsilane led to the exclusive



formation of **23b** or **24a** which was characterized by methanolysis to the lactam **24b**[23]. Finally, the use of chlorotrimethylsilane permitted the direct observation of the relatively fast rearrangement of **12a** to **23a** by ^{1}H NMR at room temperature (within 1 – 2 h) followed by slow formation of the silyl derivative (several days). It is not clear whether the rearrangement results from traces of hydrogen halide present in the reagents or from their own Lewis acidity[24]. As these results indicated that an acyl function at nitrogen may behave as an activating rather than a protecting group within the present molecular skeleton, our attention turned to the bromination/dehydrobromination of the free aziridines **19** next. Analogous procedures had previously met with success in the case of **15**[13] and 1,6-imino[10]annulene[25].



The aziridines **19a – c** yielded on addition of bromine in methylene chloride at −78°C yellow to orange-coloured syrups, foams, or amorphous solids which were not stable and therefore were dehydrobrominated immediately using potassium *tert*-butoxide in THF. The products were contaminated with considerable amounts of starting material if only one equivalent of bromine was used, since some reagent was consumed by complexation with the basic nitrogen[26] and subsequent oxidative destruction of part of the substrate. Chromatographic separation of the mixture was easily performed on alumina only in the case of the indane imine[27] **6a**, resulting in a 39% yield of the pure amine as a colourless stable liquid. If an excess of bromine was used, the hydrogen bromide produced by the oxidation of **19a** (or its dibromide) caused precipitation of a nearly equivalent amount of the dibromide hydrobromide **26** which could be obtained more efficiently by bromination of **19a** in a mixture of 48% aqueous HBr and ether (0°C, 74 – 80% yield). Its dehydrobromination under the above conditions furnished analytically pure indane imine in good yield (82 – 87%).

No crystalline dibromide hydrobromides could be obtained from **19b, c**. The use of an excess of bromine was essential in the case of **19c** as we were unable to separate the product **5c** from its precursor. All other impurities including those derived from isomeric and overreduced hydrocarbons were removed by column chromatography. Pentamethylene azepine[27] **5c** was isolated in 1.8% overall yield (from tetrahydrobenzocycloheptene) by distillation as an air-sensitive yellow liquid.

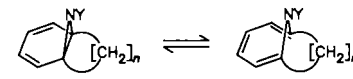
Even when an excess of bromine was used, tetramethylene azepine[27,28] could not be obtained directly free of the starting aziridine; on the other hand, however, it suffered considerable decomposition during chromatography. Even under the mildest conditions, it was partially converted into the dienone **27** and its dimer **28** which had to be removed subsequently. **28** is hardly volatile but **27** codistils with the product and forms new **28** on standing. A chemical method was therefore devised to separate these contaminants, namely their transformation into less volatile compounds by reaction with *n*-butyllithium (with concomitant deprotonation of **5b**/**6b** to form the stable *N*-anion **29b**, see below). Finally, small amounts of tetralin were removed by distillation over a spaltrohr column. Pure tetramethylene azepine resulted in 22% yield (from **19b**) as an almost colourless liquid (thick layers exhibit a weak yellowish colour) which is remarkably unstable to protic solvents. By merely leaving it in a water/methanol solution for some days, it was transformed almost quantitatively into **28** and ammonia. This reaction corresponds to the known[29] acid-catalyzed isomerization of tetralin oxide to **27** and subsequently to **28**. In the present case, too, traces of acid or surface catalysis may be involved.

N-methylation and *N*-silylation of the title compounds were performed by lithiation (*n*-BuLi, THF, −78°C) and quenching with methyl iodide and chlorotrimethylsilane, respectively[30]. The *N*-lithio derivatives **29a – c** were not examined spectroscopically so that their structures (open vs. closed) remain uncertain. Indane imine yielded a stable *N*-chloro derivative **14a** on treatment with *tert*-butyl hypochlorite (CH_2Cl_2, 0°C), while that of tetramethylene azepine could only be characterized in solution at low temperature. The *N*-chloro derivative of pentamethylene azepine was not obtained at all.

Discussion

Selected spectroscopic properties of the synthesized benzene imines and azepines are summarized in Table 1. The equilibrium positions may be deduced both from ^{1}H and ^{13}C NMR spectra. With the exception of **12a**, all examples show well-separated signals for their olefinic protons 2,5-H and 3,4-H from which the parameter $N = J_{2,3} + J_{2,4}$ may be read directly[31]. *N* has previously been correlated with

Table 1. Equilibrium positions and selected spectroscopic data of clamped 1*H*-azepines and arene imines



Compound no. (equilibrium position)			^{1}H NMR δ(2,5-H)[a]	δ(3,4-H)	N[Hz][b]	δY	Solvent, temp.[c]	^{13}C NMR δ(C-1,6)[d]	δ(C-2,5)[e]	δ(C-3,4)[e]	Solvent, temp.[c]	UV λ_{max}/(lgε)	Solvent
n = 3													
Y = H	–	**6a**	6.43	6.01	9.9[f]	−1.45	CCl_4/CD_2Cl_2	53.8	129.5	120.9	$CDCl_3$	270 (3.78)	*c*-C_6H_{12}
Me	–	**8a**	5.94	6.28	10.1	1.22	CCl_4	59.7		122.9 124.1	$CDCl_3$	271 (3.74)	CH_2Cl_2
$SiMe_3$	–	**10a**	6.40	6.00	10.0	−0.12	CCl_4	53.4	130.9	122.9	$CDCl_3$	268 (3.64)	CH_2Cl_2
COOMe	–	**12a**		6.15 (centre)		3.47	CCl_4	61.4		123.6 124.7	$CDCl_3$	261 (3.69)	CH_2Cl_2
Cl	–	**14a**	6.01	6.48	10.0	–	CCl_4	64.9		121.6 126.9	$CDCl_3$	231 (3.44) 278 (3.58)	*c*-C_6H_{12}
n = 4													
H	**5b**	**6b** (approx. 7:3)	6.07	6.34	6.6	0.3	CCl_4	109.0		121.3 125.5	$CDCl_3$	267 (3.47)	*c*-C_6H_{12}
Me	–	**8b**	5.74	6.26	10.1	1.27	CCl_4	55.8	126.9	123.9	$CDCl_3$	265 (3.71)	*n*-C_6H_{14}
$SiMe_3$	**9b**	**10b** (approx. 5:1)	6.00	6.32	5.9	−0.12	CCl_4	133.3		122.0 128.7	$CDCl_3$	[g]	
COOMe	**11b**	–	5.79	6.35	5.1	3.41	C_6D_6, +75°C[h]	130.7		120.5, 128.2 121.1, 128.6	$CDCl_3$ −20°C[i]	252 (sh) (3.37)	*n*-C_6H_{14}
Cl	–	**14b**	5.89	6.55	10.1[f]	–	CD_2Cl_2, −60°C		[j]			[j]	
n = 5[k]													
H	**5c**	–	5.15	6.04	5.5[f]	3.23	$CDCl_3$	150.2	110.5	129.7	$CDCl_3$	345 (2.75)	CH_3CN
Me	**7c**	**8c** (approx. 1:2)	5.70	6.35	8.4	1.90	$CDCl_3$	94.9		123.0 127.2	$CDCl_3$	345 (sh)[l]	CH_3CN

[a] Assignment of the 2,5-H multiplet is based on its broadening by long-range coupling with the adjacent methylene protons. – [b] $N = J_{2,3} + J_{2,4}$. – [c] Stated only if different from room temp. – [d] This signal is easily identified for arene imines and equilibrium mixtures by its chemical shift. If it is located in the sp^2 range, it can be identified by its reduced intensity due to slow relaxation (at low temperature, however, it may become the most intensive one due to much larger viscosity broadening of the others). – [e] We did not always attempt to distinguish the signals of C-2,5 and C-3,4. When this was done, assignment is based on the coupling pattern of the ^{1}H-coupled spectra[31] for arene imines, and on the assumption that C-2,5 should resonate at higher field in the case of azepines. – [f] For a complete analysis of the AA'XX' multiplet, see Experimental. – [g] Compound decomposed during measurement. – [h] At room temp., resolution is poor due to hindered rotation about the urethane N–C bond. – [i] Signal splitting for the same reason as under h). – [j] Not measured since compound is very unstable. – [k] For the purpose of comparison, the same numbering of atoms is used as in the tri- and tetramethylene series. – [l] Only a qualitative spectrum was obtained.

the equilibrium position of closely related compounds[3,32]; typical values for clamped arene oxides and norcaradienes are around 10 Hz and those for clamped oxepines and cycloheptatrienes in the region of 5 to 6.5 Hz. The higher conformational flexibility of the (hetero)cycloheptatriene vs. the (hetero)norcaradiene systems requires a careful choice of a reference compound in the former case, if possible one which has the same type of clamp. Because of its N value at the lowest end of the expected range, the urethane **11b** appears suitable in the tetramethylene series. In the ^{13}C NMR spectra, the quaternary carbon atoms C-1,6 resonate in the sp^2 region for azepines and in the region of hetero-substituted sp^3 carbons for benzene imines[33].

