Tetrahedron Vol 44, No 11, pp 3295 to 3308, 1988
Printed in Great Britain

0040-4020/88 $3.00+.00
Pergamon Press plc

[3,3] VALENCEISOMERIC AZO BRIDGED CARBOCYCLES AND CYCLIC HYDRAZONES: INTRAMOLECULAR [3+2] CYCLOADDITIONS AND [4+2] CYCLOREVERSIONS THROUGH N-METHYLATION[1]

Karin Beck[2], Siegfried Hünig* and Petra Reinold[2]

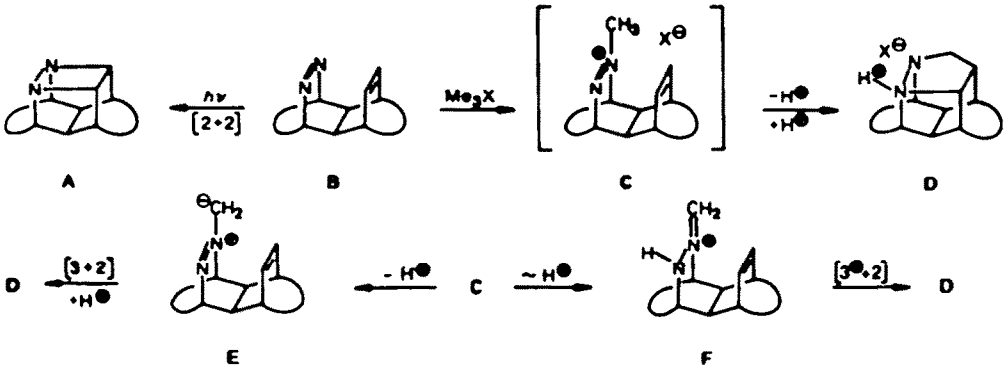
Institut für Organische Chemie der Universität Würzburg
Am Hubland, D-8700 Würzburg, Federal Republic of Germany

(*Received in USA* 16 *November* 1987)

Abstract. - Unsaturated azo bridged carbocycles 1, 2, 5, 8, 12, 14 and 16 can easily be methylated with Me_3OBF_4 or MeI. Depending on structural and steric requirements and the anion, the quaternary salts obtained are stable (1-Me$^\oplus$, 2-Me$^\oplus$, 5a-Me$^\oplus$, 14a/b-Me$^\oplus$, 16a/b-Me$^\oplus$ with $BF_4^\ominus$), undergo [4+2] cycloreversion (8a-Me$^\oplus$, 12-Me$^\oplus$) or intramolecular [3+2] cycloaddition after intermediate deprotonation, whereby the unusual hydrazine derivatives, the cage compounds 3-H$^\oplus$, 4-H$^\oplus$, 6-H$^\oplus$ and 11-H$^\oplus$ are formed. Systems which contain the N=N and C=C function in 1,5-positions are isomeric with their [3,3] rearrangement products, the hydrazones endo-7, endo-10, endo-15 and endo-17. Methylation of the latter provokes the same consecutive reactions as for their azo isomers. These have been demonstrated to be the crucial intermediates for the formation of cage compound (e.g. endo-7b-Me$^\oplus$ ⇌ 5b-Me$^\oplus$ ⇌ 6-H$^\oplus$). Intermolecular methyl migration of quaternized azo compounds has been established, explaining the high yields of cage compounds which can be produced by the "b-series" only.

GENERAL REMARKS

Recently, we described several examples of the new rigid system B which, because of laticyclic 1,5-conjugation between the parallel C=C and N=N bonds, exhibit some unusual properties.[4] The double bonds in B are ideally situated for transannular interaction and, as a consequence, both the $n_-\pi^*$ and the $\pi_-\pi^*$ transitions are conducive to an intramolecular [2+2] photocycloaddition (A).[4a,4f,5] In addition, N-alkylation - even with Me_3OBF_4 - afforded cage compounds of structure D rather than the expected salt C. This intramolecular ring closure is believed to proceed from C by either one of two possible mechanisms: deprotonation to give E, followed by a concerted 1,3-dipolar cycloaddition, or isomerisation to the hydrazonium ion F and cycloaddition.[4f]



Dedicated to Professor Ted Taylor on the occasion of his 65th birthday.

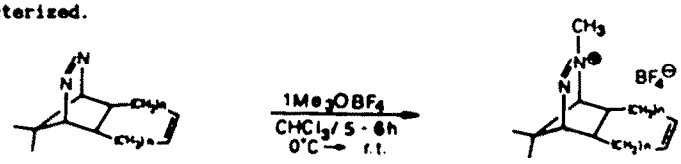
RESULTS AND DISCUSSION

I. INTRAMOLECULAR [3+2] CYCLOADDITIONS WITH DOUBLE BONDS IN DIFFERENT POSITIONS

The results mentioned above raise the question as to whether a similar [3+2] cycloaddition will occur if neighbouring azo bridge and C=C moiety are not oriented parallel to each other. These models, together with type B, are easily accessible by Diels-Alder reactions between the appropriate cyclic azines and dienes.[4]

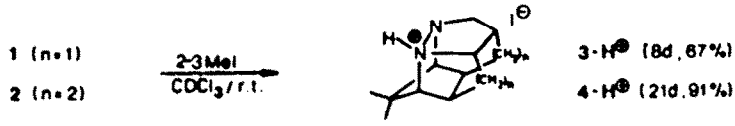
A. Systems without 1,5-related π-bonds

The first model, in which a) the azo bridge is part of a five membered ring, b) the C=C bond is held in a parallel, but structurally and conformationally rather distant position, which excludes a 1,5-relation between the π-systems, and c) the orbitals of both π-systems are not aligned with one another, is represented by compounds 1[4b] and 2.[4b] Both 1 and 2 were quantitatively N-methylated by trimethyloxonium tetrafluoroborate (Me_3OBF_4) in chloroform. These salts deposited as oils which have been fully characterized.



1 n=1
2 n=2

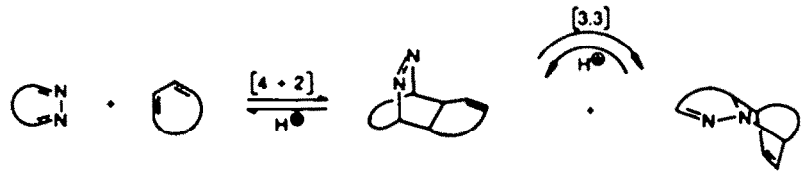
1-Me⊕ (96%)
2-Me⊕ (97%)



After reacting several days with excess of the weaker alkylating agent methyl iodide, 1 and 2 again formed organic salts. These are isomeric to 1-Me⊕ and 2-Me⊕ and possess the structures of cage compounds 3-H⊕ and 4-H⊕. Obviously, cycloaddition slows down with increasing distance between the two unsaturated systems (rate 1 > rate 2). In the methylated compound 2, only the unfavourable boat conformation will react to give 4-H⊕; the higher yield of this product compared to 3-H⊕ may be due to the larger dihedral angle of the overlapping π-systems.

B. Systems with 1,5-related π-bonds

In all other models tested and in B, the π-systems are arranged such that they are prone to undergo a [3,3] Cope rearrangement. This requires further explanation. As has been pointed out recently, [4+2] cycloadditions between two 1,3-dienes hold a special position in the realm of Diels-Alder reactions.[6,7] Applied to the systems in question, the following reaction scheme must be considered, in which equilibration is strongly proton catalysed and the position of the equilibria may be a function of the amount of acid present.

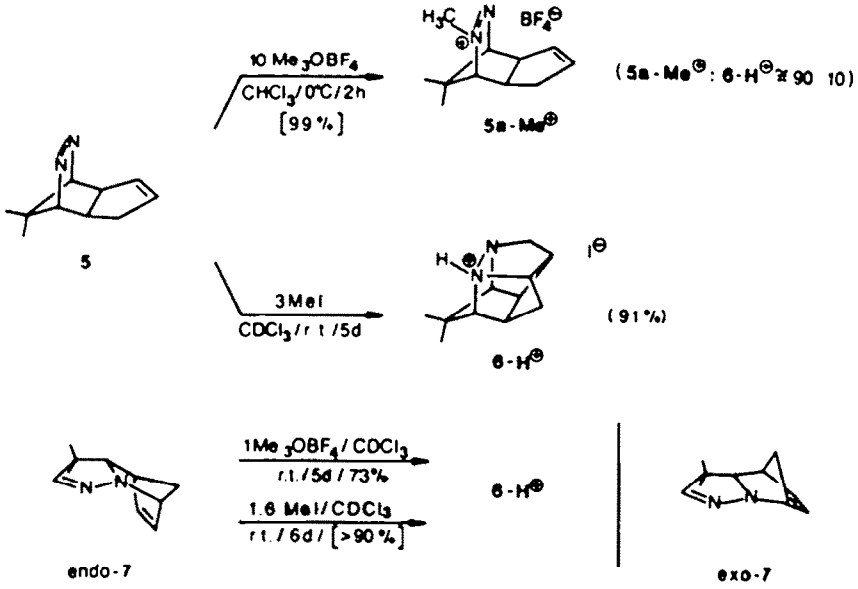


G H I K (endo)

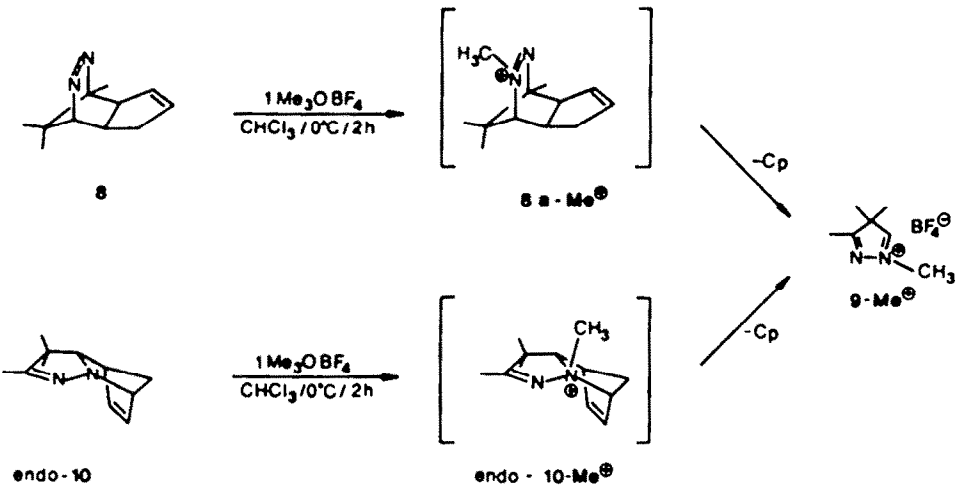
It has been shown that in all cases in which the equilibration I ⇌ H could be achieved, cycloreversion I → G + H (G + H → I: Diels-Alder reaction with the inverse electron demand) proceeded much more slowly.[6] Although the position of the catalysing proton at one of the two nitrogen atoms in G, I and H has not been established,[6] N-methylation of either I or H should catalyse equilibration of the two isomers and possibly influence the equilibria. With this in mind, the following models were selected for methylation reactions. For reasons of brevity, the systems are categorised by the size of the two rings, one of them bridged by an azo group (e.g. N^5, N^6), the other one carrying the double bond (e.g. C^5, C^6).

a) N^6-C^5 Systems and their [3,3] Isomers

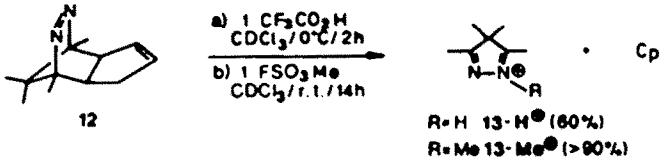
On reaction of 5[4b] with Me_3OBF_4 only one of the two isomeric quaternary salts, namely 5a-$Me^{\oplus}$ could be observed together with small amounts of the heterocyclic cage compound 6-$H^{\oplus}$. The latter was the only product obtained on alkylation with methyl iodide. This difference in behaviour due to the nature of the alkylating reagent has mechanistic implications (vide infra). Interestingly, these differences disappeared when the isomeric pyrazoline endo-7[7] was methylated. Both reagents afforded the cage compound 6-$H^{\oplus}$. It is noteworthy that exo-7[2] yielded only uncharacterised decomposition products under the same conditions.



To obtain information about the effect of bridgehead substituents, model 8[8] was investigated, which differs from 5 by one additional methyl group. Methylation of 8 with Me_3OBF_4 followed a completely different course: cycloreversion took place and the single product was the isopyrazolium salt 9-$Me^{\oplus}$, which was indentified despite some impurities. Its structure was elucidated from the ^{1}H-NMR signals of the 3-methyl and N-methyl groups [δ= 2.30 and 4.00, respectively (CD_3CN)] which are similar to those of the isopyrazolium salt 13-$Me^{\oplus}$.[4b] Cycloreversion to 9-$Me^{\oplus}$ was also observed if endo-10[9] was methylated under the same conditions. In the case of endo-10, alkylation at the more basic bridgehead position is observed, as expected; however, a plausible explanation for the preferential methylation of 8 to 8a-$Me^{\oplus}$ is not immediately apparent. Interestingly, reaction of 8 with methyl iodide followed the same path as 5 → 6-$H^{\oplus}$ by formation of the cage 11-$H^{\oplus}$. Whereas, after the methylation of endo-10 with methyl iodide a mixture of the cage product 11-$H^{\oplus}$ and the cycloreversion product 9-$Me^{\oplus}$ (69:31) was obtained.



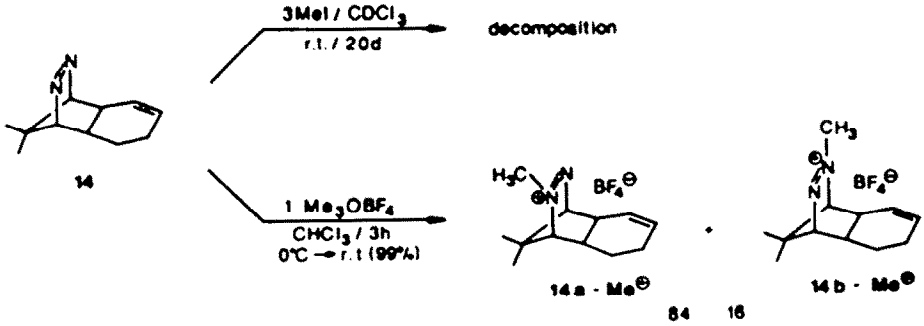
In view of the greater tendency to undergo cycloreversion on alkylation of 8 compared to 5, compound 12[4b] with methyl groups at each bridgehead carbon, should be even more prone to cyclorevert. Indeed, 12 was rapidly equilibrated with its components 13-H⊕ and cyclopentadiene.[4b]

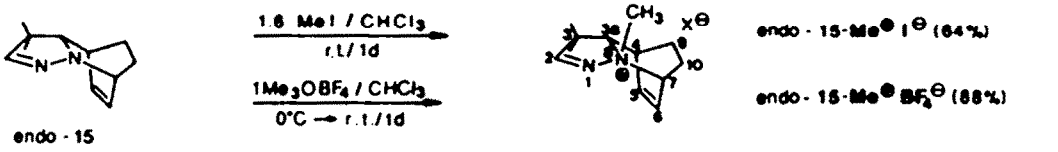


Treatment with fluorsulfonic acid methyl ester afforded 13-Me⊕ quantitatively. In 13-Me⊕ the ^{1}H-NMR signals of two methyl groups found at δ= 2.30 and 2.63 are attributed to positions 3-Me and 5-Me, respectively, because of the stronger deshielding effect of the iminium group at position 5. The N-methyl group in 13-Me⊕ resonates at δ= 3.96 ($CDCl_3$).

b) The N^9–C^5 System and its [3,3] Isomer

Formal enlargement of the olefinic ring in 5 leads to system 14.[5] In a ^{1}H-NMR experiment with methyl iodide in deuterochloroform, 14 was completely consumed, but no signals of definite products could be seen.

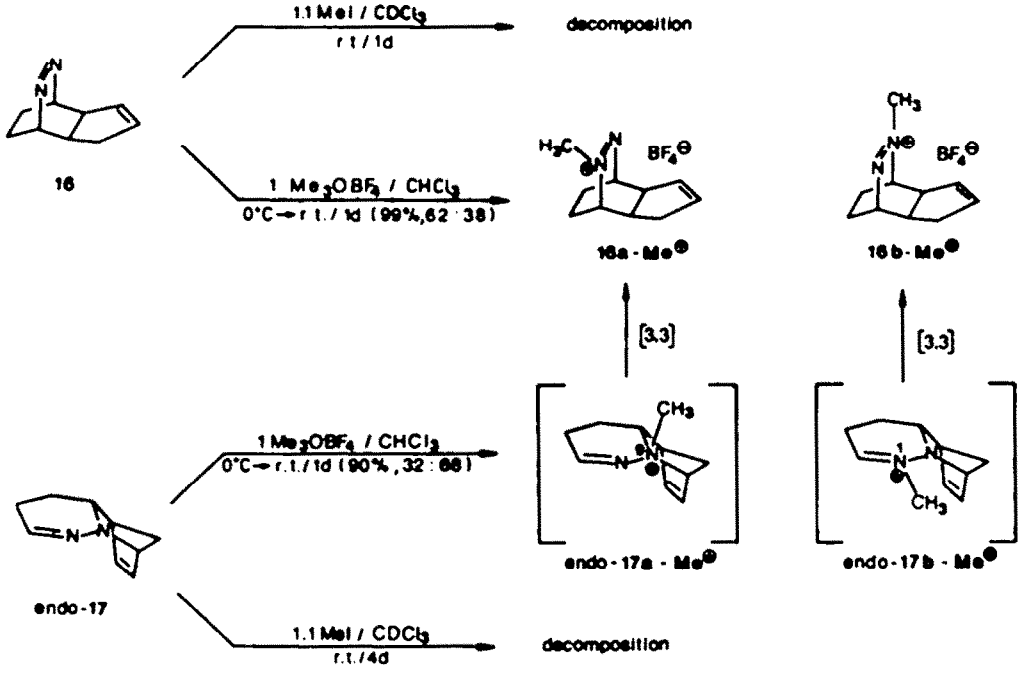




In contrast, reaction of 14 with Me_3OBF_4 yielded the two expected cations 14a-Me⊕ and 14b-Me⊕ quantitatively. The ratio 84:16 of the two isomers cannot be interpreted, since kinetically controlled reaction conditions are not fully garanteed (cf. endo-17). The [3,3] isomer of 14, endo-15,[8] was methylated by both methyl iodide and Me_3OBF_4 to give endo-15-Me⊕ as a single product.

c) **The System $N^{\oplus}$-$C^{\oplus}$ and its [3,3] Isomer**

If the number of carbon atoms in the carbocyclic rings of 14 are exchanged, one obtains system 16.[4c] It reacted with methyl iodide to give decomposition products, but with Me_3OBF_4 to afford the two expected salts 16a-Me⊕ and 16b-Me⊕ in the ratio 62:38. The selectivity of this methylation is significantly less than that of 14a-Me⊕ and 14b-Me⊕, but the N-atom further from the olefinic bond is still preferentially attacked.



The [3,3] isomer of 16, system endo-17,[8] was also methylated smoothly by Me_3OBF_4. Instead of the expected salts endo-17a-Me⊕ and endo-17b-Me⊕, the products of a [3,3] diaza-Cope rearrangement were observed, namely 16a-Me⊕ and 16b-Me⊕. These were produced in the ratio of 32:68, a reversal of that above. The more basic bridgehead nitrogen atom in 17 was methylated slower than its neighbour, probably because of steric hindrance. Again, methylation of 17 by methyl iodide led to complete decomposition.