Equilibrium positions estimated according to these criteria are included in Table 1; their accuracy is necessarily limited in the case of mixtures but the tendencies are clearly visible. As expected, they are shifted in favour of the azepine ("open") structure with increasing clamp length. In none of the examined compounds is the *N*-substituent able to override the preference of the trimethylene sytem for the benzene imine ("closed") structure. In contrast, the equilibrium positions of the tetra- and pentamethylene compounds depend on the nature of the *N*-substituents. Surprisingly, the effect of the *N*-methoxycarbonyl and *N*-chloro substituents is just opposite to that on the cycloheptatriene/norcaradiene system, while the methyl group shows parallel behaviour in both series[34]. It seems reasonable to assume that factors which increase the C^1-N-C^6 angle (which is larger in the azepine than in the benzene imine) favour the azepine isomer, and vice versa. One may conclude that the interaction of the methoxycarbonyl substituent with the lone pair on nitrogen which increases the C^1-N-C^6 angle due to amide resonance dominates over that with the Walsh orbitals of the three-membered ring[5] which would favour the closed structure. The effect of methyl substitution may be seen in analogy with the values for di- and trimethylamine which amount to 112.1° and 108.7°, respectively[35]. This simple view is, however, no longer helpful in the case of the *N*-chloro substituent, since the C–N–C angle reported for *N*-chlorodimethylamine (110.7° and 111° for 2 structure

models)[36] is only insignificantly smaller than that in dimethylamine.

The equilibrium mixture **5b/6b** was selected for low temperature ^1H and ^{13}C NMR investigations to determine the activation parameters of its valence tautomerization. Even at −147°C, however, no indication for the freezing of this process was obtained from the ^{13}C NMR spectrum (20 MHz, [D_6]dimethyl ether). An upper limit of 5 kcal/mol (21 kJ/mol) for the free activation enthalpy can be estimated from this result. There were, however, two other dynamic processes which could be frozen.

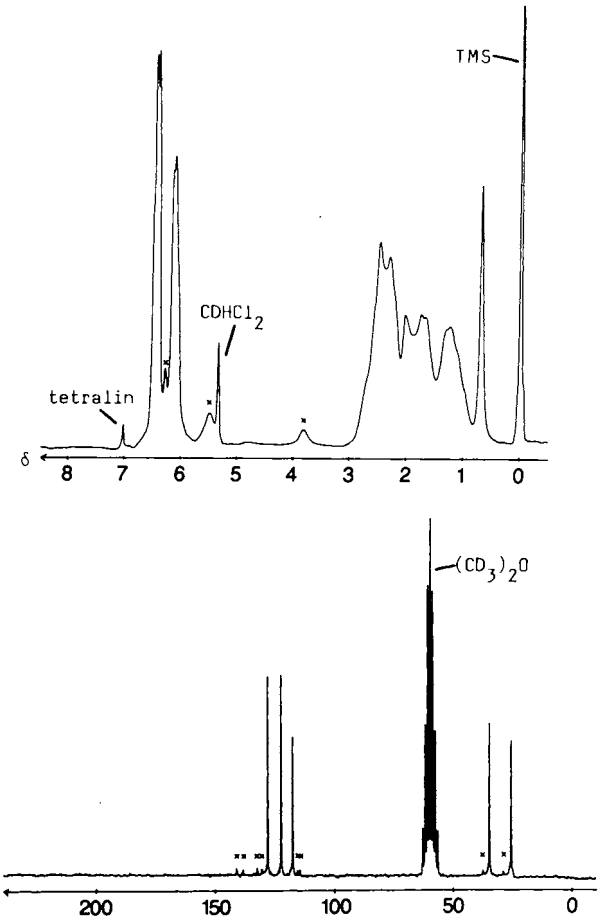
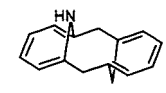


Figure 1. Low temperature ^1H and ^{13}C NMR spectra of **5b/6b** [60 MHz, CD_2Cl_2/CF_2Br_2, TMS, −112°C, and 20 MHz, $(CD_3)_2O$, −142°C]. Signals assigned to *anti*-**5b** are labelled with an asterisk. The ^1H NMR sample is contaminated with approx. 1% of tetralin.

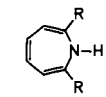
Figure 1 shows low temperature ^1H and ^{13}C NMR spectra of **5b/6b** which indicate the presence of a minor isomer which does not exhibit chemical shifts expected for **6b** (see Table 2). Instead, the two components differ by the position of their NH proton *syn* or *anti* relative to the C=C double bonds. One may expect the following ^1H NMR characteristics for *syn* and *anti* azepines: (1) The NH proton of the *syn* isomer is shielded by the $C^3=C^4$ double bond while that of the *anti* isomer is deshielded by the $C^1=C^2$ and $C^5=C^6$ double bonds. (2) *anti* configuration of the N−H proton results in an enamine-like mesomeric interaction of the nitrogen lone pair with the adjacent C=C double bonds[37] (the formation of an 8π antiaromatic system being avoided by the nonplanarity of the azepine ring[2e,38]) which should cause a high-field shift of 2,5-H. This interaction is absent in the *syn* isomer, the relevant orbitals of which are nearly orthogonal. From these considerations, the major isomer is identified as *syn* in contradiction to theoretical work[37,39]. ^{13}C NMR demonstrates further that *anti*-**5b** contains very little, if any, benzene imine isomer (*anti*-**6b**).

Comparison with further azepines included in Table 2 shows that all other representatives are at least predominantly *anti*-configurated as theory predicts[37,39]. The extent of the high-field shift of 2,5-H depends on the skeletal mobility and is maximum for the unconstrained representatives **31**, **32** where enamine resonance can attain its optimum value, and lowest for the most rigid example, *anti*-**5b**. The reason why **5b/6b** behaves different from other azepines remains uncertain but is possibly connected with the other dynamic process in its ^{13}C NMR spectrum: the olefinic signals of the *anti* isomer exhibit a 1:1 splitting at very low temperature (probably, the aliphatic ones likewise do so but part of them is hidden by other signals) which can only be explained by the freezing of the conformational inversion of the tetramethylene chain and the resulting cancellation of the plane of symmetry of the molecule.

Table 2. Selected spectroscopic data of 1*H*-azepines



30



31 (R = H), **32** (R = Me)

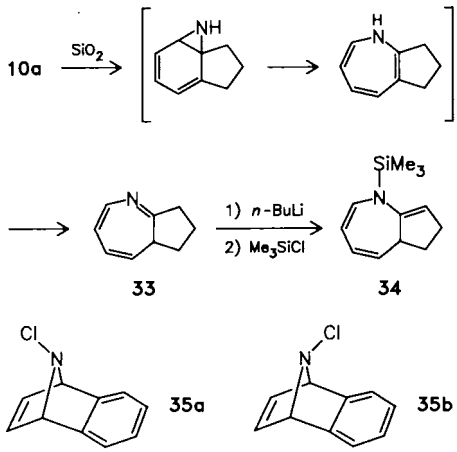
Compound	δ(2,5-H)	δ(NH)	Solvent, temp.	δ(C-1,6)	Solvent, temp.	Colour	Ref.
syn-**5b/6b**	6.1	0.7	CD_2Cl_2/CF_2Br_2, −112°C	117	$(CD_3)_2O$, −142°C }	almost	a)
anti-**5b**	5.5	3.8	CD_2Cl_2/CF_2Br_2, −112°C	138, 141[b]	$(CD_3)_2O$, −142°C }	colourless	a)
30	5.32	3.38	$CDCl_3$, room temp.	147.9	$CDCl_3$, room temp.	yellow	13
15	5.13	3.33	$CDCl_3$, room temp.	153.6	$CDCl_3$, room temp.	yellow	13
5c[c]	5.15	3.23	$CDCl_3$, room temp.	150.2	$CDCl_3$, room temp.	yellow	a)
31	4.69	3.52	$CDCl_3$, −60°C	138.0	$CDCl_3$, −60°C	red	10
32	4.72	3.06	$CDCl_3$, −50°C	148.2	$CDCl_3$, −50°C	red	52

[a] This work. — [b] Due to their quaternary nature, these signals exhibit the least viscosity broadening at −147°C and can thus be identified. — [c] See Table 1, footnote k).

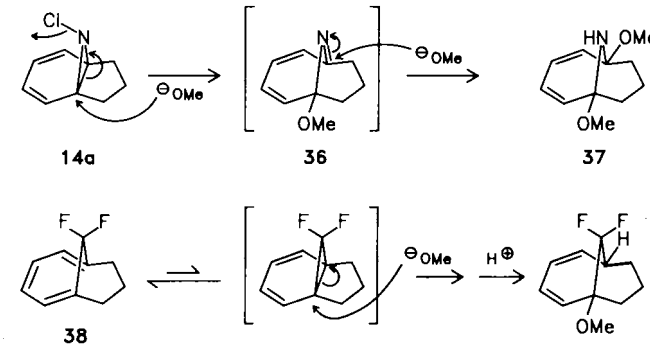
After the problem of nitrogen stereochemistry had emerged, it was interesting to obtain related information for the benzene imines. The first NMR criterion given above holds by analogous reasoning in the benzene imine series and may be extended to the *N*-methyl derivatives and, with some caution, to **10a** (where the relevant protons are more distant from the anisotropic bonds). An important difference to the azepines lies in the height of the inversion barriers; for *N*-unsubstituted and *N*-alkylated aziridines coalescence temperatures higher than room temperature are generally observed in their ^{1}H NMR spectra[19,40,41]. As there is no signal splitting or broadening in their ^{1}H and, more importantly, ^{13}C NMR spectra, we conclude that **6a** and **8a, b** (and probably also **10a**) are stereochemically homogeneous within the limits of the method. The high field resonances of their NH and CH_3 protons (see Table 1) leave no doubt that the substituents are oriented *syn* to the diene moiety in agreement with theoretical stability predictions[37,39]. A smaller but still significant shielding of the *N*-substituent is observed for **10a**. The answer is more difficult for the *N*-chloro derivative **14a** as NMR can only supply confirmation of the stereochemical homogeneity. After an attempt to use chemical methods had yielded otherwise interesting but for the present problem inconclusive results (see below), the solution was obtained through a preliminary X-ray analysis[42] which indicates again *syn* configuration at least in the solid state.

Chemical Transformations of 6a and 14a

On silica gel chromatography, indane imine undergoes a rearrangement to yield 5a,6,7,8-tetrahydrocyclopent[*b*]azepine **33**, probably by a sequence of 1,5-sigmatropic nitrogen migration, benzene imine/azepine valence tautomerization, and prototropy. **5b**/**6b** and **5c** decompose completely on silica gel. Dehydrogenation of **33** to the parent compound, cyclopent[*b*]azepine[43], failed under several conditions. A derivative which could easily be prepared is the silylation product **34**. Characteristically, deprotonation of **33** occurs at the α-position (relative to the C=N double bond) *outside* the seven-membered ring[44] avoiding formation of an antiaromatic 8π-electron system.

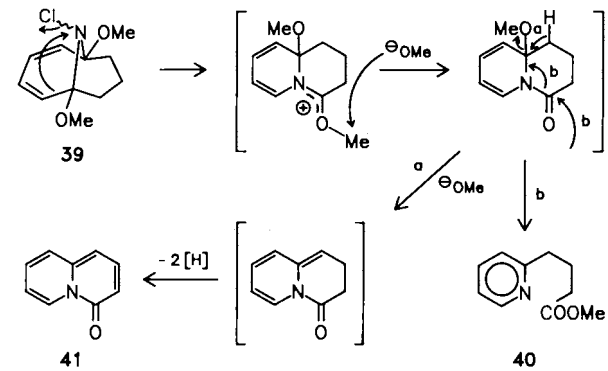


Before the nitrogen stereochemistry of **14a** had been established by X-ray analysis, an attempt was made to distinguish between the possible isomers by chemical transformation in analogy to the work of Rautenstrauch[45] who had shown that **35a, b** upon action of methoxide ion yield products derived from participation of the unsaturated group *anti* to the N–Cl bond. No products formed by neighbouring group participation were, however, found in the present case.



Instead, besides some **6a** (from N–Cl homolysis and H abstraction), the product of aziridine ring cleavage, **37**, was isolated in 61% yield. Its formation may be rationalized as shown in the formula scheme. The first step of this sequence shows strong analogy to the ring opening of **38** by methoxide[46]; in that case, however, halide elimination does not take place due to the much higher C–F bond strength.

Bridgehead azomethines like **36** are well-established as reactive intermediates[47]. **37** could be rechlorinated at nitrogen to furnish **39** which was again exposed to methoxide. This reaction yielded **37** (8%), methyl 4-(2-pyridyl)butyrate[48] (**40**) (54%), and 4*H*-quinolizin-4-one[49] (**41**) (10%). An aza-Wagner-Meerwein rearrangement[50] satisfactorily explains this transformation. Dehydrogenation leading to **41** may be caused by air (during isolation) or radicals derived from **39**.



One of us (W. T.) gratefully acknowledges a stipend granted by the *Verband der Chemischen Industrie*. We are obliged to Dr. *H. Schmickler*, Universität Köln, for the measurement of numerous NMR spectra and much help in their assignment, and to Professor Dr. *D. Cremer*, Dr. *W. Klug*, and Dr. *J. Lex*, Universität Köln, for the communication of their unpublished results. We are deeply in-

debted to Professor Dr. *E. Vogel* for the initiation of this work, his interest in it, and his consent to this publication.

Experimental

^{1}H NMR spectra were recorded on Varian EM 390 and Bruker WP 60 instruments at 90 and 60 MHz, respectively, using tetramethylsilane as the internal standard. ^{13}C NMR spectra were recorded on a Varian CFT 20 instrument at 20 MHz using the deuterium frequency of the solvent for calibration. IR and UV spectra were measured on Perkin-Elmer 283 and Beckman model 25 spectrometers, respectively. Low-resolution mass spectra were measured on a Finnigan 3200 (electron impact ionization at 70 eV), and high resolution mass spectra on Varian MAT 212 and MAT 731 instruments. Column chromatography was performed on Merck 0.063–0.2 mm neutral alumina (activity 2–3) and Merck 0.063–0.2 mm silica gel. Column dimensions (length × diameter) and eluents are indicated in the text of the individual procedures. Combustion analysis were performed by Dr. F. Pascher/E. Pascher microanalytical laboratory, Bonn. Melting points were determined on a Büchi capillary apparatus and are uncorrected.

trans-3a-Azido-7a-bromo-2,3,3a,4,7,7a-hexahydro-1H-indene (**18a**): To a mixture of 118 g (1 mol) of 2,3,4,7-tetrahydro-1*H*-indene[3,15] (**17a**) in 1 l of 1,2-dimethoxyethane and 325 g (5 mol) of NaN_3 in 200 ml of water is added in portions of 5–10 g 196 g (1.1 mol) of *N*-bromosuccinimide at −25°C with good overhead stirring at a rate slow enough that the yellow colour appearing after each portion has distinctly faded before the next one is added. After warming to room temp., 1 l of water and 800 ml of CH_2Cl_2 are added. The phases are separated, and the organic phase is washed eight times with 1 l of water each time. After drying with $MgSO_4$, the solvent is evaporated in vacuo (bath temperature should not exceed 40°C).

Note that organic azides may be explosive!

The crude, oily azide (approx. 200 g; major impurity is indane) is used in the next step without purification.

trans-4a-Azido-8a-bromo-1,2,3,4,4a,5,8,8a-octahydronaphthalene (**18b**): By the same procedure, approx. 215 g of the crude title compound is obtained from 134 g (1 mol) of 1,2,3,4,5,8-hexahydronaphthalene[3,15] and used in the next step without purification. By crystallization from 300 ml of methanol at −20°C, 116 g (45%) of the azide is obtained as colourless crystals melting at 54–56.5°C. – IR (KBr): $\tilde{\nu}$ = 3037 cm^{-1}, 2958, 2104 (N_3), 1650 (C=C), 1444, 1265 (N_3), 1216, 796, 662 (C–Br). – ^{1}H NMR (CCl_4): δ = 1.4–2.9 (m, 12H), 5.66 (narrow m, 2H, 6,7-H). – MS: *m/z* (%) = 228, 226 (0.12, 0.12), 215, 213 (0.18, 0.14), 148 (47), 133 (87), 91 (100).

$C_{10}H_{14}BrN_3$ (256.2) Calcd. C 46.89 H 5.51 Br 31.19 N 16.40
Found C 47.07 H 5.52 Br 31.54 N 16.34

trans-4a-Azido-9a-bromo-4,4a,5,6,7,8,9,9a-octahydro-1H-benzocycloheptene (**18c**): 37.0 g of 40% 4,5,6,7,8,9-hexahydro-1*H*-benzocycloheptene[3,15] (**17c**) (0.1 mol; the remainder is isomeric and overreduced material, and the starting aromatic hydrocarbon) is treated with 81.3 g (1.25 mol) of NaN_3 and 46.2 g (0.26 mol) of *N*-bromosuccinimide in 125 ml of 1,2-dimethoxyethane and 55 ml of water according to the above procedure. The crude product (54 g) should not be exposed to temperatures higher than room temp. and should be used immediately in the next step.

10-Azatricyclo[4.3.1.0^{1,6}]dec-3-ene (**19a**): **Caution!** During the hydrolysis step, large quantities of hydrogen gas are evolved accompanied by strong foaming. The reaction must be performed in a well-ventilated hood.