II. MECHANISTIC CONSIDERATIONS.

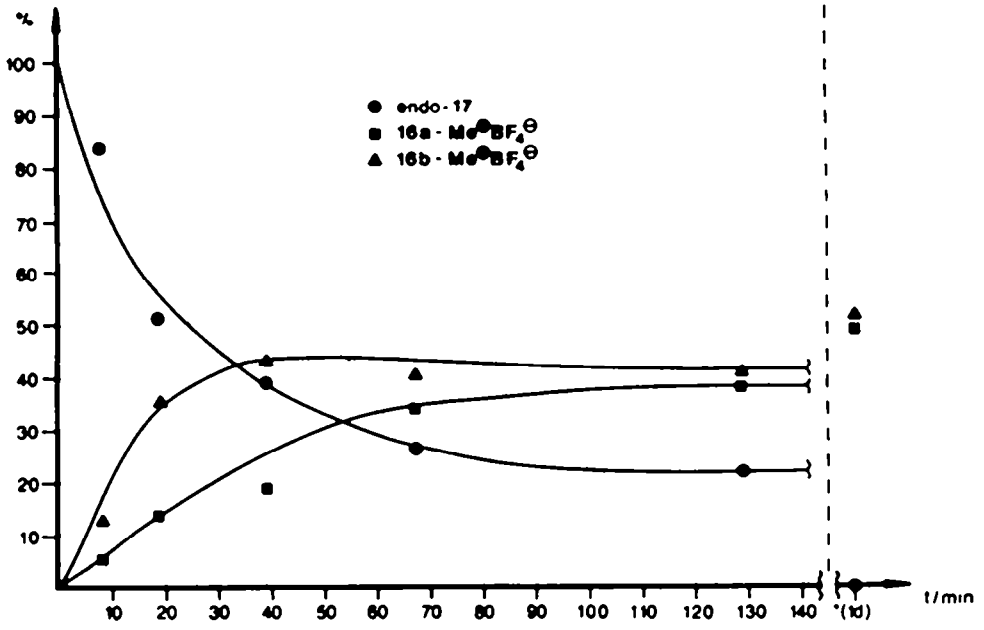
The results discussed thus far are somewhat puzzling and pose several mechanistic questions.

a) Can the methyl group in these methylation products shift from one nitrogen atom to another and if so, do they move inter- or intramolecularly?

An answer to this question was sought with the aid of some experiments.

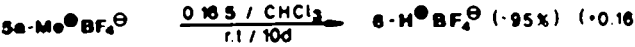
1) Methylation of endo-17 with Me_3OBF_4 was followed by ^1H-NMR spectroscopy over a period of two hours. As can be seen from Fig. 1, consumption of endo-17 led only to 16a-Me⊕ and 16b-Me⊕.

Fig. 1: Reaction of 0.121 mmol of endo-17 with 0.121 mmol Me_3OBF_4 in 0.50 ml $CDCl_3$ at 0°C monitored by the ^1H-NMR (400 MHz) signals of endo-17 (●) (proton 8-H), 16a-Me* (■) and 16b-Me* (▲) (methyl groups). * after one day at room temperature.

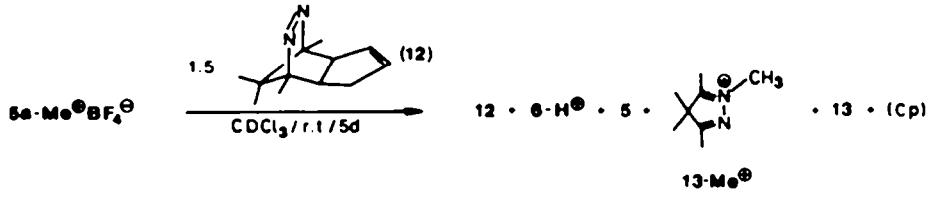


Therefore, after methylation of endo-17 a very fast [3,3] rearrangement must occur. Fig. 1 also demonstrates that 16b-Me* is formed much faster than 16a-Me*, implying that the N-atom 1 in endo-17 is methylated faster than the N-atom 9. After a longer reaction time, (e.g. after one day at room temperature when the endo-17 has been consumed), equilibration has occured and a 1:1 mixture of 16a-Me* and 16b-Me* results. This equilibration plays an important role if cage compounds are formed in a consecutive reaction. It must be born in mind, however, that only isomers 5b-Me* and 8b-Me* (unobserved) are precursors to the cages 6-H* and 11-H*. Since these cages are produced in a high yield (6-H*, 94%), equilibration of the azo-quaternary salts is prerequisite.

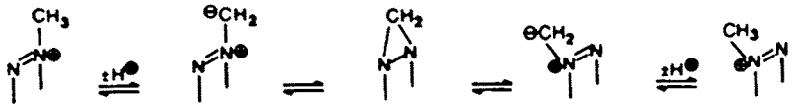
2) This equilibration and cyclisation was achieved with the small amounts of azo compound present because of the slow (and reversible?) alkylation by methyl iodide. But it occurred also when these azo compounds were added to the fluoroborate salts, as was demonstrated for example with 5a-Me* and small amounts of azo compound 5; after ten days at room temperature, the cage 6-H* was formed quantitatively.



Here, 5 can act as a base and/or as a nucleophile. Repetition of the experiment with 1.5 equivalents of 12 instead of 5 revealed that intermolecular methyl transfer to the azo group is possible.



After 10 minutes signals corresponding to new products were apparent, and after five days 5a-Me⊕ had been partially transformed into cage 6-H⊕ and partially demethylated to the azo compound 5. Formation of 13-Me⊕ indicates that the methyl group of 5a-Me⊕ has been transfered to 12, which then cycloreverts into 13-Me⊕ (vide supra) and cyclopentadiene (polymerised). Because of its high protic sensitivity,[4b] some 13 is also produced from 12. These experiments do not exclude an intramolecular 1,2-shift of the methyl group, since 12 could also act as a base. Therefore, the following reaction sequence may occur: deprotonation of the azo-quaternary salt (cf. C ⇒ E), formation of an intermediate diaziridine, ring opening and reprotonation of the isomeric dipole.



b) Does methyl migration occur with the quaternized hydrazones?
Thus far no sign of such a migration has been found; either the methylated hydrazone (for endo-7, endo-10, endo-17) cannot be isolated or the quaternized pyrazoline is stable (endo-15-Me⊕).

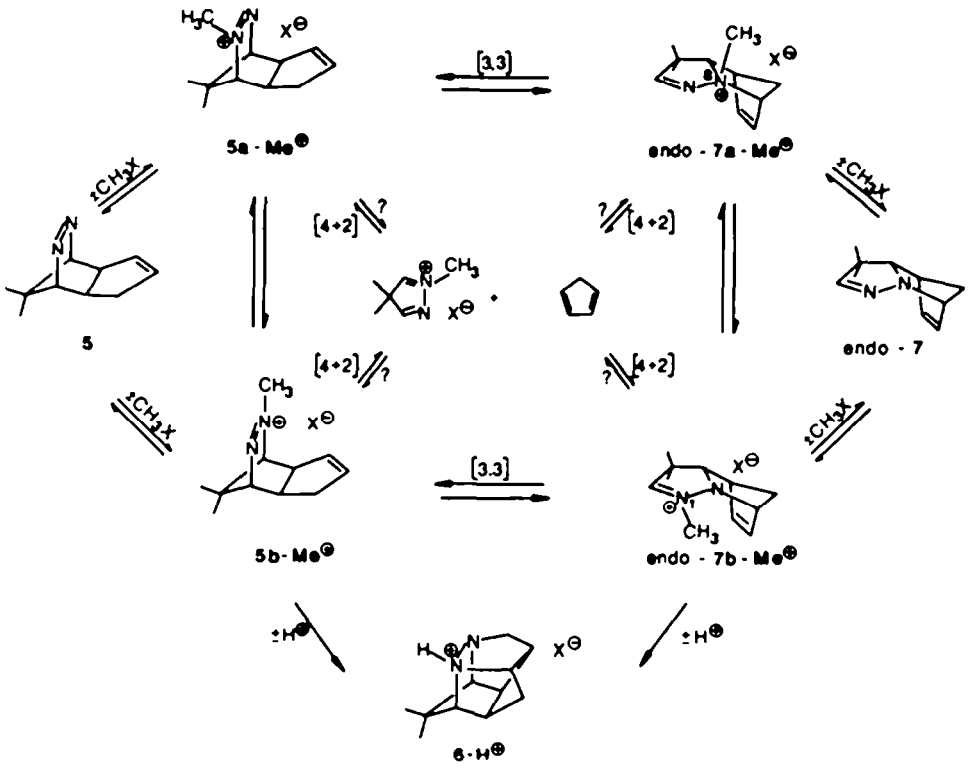
c) Does reversibility of the [4+2] cycloaddition simulate methyl migration?
If 5a-Me⊕, for example, would cyclorevert, readdition could afford the isomer 5b-Me⊕. The same holds true for the hydrazone derivatives, e.g. 17a-Me⊕ and 17b-Me⊕. This possibility has not been excluded so far. In the case of the proton catalyzed interconversion of isomeric azo compounds and hydrazones, cycloreversion was definitely ruled out.[8] Cycloreversion-addition cannot be operative for endo-7 and exo-7 because only endo-7 stereospecifically yielded the cage compound 6-H⊕.

d) Why do only some of the quaternized heterocycles isomerize?
This appears to be a question of higher thermodynamic stability within a given pair of isomeric heterocycles. Force field calculations revealed[9] the following sequence: 5 ⇒ endo-7 (+3.0 kcal/mol); 14 ⇒ endo-15 (-2.4 kcal/mol); 16 ⇒ endo-17 (+ 6.8 kcal/mol). According to these relativ stabilities, endo-7-Me⊕ and endo-17-Me⊕ rearrange very rapidly whereas endo-15-Me⊕ is perfectly stable.

e) Do the cage compounds originate both from the methylated azo compounds and pyrazolines?
In principle pyrazolines methylated at the 1-position (endo-7b-Me⊕ and endo-10b-Me⊕) could suffer an intramolecular 1,3-dipolar addition after deprotonation, thereby producing the same cage compound as from the N-methylated azo isomer (5b-Me⊕, 8b-Me⊕). With the pyrazolines, however, molecular models definitely show larger distances between the interacting groups than with the comparable azo compounds. Besides, the acidity of the methyl group should be lower if attached to N-1 at the pyrazolines. In addition, endo-7 rearranges on reaction with methyl iodide after some minutes into 5 (^{1}H-NMR control), which transforms into cage 6-H⊕ within some days. This behaviour excludes direct formation of 6-H⊕ from endo-7b-Me⊕.

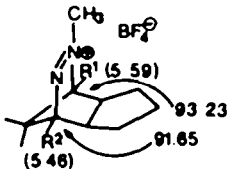
f) Why do not all the methylated azo bridges react with the intramolecular double bond present?
The fact that 5b-Me⊕ cleanly forms cage 6-H⊕, whereas the similar systems 14b-Me⊕ and 16b-Me⊕ are inert, is probably due to steric factors, i.e. the different ring sizes of these rather rigid systems. In contrast, 1-Me⊕ and 2-Me⊕ are flexible enough to adopt the boat conformation and hence bring the reacting moieties closer. Scheme 1 demonstrates all the possible reactions which may occur on alkylation, exemplified by the isomers 5 and endo-7. After methylation of 5 and endo-7, the most important step is the interconversion of 5-Me⊕ and endo-7-Me⊕ by [3,3] rearrangement and inter- (and intra?-) molecular migration of the methyl group, which probably occurs between 5a-Me⊕ and 5b-Me⊕ only. The consecutive formation of cage 6-H⊕ starts from 5b-Me⊕ and not endo-7b-Me⊕.

Scheme 1



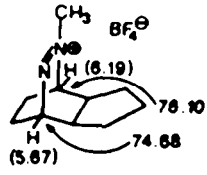
III. STRUCTURE DETERMINATIONS

For special comparisons the following azo-methyl quaternary salts 18 - 21 were chosen. They were quantitatively prepared from the corresponding azo compounds (18,[4b] 19,[3] 20,[4b] 21[4c]) and Me_3OBF_4. Due to the absence of a double bond, stable salts are formed, similar to those of diaza-bicyclo-heptene and -octene.[10]



Bridge head NMR signals for 18 (ppm)

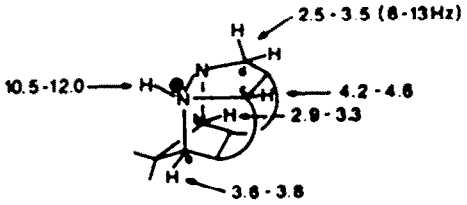
18 - Me⊕ R^1, R^2 = H (93%)
19a - Me⊕ R^1 = Me R^2 = H
and 19b - Me⊕ R^1 = H, R^2 = Me
(96%, a : b = 80 : 20)
20 - Me⊕ R^1, R^2 = Me (97%)

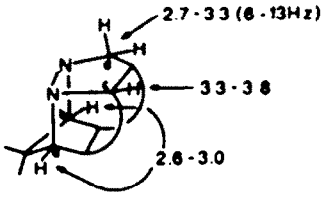


21 - Me⊕ (98%)

Because of the quaternized N-atom, the chemical shifts of the ^{1}H- and ^{13}C-NMR signals of the atoms at the bridgehead position closer to the positive charge are found at lower field than the others. Due to the double bond and the quaternized N-atom in 16a/b-Me⊕ (see 18 and 21-Me⊕), the differences $\Delta\delta$ of the bridgehead signals (^{1}H, ^{13}C-NMR) are decreased for the a-isomer in comparison to the b-isomer. Using the same arguments, the signals of the isomers 14a/b-Me⊕ have been assigned. As previously mentioned, methylation of 5 to 5a-Me⊕ is accompanied by the formation of small amounts of cage 6-H⊕. Since only one set of signals for 5-Me⊕ is to be seen, it can be assumed that they belong to isomer 5a-Me⊕ which cannot form cage 6-H⊕ directly. As discussed above, only endo-15 yields an isolable methyl quaternary salt from the various hydrazones employed, to which structure endo-15-Me⊕ can be assigned through an NOE experiment. Irradiation of the N⊕-methyl group enhances the signals of the protons 3a (8%) and 7 (10%) and one proton of the ethano bridge (8%), whereas the imino proton is only slightly influenced (2%).

From the protonated cage compounds 3-H⊕, 4-H⊕, 6-H⊕ and 11-H⊕ (type L-H⊕), potassium carbonate liberates the rather unstable bases L. This instability probably originates from the very small dihedral angle between the lone pairs in this hydrazine derivative caused by the rigid cage structure. Flexible alkyl hydrazines prefer a low energy conformation in which the two lone pairs attain a dihedral angle of about 90°.[11] In support of the proposed structures, in both the cations and the bases no double bond could be detected by spectroscopic methods. As is to be expected, ^{1}H- and ^{13}C-signals a-d in L and L-H⊕ are the most characteristic for the proposed cage structure and can easily be identified. The observed geminal coupling of J = 6-13 Hz, in both L and L-H⊕ together with δ= 2.7-3.3 (L) and δ= 2.5-3.5 (L-H⊕), respectively, has to be attributed to the H atoms of the CH_2-group (position d). Because of the small differences of the chemical shifts which are also found in the ^{13}C-NMR (L: δ= 52-54, L-H⊕: δ= 53-65), protonation obviously occurs at one nitrogen only, preferring the structure outlined in L-H⊕.





Signals of positions a and c are to be expected to show the strongest low field shift. H⊕ can be identified by its coupling pattern (multiplet) in the case of 3-H⊕ and 4-H⊕ and possesses the highest chemical shift; assignments for 6-H⊕ and 11-H⊕ have been done accordingly. Within $H^{\oplus}$-c proton $H^{\oplus}$ is assigned the smallest chemical shift. ^{13}C signals of positions a-c are found at δ= 60-80 in L-H⊕, but assignments cannot be definitely established. On deprotonation, these signals are shifted to higher field.

With methyl iodide the basic cage 6 easily forms a quarternary salt 6-Me⊕, which shows ^{1}H- and ^{13}C-NMR signals very similar to 6-H⊕. The methyl group is therefore assumed to occupy the same position as the proton in the general structure L-H⊕.

CONCLUSIONS

As expected, carbocycles with azo bridges can be quaternized by Me_3OBF_4 or methyl iodide. If these compounds include unsaturated double bonds in appropriate positions (1-Me⊕, 2-Me⊕, 5b-Me⊕, 8b-Me⊕), proton abstraction (cf. C ⇒ E) or proton shift (cf. C ⇒ F) will produce a 4π-system which undergoes an intramolecular [4+2] cycloaddition with the double bond, thereby forming a new type of cage compound (3-H⊕, 4-H⊕, 6-H⊕, 11-H⊕). In rigid systems the distance between the two functional groups is rather critical, as can be seen from 14b-Me⊕ and 15b-Me⊕, which refuse to undergo cyclisation. Formation of cages 3-H⊕ and 4-H⊕ from 1-Me⊕ and 2-Me⊕, however, indicates that the steric restrictions are less severe than anticipated from the cage formation C ⇒ D reported earlier.[4f] Systems in which azo group and double bond are arranged in a 1,5-position to one another, occupy a special position, as they are in principal capable of [4+2] cycloreversion (I ⇒ G + H) and [3,3] rearrangement (I ⇒ K). The hydrazone isomers can also be methylated. Depending on the special structure of these hydrazones, these quaternary salts are stable (endo-15-Me⊕) or they may either cyclorevert (endo-10-Me⊕ ⇒ 9) or rearrange to the quaternized azo-isomers (endo-17a/b-Me⊕ ⇒ 16a/b-Me⊕). Formation of cage compounds on methylation of hydrazones (endo-7 ⇒ 6-H⊕), proceeds via [3,3] rearrangement. In all cases, two isomers can be formed by methylation of both the azo and the hydrazone compounds. The azo quaternary salts have been shown to interconvert by intermolecular methyl migration (e.g. 5a-Me⊕, 16a/b-Me⊕) without excluding intramolecular pathways, but avoiding [4+2] cycloreversion. This isomerisation explains the high yields of cages 6-H⊕ and 11-H⊕, which can only arise from one of the two isomeric azo quaternary salts (5b-Me⊕, 8b-Me⊕).

EXPERIMENTAL

Melting points were determined using a Kofler instrument and are corrected. IR: Perkin-Elmer 1420, UV: Perkin-Elmer 330, ^{1}H- and ^{13}C-NMR: Bruker WM200 200 MHz (^{1}H)/50 MHz (^{13}C) or Bruker WM400 400 MHz (^{1}H)/100 MHz (^{13}C) Standard: TMS (0.00), $CDCl_3$ (7.26/77.0), CD_3CN (1.95/1.2, 117.8) or [d_6]-DMSO (2.50/40.6), MS: Varian MAT CH7. Elemental analyses were performed by the analytical laboratory, Institute of Inorganic Chemistry, University of Würzburg.

General procedure for the methylation with Me_3OBF_4: The freshly prepared (acid free) trimethyloxonium tetrafluoroborate was added to an ice cooled solution of the azo or hydrazone compound. The resulting suspension was stirred for the period given, while the ice bath was allowed to warm to room temperature. The resulting clear solution was filtered, and the solvent was evaporated under reduced pressure.

General procedure for the methylation with methyl iodide: Methyl iodide was dropped to a solution of the azo or hydrazone compound at room temperature. The reaction was followed by ^{1}H-NMR spectroscopy. Excess methyl iodide and solvent were evaporated at reduced pressure.

(1*a*,4*a*,4*aa*,10*aa*)-1,4,4*a*,5,8,8*a*-Hexahydro-2,9,9-trimethyl-1,4-methano-cyclohexa[*d*]pyridazinium tetrafluoroborate (1-MeBF$_4$): 80.0 mg (0.454 mmol) 1, 10 mL $CHCl_3$, 67.0 mg (0.454 mmol) Me_3OBF_4, 6 h: 121 mg [96%] 1-MeBF$_4$ as a colourless oil. IR (film): ν = 3040 cm^{-1} (C–H), 2970, 2940, 2890, 2860 (C–H), 1640 (C=C), 1465, 1450, 1385 (C(CH$_3$)$_2$), 1285, 1265, 1225, 1200–960 (BF_4^-), 890, 845, 765, 690. – ^{1}H-NMR (200 MHz, CD_3CN): δ = 0.81 and 1.21 (two s; 6H, –CH$_3$), 2.06–2.41 (m; 4H, 5,8-H), 3.30–3.59 (m; 2H, 4*a*,8*a*-H), 4.47 (s; 3H, N$^+$–CH$_3$), 6.10 (s; 1H, 1-H), 5.56–5.64 (m; 2H, 4,6-H), 5.69–6.78 (m; 1H, 7-H). – ^{13}C-NMR (50 MHz, CD_3CN): δ = 18.09 and 19.33 (two q; –CH$_3$), 22.62 and 22.89 (two t; C-5,8), 36.25 and 38.74 (two d; C-4*a*,8*a*), 53.50 (q; N$^+$–CH$_3$), 63.90 (s; C-9), 94.29 and 96.22 (two d; C-1,4), 124.6 and 128.8 (two d; C-6,7). – MS: m/z (%) = 190 (25, M$^+$-BF$_4$), 175 (100, M$^+$-HBF$_4$-CH$_3$), 109 (35), 94 (55), 79 (87), 55 (30), 49 (50), 41 (57). – Anal. Calcd. for $C_{12}H_{19}BF_4N_2$ (278.1): C, 51.83; H, 6.89; N, 10.07. Found : C, 51.89; H, 6.66; N, 9.94.