In a 4-l four-necked flask equipped with a powerful mechanical stirrer, dropping funnel, argon inlet, and thermometer, 1 l of THF is cooled to −15°C, and 41.7 g (1.1 mol) of $LiAlH_4$ is added cautiously (dissolution is exothermic). After cooling again to −15°C, the crude azide **18a** (obtained from 1 mol of tetrahydroindene) in 250 ml of THF is added dropwise within 4 h at −10 to −15°C (if the addition time is shorter or the temperature lower, the reaction may run away on warming). The reaction mixture together with the cooling bath is allowed to warm to +15°C and kept overnight at room temp. with maintenance of the inert gas atmosphere. Hydrolysis is effected by *cautious* dropwise addition of a mixture of 1.4 l of saturated potassium sodium tartrate solution and 0.4 l of 15% aqueous NaOH to the well-cooled (bath at −20°C) reaction mixture under a strong current of argon. The mixture soon becomes very viscous and difficult to stir, and care must be taken to avoid local overconcentrations of the hydrolysis solution which would cause vigorous foaming as soon as the viscosity decreases again. After the hydrogen evolution has ceased, addition of the residual hydrolysis solution may be accelerated, and cooling is stopped. The phases are separated; the aqueous phase is diluted with 1 l of water and extracted with 1 l of CH_2Cl_2. The combined solutions are washed with 2 × 200 ml of brine, evaporated, and taken up in 300 ml of cold (−30°C) pentane. The product is extracted into 600 ml of cold 1.2 M HCl, and the solution is washed with 2 × 100 ml of cold pentane. The base is liberated with 250 ml of cold 15% NaOH and extracted into 1 × 300 and 2 × 100 ml of pentane. After washing with 100 ml of brine and drying with K_2CO_3, the solvent is removed, and the residue distilled in vacuo to obtain 73.5 g (54%) of **19a** as a colourless liquid with strong amine odor; bp 37.5–39.5°C/0.9 Torr. – IR (Film): $\tilde{\nu}$ = 3281 cm^{-1} (N–H), 3033, 2928, 2894, 1654 (C=C), 872. – ^{1}H NMR (CCl_4): δ = 0.15 (br. s, 1H, NH), 1.1–2.1 (m, 6H, 7,8,9-H), 2.1–2.7 (m, 4H, 2,5-H), 5.51 (narrow m, 2H, 3,4-H). – MS: *m/z* (%) = 135 (43), 134 (58), 120 (34), 107 (100), 106 (80).

$C_9H_{13}N$ (135.2) Calcd. C 79.95 H 9.69 N 10.36
Found C 79.60 H 9.79 N 10.45

11-Azatricyclo[4.4.1.0^{1,6}]undec-3-ene (**19b**): Following the above procedure, the crude azide obtained from 1 mol of hexahydronaphthalene (**17b**) yields 68.3–73.1 g (46–49%) of **19b** as a colourless liquid with strong amine odor; bp 45–47.5°C/0.5 Torr. – IR (film): $\tilde{\nu}$ = 3272 cm^{-1} (N–H), 3026, 2931, 1654 (C=C), 1440, 1140, 857, 839. – ^{1}H NMR (CCl_4): δ = 0.3 (br. s, 1H, NH), 1.0–2.0 (m, 8H, 7-H to 10-H), 2.33 (narrow m, 4H, 2,5-H), 5.50 (narrow m, 2H, 3,4-H). – MS: *m/z* (%) = 149 (47), 148 (35), 134 (22), 121 (47), 120 (64).

$C_{10}H_{15}N$ (149.2) Calcd. C 80.48 H 10.13 N 9.39
Found C 80.38 H 10.34 N 9.49

12-Azatricyclo[5.4.1.0^{1,7}]dodec-9-ene (**19c**) *and 1a,4,4a,5,6,7,8,9-Octahydro-1H-cyclohepta[b]benzazirine* (**22**): 54 g of crude **18c** in 250 ml of THF is added dropwise at −25°C to 8.55 g (0.225 mol) of $LiAlH_4$ in 250 ml of THF. The mixture is stirred at −25°C for 3 h and allowed to warm to room temp. overnight. With the same precautions as described above, hydrolysis is effected by sequential addition of 8.5 g of water, 8.5 g of 15% NaOH, and 26.7 g of water. Stirring is continued for 1 h, 500 ml of CH_2Cl_2 is added, and the mixture is stirred for another 0.5 h. The inorganic precipitate is separated by suction filtration and carefully washed with 8 × 125 ml of CH_2Cl_2. After drying with $MgSO_4$ and removal of the solvents in vacuo, the residue is subjected to column chromatography (Al_2O_3, 60 × 4 cm). Elution with pentane affords tetrahydrobenzocycloheptene (10.1 g after distillation), further elution with ether/pentane (3:1) 10.7 g of an aziridine mixture which is fractionated in vacuo. The lowest-boiling fraction (4.75 g; bp 47–51°C/0.1 Torr) contains 50% of **19c** and is used in the following step.

From the undistilled aziridine mixture, its most polar component **22** can be isolated in low yield (1.1 g) by further twofold column chromatography (Al_2O_3, 45 × 5.5 cm, ether) and distillation; bp 50°C/0.1 Torr. – ^1H NMR ($CDCl_3$): δ = 0.64 (br. s, 1H, NH), 1.0–2.2 (m, 10H), 2.38 (narrow m, 2H, 4-H), 2.50 (narrow m, 1H, 1a-H), 5.32 (narrow m, 2H, 2,3-H). – ^{13}C NMR ($CDCl_3/CCl_4$): δ = 25.2, 26.1, 26.2, 30.4, 32.4, 36.1 ($^1J_{C,H}$ = 166 Hz, C-1a), 38.5 (C-4), 40.0 ($^1J_{C,H}$ = 125 Hz, C-4a), 40.6 (C-9a), 120.1 and 130.0 (C-2,3). – MS: *m/z* (%) = 163 (18), 148 (100).

trans-3,4-Dibromo-10-azatricyclo[4.3.1.0^{1,6}]decane Hydrobromide (**26**): 27.0 g (0.2 mol) of **19a** is dissolved in 400 ml of ether, and 25 ml (0.22 mol) of 48% hydrobromic acid is added at 0°C. To this solution 35.2 g (0.22 mol) of bromine in 20 ml of CH_2Cl_2 is added dropwise within 2 h at 0°C with good magnetic stirring. The precipitated salt appears first with a sticky consistence and later solidifies. Stirring is continued for some time to obtain a finely ground product which is then isolated by suction filtration and repeatedly washed with ether and THF until colourless, with careful crushing of remaining lumps which pertinaciously retain orange-coloured impurities. The residual fluffy white powder is sucked dry and amounts to 55.5–60 g (74–80%). The analytical sample is obtained by recrystallization from methanol (reflux to −30°C); mp 138°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2840 cm^{-1} (br., N–H), 1574, 1435, 1079, 1068. – ^1H NMR (CF_3COOH): δ = 1.5–3.0 (m, 6H, 7,8,9-H), 3.12, 3.44 and 3.18, 3.34 (AB parts of two ABX multiplets; J_{AB} = 17 and 16 Hz, resp.; only the signal at δ = 3.44 exhibits a resolved J_{AX} = 3.5 Hz; 1H each, 2,5-H), 4.71 (narrow m, 2H, 3,4-H), 5.6 and 6.7 (br. s, 2H, NH_2). – MS: *m/z* (%) = 297, 295, 293 (2, 5, 2), 216, 214 (50, 53), 134 (100).

$C_9H_{14}Br_3N$ (375.9) Calcd. C 28.76 H 3.75 Br 63.77 N 3.73
Found C 28.75 H 3.70 Br 63.90 N 3.72

10-Azatricyclo[4.3.1.0^{1,6}]deca-2,4-diene (Indane Imine, **6a**): 30.1 g (0.08 mol) of **26** is added in several portions at 0°C to 30.3 g (0.27 mol) of potassium *tert*-butoxide in 1 l of THF. The mixture is stirred overnight at room temp. under argon, then the solvent is evaporated in vacuo. 500 ml of water is added, the product is extracted into 3 × 200 ml of pentane, and the combined organic layers are washed with water and dried with K_2CO_3. The pentane is stripped off and the residue distilled in vacuo; bp 38–39.5°C/1.3 Torr. 8.7–9.3 g (82–87%) of **6a** is obtained as a colourless liquid with a characteristic unpleasant odor, which solidifies on strong cooling and then melts at 2–4°C. The compound is almost infinitely stable at −30°C, and aged, coloured samples may be recovered with little loss by distillation. – IR (film): $\tilde{\nu}$ = 3290 cm^{-1} (free N–H), 3232 (assoc. N–H), 3037, 2932, 1630 (C=C), 1444, 1312, 1082, 908, 863, 737. – ^1H NMR (CCl_4/CD_2Cl_2): δ = −1.45 (br. s, 1H, NH), 1.3–2.4 (m, 6H, 7,9-H), 6.01 (2H, 3,4-H) and 6.43 (2H, 2,5-H) (AA'XX' multiplet, $J_{2,3}$ = 9.24 Hz, $J_{2,4}$ = 0.68 Hz, $J_{2,5}$ = 1.32 Hz, $J_{3,4}$ = 6.11 Hz). – ^{13}C NMR ($CDCl_3$): δ = 18.3 (C-8), 30.1 (C-7,9), 53.8 (C-1,6), 120.9 (C-3,4), 129.5 (C-2,5). – UV (CH_3CN): λ_{max} (lgε) = 268 nm (3.77); (cyclohexane): 270 (3.78); (95% ethanol): 263 (3.77). – MS: *m/z* (%) = 133 (91), 132 (100), 118 (24), 117 (42).