(1*a*,4*a*,4*aa*,10*aa*)-1,4,4*a*,5,6,9,10,10*a*-Octahydro-2,11,11-trimethyl-1,4-methano-cycloocta[*d*]pyridazinium tetrafluoroborate (2-MeBF$_4$): 100 mg (0.489 mmol) 2, 10 mL $CHCl_3$, 72.0 mg (0.489 mmol) Me_3OBF_4, 5 h: 146 mg [97%] 2-MeBF$_4$ as a colourless oil. IR (film): ν = 3020 cm^{-1} (=C–H), 2940, 2880 (C–H), 1640, 1625 (C=C), 1465, 1450, 1430, 1400, 1385 (C(CH$_3$)$_2$), 1285, 1255, 1240, 1205, 1200–900 (BF_4^-). – ^{1}H-NMR (200 MHz, CD_3CN): δ = 0.82 and 1.18 (two s; 6H, –CH$_3$), 1.18–1.56 (m; 3H) and 2.05–2.34 (m; 5H, 5,6,9,10-H), 3.00–3.26 (m; 2H, 4*a*,10*a*-H), 4.61 (s; 3H, N$^+$–CH$_3$), 5.17 (br.s.; 1H, 4-H), 5.55 (br.s.; 1H, 1-H), 5.72–5.77 (m; 2H, 7,8-H). – ^{13}C-NMR (50 MHz, CD_3CN): δ = 18.50 and 19.35 (two q; –CH$_3$), 25.38, 25.68 and 27.50 (three t; C-5,6,9,10), 42.88 (d; C-4*a*), 44.41 (d; C-10*a*), 53.85 (q; N$^+$–CH$_3$), 63.30 (s; C-11), 96.00 (d; C-4), 96.47 (d; C-1), 132.11 and 132.45 (two d; C-7,8). – MS: m/z (%) = 218 (1, M$^+$-HBF$_4$), 203 (1, M$^+$-HBF$_4$-CH$_3$), 177 (1, M$^+$-BF$_4$-CH$_3$-N$_2$+1), 109 (14, $C_8H_{13}^+$), 83 (100), 67 (22), 54 (17), 49 (69), 41 (24). – Anal. Calcd. for $C_{14}H_{23}BF_4N_2$ (306.2): C, 54.93; H, 7.57; N, 9.15. Found: C, 54.48; H, 7.82; N, 8.61.

11,11-Dimethyl-1-azonia-9-azapentacyclo[7.3.0.0^{2,7}.0^{4,12}.0^{5,10}] dodecane iodide (3-HI): 76.0 mg (0.431 mmol) 1, 0.50 mL $CDCl_3$, 184 mg (1.29 mmol) MeI, 8 d: 90.0 mg [67%] 3-HI as light yellow crystals, m.p. 200–203 °C. IR (KBr): ν = 2930 cm^{-1}, 2870 (C–H), 2700, 2620, 2530 (N$^+$–H), 1465, 1395, 1375 (C(CH$_3$)$_2$), 1355, 1325, 1300, 1275, 1220, 1180, 1150, 1095, 1070, 1050, 925, 905, 870, 860, 830, 770, 740. – ^{1}H-NMR (400 MHZ, $CDCl_3$): δ = 1.20–1.44 (two s; 6H, –CH$_3$), 1.67–1.70 (d; J = 15 Hz, 1H, 6'-H), 1.78–1.82 (d; 1H, 6''-H), 1.90–1.94 (dd; J = 13 Hz, J = 5 Hz, 1H, 3'-H), 2.07–2.10 (d; 1H, 3''-H), 2.72–2.75 (dm; J = 9 Hz, 1H, 8'-H), 2.84 (br.s; 1H, 7-H), 2.97–3.00 (d; 1H, 8''-H), 3.07 (s; 1H, 5-H), 3.32 (s; 2H, 4,10-H), 3.77 (s; 1H, 12-H), 4.61 (br.s; 1H, 2-H), 11.70 (br.s; 1H, N$^+$-H). – ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 19.13 and 19.73 (two q; 11-CH$_3$), 23.46 and 24.53 (two t; C-3,6), 34.57, 37.03 and 39.48 (three d; C-4,5,7) 48.21 (s; C-11), 56.03 (t; C-8), 68.94, 69.17 and 77.53 (three d; C-2,10,12). – MS: m/z (%) = 190 (28, M$^+$-HI), 175 (100, M$^+$-HI-CH$_3$), 128 (37), 127 (18), 93 (22), 83 (17), 55 (6), 41 (12). – Anal. Calcd. for $C_{12}H_{19}IN_2$ (318.2): C, 45.30; H, 6.02; N, 8.80. Found: C, 45.10; H, 6.21; N, 9.15. [21.0 mg (0.0755 mmol) 1-MeBF$_4$, 2.75 mg (0.0151 mmol) 1 (0.2 eq), 0.50 mL CD_3CN; after 21 d ^{1}H-NMR spectrum shows only the proton signals of 3-HBF$_4$ and 1 (0.2 eq)].

13,13-Dimethyl-1-azonia-11-azapentacyclo[9.3.0.0^{2,9}.0^{4,14}.0^{8,12}] tetradecane iodide (4-HI): 41.0 mg (0.201 mmol) 2, 0.50 mL $CDCl_3$, 62.0 mg (0.442 mmol) MeI, 21 d: 63.0 mg [91%] 4-HI as light yellow crystals, m.p. 261–264 °C. IR (KBr): ν = 2950 cm^{-1}, 2930, 2900, 2880, 2860 (C–H), 2790, 2640, 2610 (N$^+$–H), 1475, 1460, 1405, 1390 (C(CH$_3$)$_2$), 1310, 1210, 1090, 1010, 965. – ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 1.19 and 1.54 (two s; 6H, –CH$_3$), 1.78–2.13 (m; 8H, 3,4,7,8-H), 2.63–2.68 (m; 1H, 9-H), 2.74–2.80 (m; 1H, 6-H), 2.82–2.87 (dd; J = 13 Hz, J = 6 Hz, 1H, 5-H), 2.96 (s; 1H, 12-H), 3.30–3.34 (d; J = 13 Hz, 1H, 10'-H), 3.44–3.49 (dd; J = 6 Hz, 1H, 10''-H), 3.59 (s; 1H, 14-H), 4.39 (s; 1H, 2-H), 11.29 (br.s; 1H, N$^+$-H). – ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 15.43, 17.09, 20.77 and 23.98 (four t; C-3,4,7,8), 21.85 (q; 13-CH$_3$), 29.65, 36.21 and 42.76 (three d; C-5,6,9), 50.34 (s; C-13), 52.89 (t; C-10), 60.47, 68.25 and 74.15 (three d; C-2,12,14). – MS: m/z (%) = 218 (66, M$^+$-HI), 203 (100, M$^+$-HI-CH$_3$), 138 (11), 128 (41), 127 (21), 121 (10), 93 (22), 83 (32), 67 (19), 55 (16), 41 (19). – Anal. Calcd. for $C_{14}H_{23}IN_2$ (346.3): C, 48.56; H, 6.70; N, 8.09. Found: C, 49.03; H, 6.92; N, 8.16. [188 mg (0.614 mmol) 2-MeBF$_4$, 250 mg (0.122 mmol) 2 (0.2 eq), 0.50 mL CD_3CN; after 64 d ^{1}H-NMR spectrum shows only the proton signals of 4-HBF$_4$ and 2 (0.2 eq)].

(1*a*,4*a*,4*aa*,7*aa*)-4,4*a*,5,7*a*-Tetrahydro-3,8,8-trimethyl-1,4-methano-1H-cyclopenta[*d*]pyridazinium tetrafluoroborate (5*a*-MeBF$_4$): 50.0 mg (0.308 mmol) 5, 25 mL $CHCl_3$, 456 mg (3.08 mmol) Me_3OBF_4, 0°C, 2 h: 80.0 mg [99%] of a mixture of 5*a*-MeBF$_4$ and 6-HBF$_4$ (90:10) as a colourless oil. IR (film): ν = 3100–3000 cm^{-1} (=C–H), 3000–2800 (C–H), 1475, 1460, 1450, 1440, 1430 (N=N), 1400, 1390 (C(CH$_3$)$_2$), 1290, 1200–800 (BF_4^-). – ^{1}H-NMR (Varian EM 390, 90 MHz, $CDCl_3$): δ= 1.00 and 1.30 (two s; 6H, –CH$_3$), 2.20–2.50 (m; 2H, 7-H), 3.50–3.90 and 4.10–4.40 (two m; 2H, 4*a*,7*a*-H), 4.48 (s; N$^+$–CH$_3$), 5.50–5.70 (d; 1H, N–CH), 5.70–6.00 (m; 3H, =CH, N$^+$–CH). – Anal. Calcd. for $C_{11}H_{17}BF_4N_2$ (264.1): C, 50.03; H, 6.49;

N, 10.61. Found: C, 45.32; H, 6.15; N, 11.04.

10,10-Dimethyl-1-azonia-8-azapentacyclo[6.3.0.0^{2,6}.0^{4,11}.0^{5,9}]undecane iodide (6-HI): 446 mg (2.74 mmol) 5, 4 mL $CDCl_3$, 1.17 g (8.18 mmol) MeI, 5 d: 760 mg [91%] 6-HI as yellow crystals, decomposition after 80°C; further purification wasn't successful. [241 mg (1.63 mmol) Me_3OBF_4, 528 mg (3.25 mmol) 5, 3 mL $CHCl_3$, 2 d: after removal of excess 5 289 mg [67%] 6-HBF_4 were obtained / 100 mg (0.379 mmol) 5a-$MeBF_4$, 10 mg (0.060 mmol) 5 (0.16 eq), 1 mL $CDCl_3$: after 10 d ^{1}H-NMR spectrum shows only the proton signals of 6-HBF_4 and 5 (0.16 eq) / 40.0 mg (0.160 mmol) 5a-$MeBF_4$, 0.40 mL $CDCl_3$, 40.0 mg (0.210 mmol) 12: after 5 d a mixture of 12, 6-H$^+$, 5, 13-Me$^+$, 13 and cyclopentadiene polymer was observed, utilising ^{1}H-NMR [characteristic signals (methyl group): 12: 0.35, 0.75 and 1.55, 13-Me$^+$: 1.35, 2.20, 3.50 and 3.85, 13: 1.15 and 2.20, 6-H$^+$: 1.05 and 1.30]. 6-HBF_4: IR (film): ν = 3560 cm^{-1}, 3360 (N-H), 3000-2900 (C-H), 2800-2500 (N$^+$-H), 1460, 1390, 1380, 1350, 1330, 1285, 1255, 1245, 1200-960 (BF_4^-). - ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 1.15 and 1.34 (two s; 6H, $-CH_3$), 1.93-1.96 (d; J = 12.5 Hz, 1H, 3'-H), 2.00-2.04 (dd; J = 2.5 Hz, 1H, 3''-H), 2,77-2.81 (m; 1H, 5-H), 2.93-2.96 (d; J = 6 Hz, 1H, 7'-H), 2.96 (s; 1H, 6-H), 3.11-3.13 (d; 1H, 7''-H), 3.18-3.20 (d; J = 8 Hz, 1H, 4-H), 3.21 (s; 1H, 9-H), 3.74 (s; 1H, 11-H), 4.23 (s; 1H, 2-H), 11.24 (br.s; 1H, N$^+$-H). - ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 20.61 and 21.13 (two q; $-CH_3$, 29.32 (t; C-3), 42.71 (s; C-10), 41.09, 43.82 and 50.00 (three d; C-4,5,6), 55.31 (t; C-7), 74.73, 79.28 and 82.69 (three d; C-2,9,11). - MS: m/z (%) = 176 (29, M$^+$-HBF_4), 161 (58, M$^+$-HBF_4-CH_3), 83 (100). - Anal. Calcd. for $C_{11}H_{17}BF_4N_2$ (264.1): C, 50.03; H, 6.49; N, 10.61. Found: C, 50.69; H, 6.70; N, 10.79.

Methylation of endo-7 with Me_3OBF_4: 50.0 mg (0.308 mmol) endo-7, 7 mL $CHCl_3$, 45.5 mg (0.308 mmol) Me_3OBF_4, 5 d: 59.0 mg [73%] 6-HBF_4 as a dark brown oil.

Methylation of endo-7 with MeI: 104 mg (0.641 mmol) endo-7, 0.50 mL $CDCl_3$, 148 mg (1.04 mmol) MeI. ^{1}H-NMR spectrum after 6 d showed only the proton signals of 6-H$^+$.

Methylation of exo-7 with Me_3OBF_4: 87.0 mg (0.536 mmol) exo-7, 10 mL $CHCl_3$, 79.0 mg (0.536 mmol) Me_3OBF_4, 1 d. Only decomposition was observed in ^{1}H-NMR.

Methylation of exo-7 with MeI: 100 mg (0.616 mmol) exo-7, 2 mL $CDCl_3$, 262 mg (1.85 mmol) MeI, 10 d. Only decomposition was observed in ^{1}H-NMR.

Methylation of 8 with Me_3OBF_4: 100 mg (0.567 mmol) 8, 10 mL $CHCl_3$, 84.0 mg (0.567 mmol) Me_3OBF_4, 0°C, 2 h: 80.0 mg 9-$MeBF_4$ as colourless crystals, which contain small amounts of 8 and impurities. ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 1.49 (s; 6H, $-CH_3$), 2.30 (s; 3H, $-CH_3$), 4.00 (s; 3H, $-CH_3$), 9.03-9.05 (m; 1H).

Methylation of endo-10 with Me_3OBF_4: 100 mg (0.567 mmol) endo-10, 10 mL $CDCl_3$, 84.0 mg (0.567 mmol) Me_3OBF_4, 0°C, 2 h: 103 mg [99%] 9-$MeBF_4$ as colourless crystals.

9,10,10-Trimethyl-1-azonia-8-azapentacyclo[6.3.0.0^{2,6}.0^{4,11}.0^{5,9}]undecane iodide (11-HI): 217 mg (1.23 mmol) 8, 5 mL $CHCl_3$, 524 mg (3.69 mmol) MeI, 20 d: 504 mg 11-HI as dark brown oil; further purification wasn't successful. - ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 1.05, 1.08 and 1.23 (three s; 9H, $-CH_3$), 1.85-1.90 (d; J = 11 Hz, 1H, 3'-H), 2.07-2.14 (m; 2H, 3'',5-H), 2.48-2.63 (m; J = 6 Hz, 1H, 7'-H), 2.91 (br.s; 1H, 4-H), 3.10 (s; 1H, 6-H), 3.16-3.19 (d; 1H, 7''-H), 3.74 (s; 1H, 11-H), 4.20 (s; 1H, 2-H), 10.66 (br.s; 1H, N$^+$-H). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 11.82 (q; 9-CH_3), 19.07 and 20.42 (two q; 10-CH_3), 29.68 (t; C-3), 42.41, 46.78 and 48.83 (three d; C-4,5,6), 44.84 (s; C-10), 52.84 (t; C-7), 71.83 and 79.29 (two d; C-2,11), 81.21 (s; C-9).

Methylation of endo-10 with MeI: 30.0 mg (0.170 mmol) endo-10, 72.0 mg (0.510 mmol) MeI, 0.50 mL $CDCl_3$, 4 d: 57.0 mg of a mixture of 11-HI and 9-MeI (69:31).

Cycloreversion of 12 with trifluoracetic acid yielded 13-H$^+$ and cyclopentadiene: 114 mg (1.00 mmol) trifluoracetic acid were dropped to an ice cold solution of 181 mg (1.00 mmol) 12 in 0.50 mL $CDCl_3$; within 2 h an equilibrium between 12 and 13-H$^+$, cyclopentadiene 40:60 was attained, which showed no change after a period of 65 h according to ^{1}H-NMR.

Reaction of 12 with fluorsulfonic acid methylester to 13-$MeFSO_3$ and cyclopentadiene: To an ice cold solution of 225 mg (1.21 mmol) 12 in 0.40 mL $CDCl_3$ were dropped 180 mg (1.80 mmol) fluorsulfonic acid methylester. After 14 h at room temperature, complete cycloreversion of 12 was achieved yielding 13-$MeFSO_3$ and cyclopentadiene polymer. - ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 1.48 (s; 6H), 2.30 (s; 3H), 2.63 (m; 3H), 3.95 (m; 3H).

Methylation of 14 with MeI: 27.0 mg (0.153 mmol) 14, 0.50 mL $CDCl_3$, 65.0 mg (0.459 mmol) MeI. Only decomposition was observed in ^{1}H-NMR within 20 d.

(1a,4a,4aa,8aa)-1,4,4a,7,8,8a-Hexahydro-2,9,9-trimethyl-1,4-methano-phthalazinium tetrafluoroborate (14a-$MeBF_4$) and (1a,4a,4aa,8aa)-1,4,4a,7,8,8a-Hexahydro-3,9,9-trimethyl-1,4-methano-phthalazinium tetrafluoroborate (14b-$MeBF_4$): 81.0 mg (0.459 mmol) 14, 10 mL $CDCl_3$, 68.0 mg (0.459 mmol) Me_3OBF_4, 3 h: 127 mg [96%] 14-$MeBF_4$ as a yellow oil (a:b = 84:16). ^{1}H-NMR (200 MHz, CD_3CN): a: δ= 0.87 and 1.22 (two s; 6H, $-CH_3$), 1.38-1.58 (m; 2H, 8-H), 1.76-1.93 (m; 2H, 7-H), 3.44-3.51 (m; 2H, 4a,7a-H), 4.42 (s; 3H, N$^+$-CH_3), 5.30 and 5.64 (two br.s; 2H, 1,4-H), 5.80-5.86 and 6.03-6.11 (two m; 2H, 5,6-H). - b: δ = 4.55 (s; 3H, N$^+$-CH_3). - ^{13}C-NMR (50 MHz, CD_3CN): a: δ= 18.80 and 19.29 (two q; $-CH_3$), 21.86 (t; C-8), 23.59 (t; C-7), 38.50 and 39.93 (two d; C-4a,8a), 53.79 (d; N$^+$-CH_3), 62.74 (s; C-9), 93.31 and 94.36 (two d; C-1,4), 123.7 and 134.8 (two d; C-5,6). b: δ = 92.80 (d; C-1), 96.19 (d; C-4), 124.3 and 132.0 (two d; C-5,6).

Endo-3,3a,4,7-Tetrahydro-3,3,8-trimethyl-4,7-ethanopyrazolo[1,5-a]pyridinium iodide (endo-15·MeI): 438 mg (2.60 mmol) endo-15, 2.0 mL $CHCl_3$, 604 mg (4.26 mmol) MeI, 1 d. The yellow residue was washed with acetone and dried for 4 h (100–120°C) at reduced pressure (0.01 Torr) to give 530 mg [64%] endo-15·MeI as colourless crystals, m.p. 183–185°C. IR (KBr): ν= 3050 cm^{-1}, 3040, 3030 (=C-H), 3000, 2955, 2880 (C-H), 1635 (C=N), 1480, 1470, 1455, 1440, 1380, 1365, 1315, 1305, 1275, 1260, 1225, 1170, 935, 905, 885, 795, 770, 740. – ^{1}H-NMR (400 MHz, [d_6]-DMSO): δ = 1.21 and 1.38 (two s; 6H, $-CH_3$), 1.30–1.38 and 1.46–1.53 (two m; 2H, 9-H), 1.88–1.95 and 2.41–2.52 (two mc; 2H, 10-H), 3.08 (br.s.; 1H, 4-H), 3.56 (s; 3H, N^+-CH_3), 3.92 (s; 1H, 3a-H), 4.78–4.80 (br.s.; 1H, 7-H), 6.19–6.23 and 6.60–6.64 (two t; 2H, 5,6-H). – ^{13}C-NMR (100 MHz, [d_6]-DMSO): δ= 18.05 (q; $-CH_3$), 19.07 and 19.20 (two t; C-9,10), 27.01 (q; $-CH_3$), 31.18 (d; C-4), 52.40 (q; N^+-CH_3), 54.35 (s; C-3), 64.43 (d; C-3a), 80.13 (d; C-7), 128.8 (d; C-5,6), 134.6 (d; C-5,6), 173.3 (d; C-2). – MS: m/z (%) = 191 (0.1, M^+-I), 176 (1, M^+-I-CH_3), 142 (90), 127 (34), 109 (61), 95 (41, $C_5H_7N_2^+$), 79 (100, $C_6H_7^+$), 66 (18), 51 (18), 42 (22), 39 (27). – Anal. Calcd. for $C_{12}H_{19}IN_2$ (318.2): C, 45.30; H, 6.02; N, 8.80. Found: C, 45.14; H, 5.89; N, 8.87.