$C_9H_{11}N$ (133.2) Calcd. C 81.16 H 8.32 N 10.52
Found C 80.85 H 8.30 N 10.79

11-Azabicyclo[4.4.1]undeca-1,3,5-triene (Tetramethylene Azepine)/*11-Azatricyclo[4.4.1.0^{1,6}]undeca-2,4-diene* (**5b**/**6b**): 16.8 g (0.105 mol) of bromine in 200 ml of CH_2Cl_2 is added dropwise within 2.5 h to 14.9 g (0.1 mol) of **19b** in 200 ml of CH_2Cl_2 at −78°C. The mixture is allowed to warm to room temp., the solvent evaporated in vacuo (heating must be avoided), and the viscous, coloured residue dissolved in 500 ml of THF. 28.1 g (0.25 mol) of potassium *tert*-butoxide is added in several portions at −25°C, and the mixture is stirred without further cooling for 4 h under an argon atmosphere. The solvent is evaporated, and the residue partitioned between 1 l of water and 200 ml of pentane (poor phase separation). After a further pentane extraction, the combined organic layers are washed with water and dried with K_2CO_3. Evaporation and distillation in vacuo affords 8.5–9.3 g of very impure product which is subjected to column chromatography (Al_2O_3, 20 × 6 cm, acetone/hexane, 1:15). The azepine is eluted together with or immediately after some tetralin. The elution must be quite rapid in order to minimize decomposition, and any fraction containing residual **19b** (more polar than the azepine; detection on TLC plates by exposure to iodine vapours) must be discarded. The resulting solution is concentrated and distilled to obtain 4.7–4.9 g of **5b**/**6b** contaminated with tetralin, **27**, and **28**. 19.3 g of this material (collected from 4 runs) is dissolved in 400 ml of THF, and 10 ml of *n*-butyllithium (1.25 M in hexane) is added at −78°C under argon. After stirring at 0°C for 20 min, 0.5 ml of water is added, the solvent stripped off, 200 ml of pentane added, and the solution dried with Na_2SO_4. The pentane is removed, and the residue distilled again. Finally, tetralin is removed by distillation over a 30-cm spaltrohr column, the purity of the fractions being monitored by ^1H NMR (traces of tetralin may be detected by its singlet at δ = 6.87 in CCl_4). 13.0 g (22%) of **5b**/**6b** is obtained as an almost colourless liquid with a sweetish-foul odor; bp 50–50.5°C/0.65 Torr. The storage stability is similar to that of **10a**. – IR (film): $\tilde{\nu}$ = 3266 cm^{-1} (N–H), 3036, 2934, 1598 (C=C), 1497, 1441, 1167, 997, 969, 839, 731. – ^1H NMR (CCl_4): δ = 0.3 (br. s, 1H, NH), 0.9–2.8 (m, 8H, 7-H to 10-H), 6.07 (2H, 2,5-H) and 6.34 (2H, 3,4-H) (AA'XX' multiplet, *N* = 6.6 Hz). – ^{13}C NMR ($CDCl_3$): δ = 23.6 (C-8,9), 33.1 (C-7,10), 109.0 (C-1,6), 121.3 and 125.5 (C-2 to 5). – UV (cyclohexane): λ_{max} (lgε) = 219 nm (4.21), 267 (3.47). – MS: *m/z* (%) = 147 (96), 146 (33), 132 (17), 119 (100), 118 (73).

$C_{10}H_{13}N$ (147.2) Calcd. C 81.59 H 8.90 N 9.51
Found C 81.37 H 8.77 N 9.21

Dispiro[dicyclopentane-1,1':1",9'-[1,2,4a,5,8,8a]hexahydro[5,8]-ethenonaphthalene]-2,10-dione (**28**): 0.15 g (1 mmol) of **5b**/**6b** is dissolved in 2 ml of methanol and 1 ml of water and allowed to stand at room temp. for 7 d. The odor of the azepine is replaced by that of ammonia, and impure **28** crystallizes almost quantitatively. Recrystallization from methanol yields 0.09 g (60%) of brownish plates; mp 137–140°C (ref.[29a] 143°C). – IR (KBr): $\tilde{\nu}$ = 3038 cm^{-1}, 2953, 2903, 1713 (isol. C=O), 1682 (conjug. C=O). – ^1H NMR ($CDCl_3$): δ = 1.0–2.7 (m, 18H), 3.1–3.4 (m, 2H), 5.8–6.6 (m, 4H). – MS: *m/z* (%) = 296 (3), 200 (17), 148 (100), 117 (58), 96 (87), 91 (92).

12-Azabicyclo[5.4.1]dodeca-1(11),7,9-triene (Pentamethylene Azepine, **5c**): All operations must be performed under argon and with argon-saturated solvents. 4.08 g (25 mmol) of the aziridine mixture containing 50% of **19c** is dissolved in 40 ml of CH_2Cl_2 and cooled to −78°C, and 5.2 g (32.5 mmol) of bromine in 10 ml of CH_2Cl_2 is added dropwise. Stirring at −78°C is continued for 30 min, and the mixture is evaporated in vacuo with ice cooling. The residue is dissolved in 50 ml of ice-cold THF, and 8.4 g (75 mmol) of freshly sublimed potassium *tert*-butoxide is added in several portions within 1 min, maintaining the temperature at 0°C. After 5 min, the solvent is removed in vacuo at 0°C, the residue partitioned between 100 ml each of ether and water, and the aqueous layer extracted with further 50 ml of ether. The combined organic layers are washed with 3 × 75 ml of water, dried with Na_2SO_4, and evaporated. Column chromatography (Al_2O_3, 30 × 3 cm, pentane/ether, 2:1) yields a yellow fraction (R_f approx. 0.35) which is again chromatographed (Al_2O_3, 40 × 3 cm, benzene/ether, 4:1), evaporated, and distilled in a short-path apparatus (50°C/0.1 Torr; con-

denser 0°C) to yield 0.51 g (1.8% overall from tetrahydrobenzocycloheptene) of **5c** as a yellow, air-sensitive liquid. It is best stored as a dilute solution in argon-saturated $CDCl_3$ at −20°C. – IR (film): $\tilde{\nu}$ = 3366 cm^{-1} (N−H), 3019, 2928, 1665 (C=C), 1419, 750. – ^1H NMR ($CDCl_3$): δ = 1.1−2.5 (m, 10H, 2-H to 6-H), 3.23 (br. s, 1H, NH), 5.15 (2H, 8,11-H) and 6.04 (2H, 9,10-H) (AA'XX' multiplet, $J_{8,9}$ = 5.21 Hz, $J_{8,10}$ = 0.30 Hz, $J_{8,11}$ = 0.00 Hz, $J_{9,10}$ = 10.91 Hz). – ^{13}C NMR ($CDCl_3$): δ = 28.9 (C-4), 33.7 (C-3,5), 38.5 (C-2,6), 110.5 (C-8,11), 129.7 (C-9,10), 150.2 (C-1,7). – UV (CH_3CN): λ_{max} (lgε) = 212 nm (4.29), 265 (sh, 2.80), 345 (2.75). – MS: *m/z* (%) = 161 (100), 146 (40), 132 (54), 106 (100).

$C_{11}H_{15}N$ Calcd. 161.1204 Found 161.1203 (MS)

10-Methyl-10-azatricyclo[4.3.1.0^{1,6}]deca-2,4-diene (**8a**): 5.5 ml (7.2 mmol) of *n*-butyllithium (1.3 M in hexane) is added dropwise with a syringe at −78°C under argon to 0.80 g (6 mmol) of **6a** in 10 ml of THF, and the resulting suspension of the *N*-lithio derivative is stirred at −78°C for 30 min. 0.7 ml (11 mmol) of CH_3I is then added, the cooling bath is removed, and the mixture stirred for another 30 min. Water and pentane are added, and the organic phase is separated and dried with K_2CO_3. Concentration and distillation in vacuo afford 0.74 g (84%) of a colourless, musty-smelling liquid; bp 28−29°C/0.65 Torr. – IR (film): $\tilde{\nu}$ = 3032 cm^{-1}, 2922, 1621 (C=C), 1440, 1290, 1170, 1043, 742, 720 cm^{-1}. – ^1H NMR (CCl_4): δ = 1.22 (s, 3H, CH_3), 1.3−2.4 (m, 6H, 7,8,9-H), 5.94 (2H, 2,5-H) and 6.28 (2H, 3,4-H) (AA'XX' multiplet, *N* = 10.1 Hz). – ^{13}C NMR ($CDCl_3$): δ = 18.6 (C-8), 30.2 (CH_3), 31.7 (C-7,9), 59.7 (C-1,6), 122.9 and 124.1 (C-2 to 5). – UV (CH_2Cl_2): λ_{max} (lgε) = 271 nm (3.74). – MS: *m/z* (%) = 147 (73), 132 (95), 117 (68), 91 (59).

$C_{10}H_{13}N$ (147.2) Calcd. C 81.59 H 8.90 N 9.51
Found C 81.36 H 8.84 N 9.75

11-Methyl-11-azatricyclo[4.4.1.0^{1,6}]undeca-2,4-diene (**8b**): Following the above procedure, 0.88 g (6 mmol) of **5b**/**6b** yields 0.82 g (85%) of **8b** as a yellowish, musty-smelling liquid; bp 36−37°C/0.28 Torr. – IR (film): $\tilde{\nu}$ = 3027 cm^{-1}, 2925, 1436, 751, 724. – ^1H NMR (CCl_4): δ = 0.9−1.85 and 2.1−2.5 (m, 8H, 7-H to 10-H), 1.27 (s, 3H, CH_3), 5.74 (2H, 2,5-H) and 6.26 (2H, 3,4-H) (AA'XX' multiplet, *N* = 10.1 Hz). – ^{13}C NMR ($CDCl_3$): δ = 20.9 (C-8,9), 29.9 (CH_3), 32.6 (C-7,10), 55.8 (C-1,6), 123.9 (C-3,4), 126.9 (C-2,5). – UV (*n*-hexane): λ_{max} (lgε) = 265 (3.71). – MS: *m/z* (%) = 161 (39), 146 (26), 120 (64), 91 (100).

$C_{11}H_{15}N$ Calcd. 161.1204 Found 161.1247 (MS)

12-Methyl-12-azabicyclo[5.4.1]dodeca-1(11),7,9-triene/12-Methyl-12-azatricyclo[5.4.1.0^{1,7}]dodeca-8,10-diene (**7c**/**8c**): All operations must be performed under argon and with argon-saturated solvents. To 32 mg (0.2 mmol) of **5c** in 50 ml of THF is added at −78°C from a syringe 0.25 ml of *n*-butyllithium (1.0 M in hexane). The red solution is stirred at −78°C for 20 min, 0.18 ml (0.3 mmol) of CH_3I is added, and the mixture is allowed to warm to room temp. The solvent is removed in vacuo, and the residue taken up in 75 ml of ether, washed with 3 × 75 ml of water, and dried with Na_2SO_4. After concentration in vacuo, the residue is distilled in a short-path apparatus (50°C/0.25 Torr) to obtain 25 mg (71%) of **7c**/**8c** as a yellow, air-sensitive liquid. – IR (film): $\tilde{\nu}$ = 3037 cm^{-1}, 2925, 1637, 1618, 1591, 1441. – ^1H NMR ($CDCl_3$): δ = 1.1−2.4 (m, 10H, 2,6-H), 1.90 (s, 3H, CH_3), 5.70 (2H, 8,11-H) and 6.35 (2H, 9,10-H) (AA'XX' multiplet, *N* = 8.4 Hz). – ^{13}C NMR ($CDCl_3$): δ = 29.5 (C-3,5), 29.6 (C-4), 32.8 (CH_3), 36.2 (C-2,6), 94.9 (C-1,7), 123.0 and 127.2 (C-8 to 11). – UV (CH_3CN, qualitative): λ_{max} = 226 nm, 262, 345 (sh). – MS: *m/z* (%) = 175 (43), 160 (18), 146 (38), 120 (61), 91 (95), 68 (100).

10-Trimethylsilyl-10-azatricyclo[4.3.1.0^{1,6}]deca-2,4-diene (**10a**): The reaction is run under argon in a flask fitted with a Zincke distillation apparatus. 12 ml (13 mmol) of *n*-butyllithium (1.1 M in hexane) is added with a syringe at −78°C to 1.33 g (10 mmol) of **6a** in 10 ml of THF, and stirring at −78°C is continued for 30 min. 2.3 ml (18 mmol) of Me_3SiCl is added, the mixture allowed to warm to room temp., and all low-boiling material cautiously stripped off, applying a gradually increasing vacuum. The residue is then distilled in the same apparatus, yielding 1.91 g (93%) of **10a** as a colourless oil; bp 38.5−39.5°C/0.83 Torr (unchanged on repeated distillation). – IR (film): $\tilde{\nu}$ = 3033 cm^{-1}, 2954, 1300, 1249, 1163, 1017, 840, 740, 626. – ^1H NMR (CCl_4): δ = −0.12 (s, 9H, $SiMe_3$), 1.2−2.2 (m, 6H, 7,8,9-H), 6.00 (2H, 3,4-H) and 6.40 (2H, 2,5-H) (AA'XX' multiplet, *N* = 10.0 Hz). – ^{13}C NMR ($CDCl_3$): δ = −0.1 ($SiMe_3$), 18.6 (C-8), 31.5 (C-7,9), 53.4 (C-1,6), 122.9 (C-3,4), 130.9 (C-2,5). – UV (CH_2Cl_2): λ_{max} (lgε) = 268 nm (3.64). – MS: *m/z* (%) = 205 (17), 132 (11), 117 (7), 73 (100).

$C_{12}H_{19}NSi$ (205.4) Calcd. C 70.18 H 9.32 N 6.82
Found C 69.97 H 9.40 N 6.90

11-Trimethylsilyl-11-azabicyclo[4.4.1]undeca-1,3,5-triene/11-Trimethylsilyl-11-azatricyclo[4.4.1.0^{1,6}]undeca-2,4-diene (**9b**/**10b**): Following the above procedure, 0.88 g (6 mmol) of **5b**/**6b** yields 1.22−1.27 g (93−97%) of the little compound as a syrup which solidifies to a glass slightly below room temp.; bp 53.5−54°C/0.15 Torr. The compound should be stored at −30°C. – IR (film): $\tilde{\nu}$ = 3018 cm^{-1}, 2935, 1611 (C=C), 1250, 1176, 1019, 846, 737 cm^{-1}. – ^1H NMR (CCl_4): δ = −0.12 (s, 9H, $SiMe_3$), 0.9−1.4 and 1.6−2.0 (m, 4H, 8,9-H), 2.34 (m, 4H, 7,10-H), 6.00 (2H, 2,5-H) and 6.32 (2H, 3,4-H) (AA'XX' multiplet, *N* = 5.9 Hz). – ^{13}C NMR ($CDCl_3$): δ = 0.2 ($SiMe_3$), 25.8 (C-8,9), 36.1 (C-7,10), 122.0 and 128.7 (C-2,5), 133.3 (C-1,6). – MS: *m/z* (%) = 219 (24), 73 (100).

10-Methoxycarbonyl-10-azatricyclo[4.3.1.0^{1,6}]dec-3-ene[11] (**20a**): 31.5 g (0.33 mol) of $ClCOOCH_3$ in 150 ml of ether is added dropwise with ice cooling to 40.6 g (0.3 mol) of **19a** in 150 ml of ether within 70 min. Together with the second half of the chloroformate, 95 g of 15% NaOH is added dropwise, and stirring at 0°C is continued for 30 min. The layers are separated, the ethereal one washed with 2 × 200 ml of water, the combined aqueous phases extracted with 50 ml of CH_2Cl_2, and the combined organic phases dried with $MgSO_4$. After removal of the solvent, the residue is distilled in vacuo to obtain 45.9 g (79%) of **20a** as a colourless syrup; bp 70−83°C/0.1−0.15 Torr. The compound solidifies on prolonged cooling and then melts at 30−33°C. A small sample was redistilled; bp 62−63°C/0.1 Torr.

$C_{11}H_{15}NO_2$ (193.3) Calcd. C 68.37 H 7.82 N 7.25
Found C 67.90 H 7.82 N 7.25

10-Methoxycarbonyl-10-azatricyclo[4.3.1.0^{1,6}]deca-2,4-diene (**12a**): This compound is prepared by a modification of Paquette's procedure[11]. 16.5 g (0.103 mol) of bromine in 150 ml of CH_2Cl_2 is added dropwise to 19.3 (0.1 mol) of **20a** in 150 ml of CH_2Cl_2 at −78°C within 1.5 h. The mixture is warmed to room temp., the solvent stripped off, the residue dissolved in 300 ml of THF, and 23.6 g (0.21 mol) of potassium *tert*-butoxide added at once. The mixture begins to boil and is refluxed under an argon atmosphere for 2 h. 200 g of Al_2O_3 (ICN pharmaceuticals, basic, activity 1) is deactivated with 30 ml of water, and half of it is added to the cooled reaction mixture. The solvent is stripped off, and the residue is filtered over the second half of the alumina, using pentane/ether (9:1) as the eluent. After removal of the solvent, the crude product is distilled (bp 48−65°C/3−7 · 10^{-5} mbar), and the semi-solid distillate is taken up in hexane. Crystallization at −30°C affords 10.1 g (53%) of **12a** as colourless needles. The analytical sample is obtained by 2 further crystallizations from hexane; mp 63−64°C. – IR (KBr): $\tilde{\nu}$ = 3042 cm^{-1}, 2951, 1713 (C=O), 1427,

1312, 1233, 736. – ^{1}H NMR (CCl_4): δ = 1.4–2.0 and 2.1–2.5 (m, 6H, 7,8,9-H), 3.47 (s, 3H, CH_3), 6.15 (centre of an AA'BB' multiplet, 4H, 2-H to 5-H). – ^{13}C NMR ($CDCl_3$): δ = 19.8 (C-8), 30.3 (C-7,9), 52.0 (CH_3), 61.4 (C-1,6), 123.6, 124.7 (C-2 to 5), 157.3 (C=O). – UV (CH_2Cl_2): λ_{max} (lgε) = 261 nm (3.69). – MS: *m/z* (%) = 191 (17), 132 (100), 117 (36).