Endo-3,3a,4,7-Tetrahydro-3,3,8-trimethyl-4,7-ethanopyrazolo[1,5-a]pyridinium tetrafluoroborate (endo-15·$MeBF_4$): 96.0 mg (0.545 mmol) endo-15, 10 mL $CDCl_3$, 80.6 mg (0.545 mmol) Me_3OBF_4, 1 d: 134 mg [88%] endo-15·$MeBF_4$ as colourless crystals, m.p. 187–189°C.

Methylation of 15 with MeI: 20.0 mg (0.135 mmol) 15, 0.50 mL $CDCl_3$, 21.0 mg (0.148 mmol) MeI. Complete decomposition was observed in ^{1}H-NMR after 1 d.

(1α,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-2-methyl-1,4-ethano-1H-cyclopenta[d]pyridazinium tetrafluoroborate (16a·$MeBF_4$) and (1α,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-3-methyl-1,4-ethano-1H-cyclopenta[d]pyridazinium tetrafluoroborate (16b·$MeBF_4$): 100 mg (0.675 mmol) 16, 10 mL $CHCl_3$, 100 mg (0.675 mmol) Me_3OBF_4, 1 d: 187 mg [99%] 16·$MeBF_4$ as light yellow crystals (a:b = 62:38), m.p. 120–125°C. – IR (KBr): ν = 3050 cm^{-1} (=C-H), 2940, 2910 (C-H), 1640 (C=C), 1590, 1500, 1460, 1390 (C(CH_3)$_2$), 1360, 1300, 1280, 1265, 1200–960 (BF_4^-). – ^{1}H-NMR (400 MHz, CD_3CN): a: δ = 1.43–1.50 (m; 1H), 1.81–1.87 (m; 1H) and 2.08–2.34 (m; 3H, 7,8,9-H), 2.56–2.65 (m; 1H, 7-H), 3.11–3.17 (m; 1H, 7a-H), 3.62–3.65 (mc; 1H, 4a-H), 4.34 (s; 3H, N^+-CH_3), 5.46–5.47 (m; 1H, 4-H), 5.61–5.64 (m; 1H) and 5.77–5.80 (mc; 1H, 5,6-H), 5.93–5.94 (br.s.; 1H, 1-H). – b: δ = 1.52–1.59 (mc; 1H), 1.68–1.80 (mc; 1H) and 2.08–2.34 (m; 3H, 7,8,9-H), 2.67–2.74 (m; 1H, 7-H), 3.11–3.17 (m; 1H, 7a-H), 3.62–3.65 (mc; 1H, 4a-H), 4.55 (s; 3H, N^+-CH_3), 5.40–5.41 (m; 1H, 1-H), 5.54–5.57 (m; 1H, 6-H), 5.61–5.64 (m; 1H, 5-H), 6.12–6.14 (m, 1H, 4-H). – ^{13}C-NMR (100 MHz, CD_3CN): a: δ= 23.14 and 23.60 (two t; C-8,9), 39.01 (t; C-7), 40.54 (d; C-7a), 53.72 (d; C-4a), 58.61 (q, N^+-CH_3), 74.93 (d; C-1,4), 127.9 and 136.5 (two d; C-5,6). – b: δ = 23.09 and 24.75 (two t; C-8,9), 38.04 (t; C-7), 41.13 (d; C-7a), 52.16 (d; C-4a), 59.25 (q; N^+CH_3), 73.33 (d; C-1), 76.97 (d; C-4), 130.0 and 134.0 (two d; C-5,6). – MS : m/z (%) = 162 (31, M^+-HBF_4), 150 (47 M^+-BF_4-CH_2+H), 97 (48), 91 (35), 83 (98), 80 (58, $C_4H_4N_2^+$), 66 (48, $C_5H_6^+$), 57 (100), 49 (60), 41 (59). – Anal. Calcd. for $C_{10}H_{15}BF_4N_2$ (250.0): C, 48.04; H, 6.05; N, 11.20. Found: C, 47.96; H, 6.41; N, 10.94.

Methylation of endo-17 with Me_3OBF_4: 48.0 mg (0.324 mmol) endo-17, 5 mL $CHCl_3$, 48.0 mg (0.324 mmol) Me_3OBF_4, 1 d: 73.0 mg [90%] 16·$MeBF_4$ as a light yellow paste (a:b = 32:68).

Methylation of endo-17 with MeI: 52.0 mg (0.361 mmol) endo-17, 0.50 mL $CDCl_3$, 55.0 mg (0.386 mmol) MeI. Decomposition was observed within 4 d in ^{1}H-NMR.

(1α,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-2,8,8-trimethyl-methano-1H-cyclopenta[d]pyridazinium tetrafluoroborate (18·$MeBF_4$): 32.0 mg (0.196 mmol) 18, 5 mL $CHCl_3$. 29.0 mg (0.196 mmol) Me_3OBF_4, 0°C, 1 h: 48.0 mg [93%] 18·$MeBF_4$ as a colourless oil. – IR (film): ν= 3000–2800 cm^{-1} (C-H), 1480, 1460, 1450 (N=N), 1400, 1380 (C(CH_3)$_2$), 1290, 1280, 1250, 1200–800 (BF_4^-). – ^{1}H-NMR (Varian EM 390, 90 MHz, $CDCl_3$): δ= 0.90 and 1.25 (two s; 6H, $-CH_3$), 1.35–2.00 (m; 6H, 5,6,7-H), 3.37–3.73 (m; 2H, 4a,7a-H), 4.68 (s; 3H, N^+-CH_3), 5.46 (d; J = 3 Hz, 1H, 4-H), 5.59 (d; J = 2 Hz, 1H, 1-H). – ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 18.45 and 19.40 (two q; $-CH_3$), 25.78 and 27.10 (two t; C-5,6,7), 27.07 (q; N^+-CH_3), 46.91 (d; C-4a), 46.21 (d; C-7a), 53.34 (s; C-8), 91.65 (d; C-4), 93.23 (d; C-1). – MS: m/z (%) = 178 (5, M^+-HBF_4), 163 (10, M^+-HBF_4-CH_3), 107 (100). – Anal. Calcd. for $C_{11}H_{19}BF_4N_2$ (266.9): C, 49.68; H, 7.20; N, 10.53. Found: C, 47.73; H, 7.05; N, 9.70.

(1α,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1,2,8,8-tetramethyl-1,4-methano-1H-cyclopenta[d]pyridazinium tetrafluoroborate (19a·$MeBF_4$) and (1α,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1,3,8,8-tetramethyl-1,4-methano-1H-cyclopenta[d]pyridazinium tetrafluoroborate (19b·$MeBF_4$): 130 mg (0.729 mmol) 19, 15 mL $CHCl_3$, 108 mg (0.729 mmol) Me_3OBF_4, 4.5 h: 198 mg [96%] 19·$MeBF_4$ as light yellow crystals (a:b = 80:20), m.p. 144–146°C. – IR (KBR): ν = 2960 cm^{-1}, 2870 (C-H), 1440, 1396, 1380, 1335, 1300, 1250–960 (BF_4^-). – ^{1}H-NMR (200 MHz, CD_3CN): a: δ = 0.77 (s; 3H, $-CH_3$), 1.01–1.25 (m; 2H, 6-H), 1.13 (s; 3H, $-CH_3$), 1.46–1.89 (m; 2H, 5,7-H), 1.81 (s; 3H, 1-CH_3), 3.22–3.33 and 3.41–3.56 (two m; 2H, 4a,7a-H), 4.56 (s; 3H, N^+-CH_3), 5.27–5.29 (d; J = 3 Hz, 1H, 4-H). – b: δ = 0.73, 1.13 and 1.72 (three s; 9H, $-CH_3$), 4.47 (s; N^+-CH_3), 5.63–5.64 (d; J = 3.5 Hz, 1H, 1-H).– ^{13}C-NMR (50 MHz, CD_3CN): a: δ = 11.12, 17.17 and 18.45 (three q; $-CH_3$), 25.05, 26.75 and 27.65 (three t; C-5,6,7), 47.28 and 52.16 (two d; C-4a,7a), 53.81 (q; N^+-CH_3), 68.70 (s; C-8), 94.87 (d; C-4), 97.54 (s; C-1). – b: δ = 9.81, 17.17 and 19.10 (three q; $-CH_3$), 25.41, 26.63 and 27.38 (three t; C-5,6,7), 47.19 and 51.33 (two d; C-4a,7a), 51.16 (q; N^+-CH_3), 68,18 (s; C-8), 91.10 (d; C-4), 100.3 (s; C-1). – MS: m/z (%) = 192 (0.4, M^+-HBF_4), 180 (4, M^+-BF_4-CH_2+H), 163 (2, M^+-BF_4-2CH_3), 148 (2, M^+-BF_4-3CH_3), 135 (9), 123 (8), 111 (16), 97 (14, $C_5H_9N_2^+$), 67 (100, $C_5H_7^+$) 53 (39), 41 (37). – Anal. Calcd. for $C_{12}H_{21}BF_4N_2$ (280.1): C, 51.46; H, 7.55; N, 10.00. Found: C, 51.22; H, 7.30; N, 9.73.

(1a,4a,4aa,7aa)-4,4a,5,6,7,7a-Hexahydro-1,2,4,8,8-pentamethyl-methano-1H-cyclopenta[d]pyridazinium tetrafluoroborate (20-$MeBF_4$): 32.6 mg (0.220 mmol) 20, 0.40 mL $CDCl_3$, 33.0 mg (0.220 mmol) Me_3OBF_4, 24 h: 63.0 mg [97%] 20-$MeBF_4$ as light yellow crystals, m.p. 132-133°C. IR (KBr): ν = 2950 cm^{-1}, 2860 (C-H), 1460, 1456 (N=N), 1395, 1380 ($C(CH_3)_2$), 1150-1000 cm (BF_4^-). - ^{1}H-NMR (Varian EM 390, 90 MHz, $CDCl_3$): δ= 0.61 (s; 3H, $-CH_3$), 1.00 (s; 3H, $-CH_3$), 1.29-1.90 (m; 6H, $3CH_2$), 1.72 (s; 3H, $-CH_3$), 1.78 (s; 3H, N^+-CH_3), 3.00-3.30 (m; 2H, 4a, 7a-H), 4.45 (s; 3H, N^+-CH_3). - Anal. Calcd. for $C_{13}H_{23}BF_4N_2$ (294.1). C, 53.08; H, 7.88; N, 9.52. Found: C, 53.05; H, 8.16; N, 9.11.