$C_{11}H_{13}NO_2$ (191.2) Calcd. C 69.09 H 6.85 N 7.32
Found C 68.80 H 6.81 N 7.32

8-Methoxy-7-oxa-9-azatricyclo[4.3.3.0^{1,6}]dodeca-2,4,8-triene (**23a**): 1.15 g (6 mmol) of **12a** in 15 ml of CCl_4 is stirred at room temp. with a catalytic amount of *p*-toluenesulfonic acid until ^{1}H NMR indicates the completion of the rearrangement. The solution is washed with aqueous $NaHCO_3$, dried with Na_2SO_4, and evaporated, and the residue is distilled in vacuo to afford 0.97 g (84%) of **23a** as a colourless syrup which solidifies on cooling and then melts at 38–40.5°C; bp 36.5–39°C/0.06 Torr. – IR (film): $\tilde{\nu}$ = 3041 cm^{-1}, 2960, 1667 (C=N), 1444, 1350, 1318, 1058, 928 cm^{-1}. – ^{1}H NMR (CCl_4): δ = 1.2–2.5 (m, 6H, 10,11,12-H), 3.83 (s, 3H, CH_3), 5.6–6.1 (m, 4H, 2-H to 5-H). – ^{13}C NMR ($CDCl_3$): δ = 16.6 (C-11), 41.8 and 42.2 (C-10,12), 56.9 (CH_3), 74.5 (C-1), 91.7 (C-6), 117.7, 122.0, 124.9, 131.9 (C-2 to 5), 162.9 (C-8). – UV (cyclohexane): λ_{max} (lgε) = 249 nm (3.43), 256 (sh, 3.41). – MS: *m/z* (%) = 191 (38), 132 (100), 117 (30).

$C_{11}H_{13}NO_2$ Calcd. 191.0946 Found 191.0952 (MS)

7-Oxa-9-azatricyclo[4.3.3.0^{1,6}]dodeca-2,4-dien-8-one (**24b**): To 0.96 g (5 mmol) of **13a** in 12 ml of $CHCl_3$ (dried over activity 1 basic alumina) is added dropwise under argon at 0°C within 30 min 0.7 ml (5.4 mmol) of $BrSiMe_3$ in 2 ml of dry $CHCl_3$. Stirring at 0°C is continued for 30 min, and all volatile material is removed in vacuo. The residue is taken up in 10 ml of CH_2Cl_2, 1 ml of methanol is added, and the mixture is stirred at room temp. for 1 day. After removal of the solvent, crystallization from CH_2Cl_2/pentane affords 0.50 g (56%) of a colourless powder melting at 116.5–118°C. The analytical sample is obtained by further crystallization from much CCl_4 (reflux to –30°C); mp 119–120°C. – IR (KBr): $\tilde{\nu}$ = 3514 cm^{-1}, 3438, 3194, 3115, 2972, 1715 (C=O), 1646 (C=C), 1082, 995, 749. – ^{1}H NMR ($CDCl_3$): δ = 1.4–2.7 (m, 6H, 10,11,12-H), 5.93 (narrow m, 4H, 2-H to 5-H), 6.4 (br. s, NH and H_2O). – ^{13}C NMR ($CDCl_3$): δ = 16.4 (C-11), 41.6, 41.8 (C-10,12), 64.1 (C-1), 88.5 (C-6), 119.0, 121.4, 125.8, 128.6 (C-2 to 5), 159.1 (C-8). – UV (CH_2Cl_2): λ_{max} (lgε) = 256 nm (sh, 3.56), 260 (3.57). – MS: *m/z* (%) = 177 (26), 148 (32), 135 (100), 132 (53), 106 (93), 91 (62).

$C_{10}H_{11}NO_2 \cdot H_2O$ (195.2) Calcd. C 61.53 H 6.71 N 7.17
Found C 61.62 H 6.67 N 7.17

11-Methoxycarbonyl-11-azabicyclo[4.4.1]undeca-1,3,5-triene[11] (**11b**): 14.9 g (0.1 mol) of **19b** is transformed into the urethane **20b** as described for **19a**, but omitting the distillation. The crude product (18.7 g, 90%) is brominated as described for **20a** using 14.5 g (0.09 mol) of bromine, and the crude bromide is dissolved in 150 ml of THF. This solution is added dropwise to a suspension of sodium methoxide [freshly prepared from 6.9 g (0.3 mol) of sodium] in 150 ml of THF within 30 min. and refluxed for 4.5 h. After cooling, the solvent is evaporated in vacuo, 1 l of water added, and the product extracted into 1 × 200 and 4 × 100 ml of ether. The combined organic layers are washed with 100 ml of brine, dried with $MgSO_4$/charcoal, concentrated to 30 ml, and diluted with 50 ml of hexane. Crystallization at –30°C affords 7.9 g (38% from **19b**) of **11b** as colourless crystals; mp 52–59°C (ref.[11] 57.5–59°C). – ^{1}H NMR (C_6D_6, +75°C): δ = 0.8–1.8 (m, 4H, 8,9-H), 2.0–2.3 and 2.4–3.2 (m, 4H, 7,10-H), 3.41 (s, 3H, CH_3), 5.83 (2H, 2,5-H) and 6.35 (2H, 3,4-H) (AA'XX' multiplet, *N* = 5.1 Hz). – ^{13}C NMR ($CDCl_3$, –20°C): δ = 24.4 and 24.6 (C-8,9), 30.7 and 31.5 (C-7,10), 51.9 (CH_3), 120.5 and 121.1 (C-2,5), 128.2 and 128.6 (C-3,4), 130.7 (C-1,6), 152.3 (C=O). – UV (*n*-hexane): λ_{max} (lgε) = 220 nm (3.94), 252 (sh, 3.37).

10-Chloro-10-azatricyclo[4.3.1.0^{1,6}]deca-2,4-diene (**14a**): 3.0 g (27.5 mmol) of *tert*-butyl hypochlorite in 20 ml of CH_2Cl_2 is added dropwise with ice cooling to 3.33 g (25 mmol) of **6a** in 20 ml of CH_2Cl_2. Stirring is continued for 5 min, and all volatile materials are removed in vacuo without heating. Filtration through Al_2O_3 (15 × 5 cm, CH_2Cl_2) affords crude **14a** which is dissolved in 25 ml of hexane. Crystallization at –30°C yields 2.31 g of a greenish solid, mp 42–43°C; a second green-brownish fraction (0.73 g), mp 39–42°C, is obtained by concentration of the mother liquid and cooling (together: 72%). Colourless crystals, mp 42–43°C, are obtained from the first fraction by another recrystallization from hexane. The compound is stable at –30°C. – IR (film): $\tilde{\nu}$ = 3041 cm^{-1}, 2953, 1437, 1058, 749, 693 (N–Cl). – ^{1}H NMR (CCl_4): δ = 1.4–2.8 (m, 6H, 7,8,9-H), 6.01 (2H, 2,5-H), 6.48 (2H, 3,4-H) (AA'XX' multiplet, *N* = 10.0 Hz). – ^{13}C NMR ($CDCl_3$): δ = 18.8 (C-8), 32.8 (C-7,9), 64.9 (C-1,6), 121.6, 126.9 (C-2 to 5). – UV (cyclohexane): λ_{max} (lgε) = 231 nm (3.44), 278 (3.58). – MS: *m/z* (%) 169, 167 (5, 14), 132 (76), 118 (45), 117 (100).

$C_9H_{10}ClN$ (167.6) Calcd. C 64.48 H 6.01 Cl 21.15 N 8.36
Found C 64.54 H 6.12 Cl 20.56 N 8.24

11-Chloro-11-azatricyclo[4.4.1.0^{1,6}]undeca-2,4-diene (**14b**): In an NMR tube 2.2 mg of **5b**/**6b** is dissolved in 0.45 ml of CD_2Cl_2, and 1 drop of TMS/CCl_4 is added. The solution is cooled to –78°C, a slight excess of *tert*-butyl hypochlorite is added, and the solution is shaken and immediately recooled. *N*-chlorination takes place at –60°C within approx. 1 h and is monitored by ^{1}H NMR spectroscopy (60 MHz, PFT technique). Immediately after the disappearance of the starting material, the following spectrum was recorded: δ = 1.0–2.8 (m, 8H, 7-H to 10-H), 5.89 (2H, 2,5-H) and 6.55 (2H, 3,4-H) (AA'XX' multiplet, $J_{2,3}$ = 9.18 Hz, $J_{2,4}$ = 0.88 Hz, $J_{2,5}$ = 0.96 Hz, $J_{3,4}$ = 6.26 Hz). On further standing at –60°C slow decomposition occurs which becomes rapid at –30°C.

5a,6,7,8-Tetrahydrocyclopent[b]azepine (**33**): 0.80 g (6 mmol) of **6a** is dissolved in CH_2Cl_2 and filtered through a *short* column of silica gel (2.5 × 3.5 cm, CH_2Cl_2). The eluate is evaporated and distilled in vacuo, yielding 0.46–0.64 g (58–80%) of **33** as a colourless liquid which decomposes within several days even at –30°C; bp 34.5–35.5°C/0.2 Torr. – IR (film): $\tilde{\nu}$ = 3020 cm^{-1}, 2960, 1629 (C=C), 1176, 730. – ^{1}H NMR (CCl_4): δ = 1.4–2.8 (m, 7H, 5a,6,7,8-H), 4.79 (dd, 1H, 5-H), 5.9–6.3 (m, 2H, 3,4-H), 7.28 (d, 1H, 2-H). 3,4,5a-H are assigned by double resonance to the signals at δ = 6.04, 6.21, and approx. 1.5, resp. $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 6.3 Hz, $J_{4,5}$ = 7.8 Hz, $J_{4,5a} \approx$ 2 Hz, $J_{5,5a}$ = 3.8 Hz. – ^{13}C NMR ($CDCl_3$): δ = 23.6, 30.3, 32.7 (C-6,7,8), 44.4 (C-5a), 115.3, 119.0 (C-3,4), 125.3 (C-5), 140.5 (C-2), 160.7 (C-8a). – UV (cyclohexane): λ_{max} (lgε) = 206 nm (3.79), 242 (3.59), 264 (sh, 3.54). – MS: *m/z* (%) = 133 (44), 132 (100), 117 (33), 105 (46).

$C_9H_{11}N$ Calcd. 133.0891 Found 133.0897 (MS)

1-Trimethylsilyl-1,5a,6,7-tetrahydrocyclopent[b]azepine (**34**): 0.46 g (3.5 mmol) of **33** is silylated following the same procedure as described for **6a**, to obtain 0.59–0.66 g (83–93%) of **34** as a colourless oil with the same low stability as for **33**; bp 47–48°C/0.1 Torr. – IR (film): $\tilde{\nu}$ = 3022 cm^{-1}, 2962, 1629 (C=C), 1585 (C=C), 1337, 1255, 1109, 842. – ^{1}H NMR (CCl_4): δ = 0.27 (s, 9H, $SiMe_3$), 1.7–2.3 (m, 4H, 6,7-H), 2.87 (m, 1H, 5a-H), 4.7–4.9 (m, 2H, 3,8-H), 5.4–5.9 (m, 2H, 4,5-H), 6.07 (d, 1H, 2-H). 3,4,5,8-H are assigned by double resonance to the signals at δ = 4.77, 5.71, 5.52,

and 4.79, resp. $J_{7,8} \approx 1.5-2$ Hz, $J_{2,3} = 9.7$ Hz, $J_{3,4} = 6.3$ Hz, $J_{4,5} = 10.1$ Hz, $J_{4,5a} = 2.6$ Hz, $J_{5,5a} \approx 3$ Hz. – UV (cyclohexane): λ_{max} (lgε) = 248 nm (sh, 3.57), 308 (3.74). – MS: *m/z* (%) = 205 (28), 204 (22), 190 (10), 73 (100).

1,6-Dimethoxy-10-azabicyclo[4.3.1]deca-2,4-diene (**37**): 2.01 g (12 mmol) of **14a** in 10 ml of hexane and a solution of sodium methoxide freshly prepared from 0.92 g (40 mmol) of sodium and 40 ml of methanol are stirred together at room temp. for 3 weeks. The solvent is removed, 50 ml of water added, and the crude product extracted into 1 × 50 and 2 × 20 ml of CH_2Cl_2. After drying with K_2CO_3, the solvent is evaporated and the residue chromatographed on Al_2O_3 (20 × 4.5 cm, ether/hexane, 1:1). After a forerun of unreacted starting material, **37** is eluted together with some **6a**. Evaporation and recrystallization from hexane (room temp. to −30°C) affords 1.43 g (61%) of **37** as colourless transparent crystals; mp 73.5–74.5°C. – IR (KBr): $\tilde{\nu}$ = 3288 cm^{-1} (N–H), 3025, 2945, 1093, 1057, 963, 837, 711. – ^1H NMR (CCl_4): δ = 1.4–1.9 (m, 7H, 7,8,9-H, and NH), 3.31 (s, 6H, CH_3), 5.71 (s, 4H, 2-H to 5-H). – UV (cyclohexane): λ_{max} (lgε) = 246 nm (3.84), 252 (sh, 3.82), 2.64 (sh, 3.58). – MS: *m/z* (%) = 195 (24), 180 (100), 164 (46), 148 (44), 120 (68).

$C_{11}H_{17}NO_2$ (195.3) Calcd. C 67.66 H 8.78 N 7.17
Found C 68.07 H 8.96 N 7.40

10-Chloro-1,6-dimethoxy-10-azabicyclo[4.3.1]deca-2,4-diene (**39**): To 0.39 g (2 mmol) of **37** in 3 ml of CH_2Cl_2 is added dropwise at 0°C 0.25 g (2.3 mmol) of *tert*-butyl hypochlorite in 1 ml of CH_2Cl_2. Stirring is continued for 5 min, and all volatiles are removed in vacuo. Chromatography on Al_2O_3 (7 × 4 cm, CH_2Cl_2) affords 0.43 g (94%) of **39** which is recrystallized from hexane (room temp. to −30°C) to yield 0.37 g (81%) of **39** as colourless plates; mp 87.5–88.5°C. – IR (KBr): $\tilde{\nu}$ = 3028 cm^{-1}, 2950, 1168, 1090, 1055, 696, 679. – ^1H NMR (CCl_4): δ = 1.3–2.2 (m, 6H, 7,8,9-H), 3.32 (s, 6H, CH_3), 5.40, 5.70 (AA'BB' multiplet, 4H, 2-H to 5-H, *N* = 13.6 Hz). – UV (cyclohexane): λ_{max} (lgε) = 204 nm (3.59), 248 (sh, 3.73), 254 (3.74). – MS: *m/z* (%) = 231, 229 (0.02, 0.05), 216, 214 (0.08, 0.3), 194 (38), 167 (100).

$C_{10}H_{13}{}^{35}ClNO_2$ (M − CH_3)
Calcd. 214.0634 Found 214.0627 (MS)

Methyl-4-(2-Pyridyl)butyrate (**40**) *and 4H-Quinolizin-4-one* (**41**): 1.95 g (10 mmol) of **37** is converted into **39** according to the above procedure, omitting the purification. The crude **39** is taken up in 20 ml of methanol, and this solution is added dropwise to a solution of sodium methoxide in methanol freshly prepared from 1.65 g (72 mmol) of sodium and 80 ml of methanol. The mixture is refluxed for 15 h under argon, the solvent removed in vacuo, and the residue chromatographed on SiO_2 (20 × 4.5 cm, ether), eluting subsequently: (1) a forerun; (2) 0.15 g (8%) of **37**; (3) traces of byproducts which were not examined; (4) compound **40**; (5) compound **41**. Fraction 4 is evaporated and distilled in vacuo to yield 0.96 g (54%) of **40** as a yellowish liquid; bp 59–62°C/0.07 Torr. – IR (film): $\tilde{\nu}$ = 3009 cm^{-1}, 2951, 1734 (C=O), 1590 and 1569 (pyridine ring), 1473, 1433, 757 cm^{-1}. – ^1H NMR (CCl_4): δ = 1.85–2.4 (m, 4H, CH_2), 2.77 (t, 2H, CH_2), 3.63 (s, 3H, CH_3), 6.95–7.2 (m, 2H, 3,5-H), 7.54 (ddd, 1H, 4-H), 8.51 (br. d, 1H, 6-H). $J_{3,4}$, $J_{4,5}$ = 7.9, 7.1 Hz (assignment uncertain), $J_{4,6}$ = 1.9 Hz, $J_{5,6}$ = 4.7 Hz. – MS: *m/z* (%) = 148 (7), 120 (24), 106 (36), 93 (100). – Fraction 5 is evaporated and sublimed at 60–70°C/0.15 Torr to yield 0.15 g (10%) of **41** as a yellow, hygroscopic solid; mp 60–69°C (ref.[47a] 71–72°C). – ^1H NMR (CCl_4; for assignment see ref.[50b]): δ = 6.4–6.5 (m, 2H, 1,3-H), 6.91 (dt, 1H, 7-H), 7.15–7.7 (m, 3H, 2,8,9-H), 9.07 (d, 1H, 6-H). – MS: *m/z* (%) = 145 (52), 117 (100), 90 (39).

CAS Registry Numbers

5a: 121056-49-3 / **5c**: 121056-51-7 / **6a**: 75863-29-5 / **6b**: 121056-50-6 / **7c**: 121072-68-2 / **8a**: 121056-52-8 / **8b**: 121056-53-9 / **8c**: 121056-54-0 / **9b**: 121056-61-9 / **10a**: 121056-55-1 / **10b**: 121072-70-6 / **11b**: 20646-46-2 / **12a**: 20646-52-0 / **14a**: 121056-62-0 / **14b**: 121056-63-1 / **17a**: 7603-37-4 / **17b**: 36231-13-7 / **17c**: 30483-09-1 / **18a**: 121072-66-0 / **18b**: 121056-45-9 / **18c**: 121072-67-1 / **19a**: 121056-46-0 / **19b**: 121056-47-1 / **19c**: 121056-48-2 / **20a**: 20646-47-3 / **20b**: 20646-51-9 / **21**: 121056-56-2 / **22**: 121056-57-3 / **23a**: 121072-69-3 / **24a**: 121072-71-7 / **24b**: 121056-58-4 / **25**: 35342-88-2 / **26**: 121056-59-5 / **27**: 64129-41-5 / **28**: 121056-60-8 / **33**: 121056-64-2 / **34**: 121056-65-3 / **37**: 121056-66-4 / **39**: 121056-67-5 / **40**: 121056-68-6 / **41**: 491-42-9 / tetralin: 119-64-2 / tetrahydrobenzocycloheptene: 16189-49-4

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[24] The subsequent fragmentation in the case of iodotrimethylsilane obviously needs additional acid for the delivery of the NH proton in **25**. As the amount of HI formed during the transfer of the reagent varies from one experiment to another, the irreproducible extent of this side reaction is easily understood. The reaction may be rationalized by nucleophilic attack of I^- on silylated **23b**/**24a** (with or without allylic rearrangement) and reduction of the resulting intermediate by further I^- as shown in the formulas, or silylation and protonation may occur in the reverse order.

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