(1a,4a,4aa,7aa)-4,4a,5,6,7,7a-Hexahydro-2-methyl-1,4-ethano-1H-cyclopenta[d]pyridazinium tetrafluoroborate (21-$MeBF_4$): 57.0 mg (0.379 mmol) 21, 10 mL $CHCl_3$, 56.0 mg (0.379 mmol) Me_3OBF_4, 1 d: 94.0 mg [98%] 21-$MeBF_4$ as light yellow crystals, m.p. 109-115°C. IR (KBr): ν = 2980 cm^{-1}, 2870 (C-H), 1440, 1396, 1315, 1300, 1285, 1240, 1200-950 (BF_4^-). - ^{1}H-NMR (200 MHz, CD_3OD): δ = 1.43-1.54, 1.68-1.80, 1.92-2.09, 2.11-2.33 (four m; 10H, 5,6,7,8,9-H), 3.07-3.12 (m; 2H, 4a,7a-H), 4.84 (s; 3H, N^+-CH_3), 5.66 5.68 (d; 1H, 4-H), 6.19 (br.s.; 1H, 1-H). - ^{13}C-NMR (50 MHz, CD_3OD): δ = 23.60, 24.75 and 26.15 (three t; C-5,6,7), 31.54 and 32.17 (two t; C-8,9), 45.63 (d; C-4a), 46.14 (d; C-7a), 58.87 (q; N^+-CH_3), 74.68 (d; C-4), 76.10 (d; C-1). - MS: m/z (%) = 165 (24, M^+-BF_4), 152 (41), 150 (3, $M^+-BF_4-CH_3$), 122 (10, $M^+-BF_4-CH_3-N_2$), 93 (32), 83 (100), 67 (45, $C_5H_7^+$), 56 (62), 41 (45). - Anal. Calcd. for $C_{10}H_{17}BF_4N_2$ (252.1): C, 47.65; H, 6.80; N, 11.11. Found: C, 47.85; H, 7.01; N, 10.76.

General procedure for the deprotonation of L-H$^+$:
L-H$^+$ in $CHCl_3$ was shaken with an aqueous solution of K_2CO_3. The organic layer was dried over K_2CO_3 and the solvent was evaporated.

11,11-Dimethyl-1,9-diazapentacyclo[7.3.0.$0^{2,7}$.$0^{4,12}$.$0^{5,10}$]dodecane (3): 100 mg (0.314 mmol) 3-HI; 13.0 mg [22%] 3 as colourless crystals. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.10 and 1.36 (two s; 6H, $-CH_3$), 1.36-1.41 (d; 1H), 1.56-1.61 (m; 2H) and 1.78-1.84 (d; J = 12 Hz, 1H, 3,6-H), 2.31-2.37 (m; 2H, 5,7 H), 2.55-2.59 (d; 1H, 4-H), 2.59 (s; 1H, 10-H), 2.85 (s; 1H, 12-H), 2.90-2.96 (d; 12 Hz, 1H, 8'-H), 3.04-3.10 (br.d; 1H, 8''-H), 3.66-3.71 (mc; 1H, 2-H).

13,13-Dimethyl-1,11-diazapentacyclo[9.3.0.$0^{2,9}$.$0^{5,14}$.$0^{6,12}$]tetradecane (4): 50.0 mg (0.144 mmol) 4-HI; 20.0 mg 4 as light yellow oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.09 and 1.46 (two s; 6H, $-CH_3$), 1.62-2.10 (m; 8H, 3,4,7,8-H), 2.43-2.58 (m; 3H, 5,6,9-H), 2.60-2.61 (d; J = 2.5 Hz, 1H, 12-H), 2.93 (s; 1H, 14-H), 3.06-3.12 (d; J = 13 Hz, 1H, 10'-H), 3.21-3.32 (ddd; J = 6.5 Hz, J = 1.5 Hz, 1H, 10''-H), 3.71-3.77 (mc; 1H, 2-H).

10,10-Dimethyl-1,8-diazapentacyclo[6.3.0.$0^{2,6}$.$0^{4,11}$.$0^{5,9}$]undecane (6): 289 mg (1.09 mmol) 6-HI; 121 mg [42%] 6 as colourless crystals, m.p. 40-41°C. IR ($CDCl_3$): ν = 2980 cm^{-1}, 2960, 2940 (C-H), 1460, 1450, 1390, 1370 ($C(CH_3)_2$), 1300, 1240, 1200. - ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 1.06 and 1.36 (two s; 6H, $-CH_3$), 1.53-1.56 (d; J = 11 Hz, 1H, 3'-H), 1.69-1.70 (dd; J = 2 Hz, 1 H, 3''-H), 2.19-2.22 (m; 1H, 5-H), 2.59-2.63 (m; 2H, 4,6-H), 2.69-2.70 (d; J = 6 Hz, 1H, 7'-H), 2.71 (s; 1H, 9-H), 2.81-2.83 (d; 1H, 7''H), 2.84 (s; 1H, 11-H), 3.29 (s; 1H, 2-H). - ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.59 and 22.13 (two q; $-CH_3$), 29.83 (t, C-3), 43.45 (s; C-10), 41.51, 44.88 and 50.96 (three d; C-4,5,6), 54.44 (t; C-7), 68.26, 77.30 and 80.03 (three d; C-2,9,11). - MS: m/z (%) = 176 (35, M^+), 161 (65, M^+-CH_3). Anal. Calcd. for $C_{11}H_{16}N_2$ (176.3): C, 74.96; H, 9.15; N, 15.89. Found: C, 75.31; H, 9.40; N, 16.20.

9,10,10-Trimethyl-1,8-diazapentacyclo[6.3.0.$0^{2,6}$.$0^{4,11}$.$0^{5,9}$]undecane (11): 504 mg (1.58 mmol) 11-HI; 300 mg [10%] 11 as yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.95, 0.96 and 1.18 (three s; 3H, $-CH_3$), 1.55-1.62 (d; J = 11 Hz, 1H, 3'-H), 1.69-1.76 (dd; J = 2 Hz, 1H, 3''-H), 1.89-1.94 (m; J = 6 Hz, 1H, 4-H), 1.94 (s; 1H, 6-H), 2.56-2.59 (d; 1H, 5-H), 2.68-2.71 (dm; J = 6 Hz, 1H, 7'-H), 2.77-2.81 (d; 1H, 7''-H), 2.91 (s; 1H, 11-H), 3.45 (s; 1H, 2-H). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 12.73 (q; 9-CH_3), 19.81 and 21.53 (two q; 10-CH_3), 30.31 (t; C-3), 43.96, 46.22 and 50.28 (three d; C-4,5,6), 45.26 (s; C-10), 52.04 (t; C-7), 67.86 and 76.40 (two d; C-2,11), 80.40 (s; C-9).

1,10,10 Trimethyl-1,8-diazapentacyclo[6.3.0.$0^{2,6}$.$0^{4,11}$.$0^{5,9}$]undecanium iodide: 100 mg (0.567 mmol) 6, 0.40 mL $CDCl_3$, excess of MeI, 30 min: 171 mg [95%] of yellow crystals, decomposition after 80°C. IR ($CDCl_3$): ν = 3000-2800 cm^{-1} (C-H), 1455, 1440, 1395, 1370 ($C(CH_3)_2$), 1310, 1280, 1260, 1250, 1240, 1150, 1030. - ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 and 1.48 (two s; 6H, $-CH_3$), 2.04-2.08 (dd; J = 3 Hz, 1H, 3'-H), 2.55-2.58 (d; J = 12 Hz, 1H, 3''-H), 2.88-2.91 (m; 1H, 5-H), 3.01-3.04 (m; 2H, 7',6-H), 3.25-3.28 (m; 2H, 4,9-H), 3.44 (s; 3H, N^+-CH_3), 3.70-3.73 (d; J = 12 Hz, 1H, 7''-H), 4.13 and 4.58 (two s, 2H, 2,11-H). - ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.43 and 21.71 (two q; CH_3), 28.83 (t; C-3), 43.82 (s; C-10), 49.88 (q; N^+-CH_3), 40.85, 44.94 and 51.07 (three d; C-4,5,6), 54.98 (t; C-7), 79.83, 85.34 and 90.58 (three d; C-2,9,11). Anal. Calcd. for $C_{12}H_{19}IN_2$ (318.2): C, 45.30; H, 6.02; N, 8.80. Found: C, 45.39; H, 6.20; N, 8.67.

ACKNOWLEDGEMENTS
Financial support by Fonds der Chemischen Industrie and BASF AG, Ludwigshafen/Rhein, is gratefully acknowledged.

LITERATURE

1 Paper VIII in the series Azo Bridges from Azines.

2 Taken partly from the K.Beck, Ph.D. Thesis, Würzburg (1986).

3 Taken partly from the P. Reinold, Diploma Thesis, Würzburg (1986) and from unpublished results.

4 a) K. Beck, S. Hünig, Angew. Chem. 98 (1986) 193; Angew. Chem. Int. Ed. Engl. 25 (1986) 187; b) K. Beck, A. Böhm, S. Hünig, F. Prokschy, Chem. Ber. 117 (1984) 517; c) S. Hünig, F. Prokschy, Chem. Ber. 117 (1984) 534; d) W. Berning, S. Hünig, F. Prokschy, Chem. Ber. 117 (1984) 1455; e) B. Albert, W. Berning, Ch. Burschka, S. Hünig, F. Prokschy, Chem. Ber. 117 (1984) 1465; f) F. Prokschy, S. Hünig, Chem. Ber. 117 (1984) 2099; g) K. Beck, S. Hünig, Chem. Ber. 120 (1987) 477; h) K. Beck, F.-G. Klärner, P. Kraft, S. Hünig, U. Artschwager-Perl, Chem. Ber. 1987, issue 12.

5 K. Beck, S. Hünig, G. Kleefeld, H.-D. Martin, K. Peters, F. Prokschy, H.G. von Schnering, Chem. Ber. 119 (1986) 543.

6 The first example was definitely established by R.B. Woodward and T.J. Katz (Tetrahedron Lett. 1959, 5; Tetrahedron 5 (1959) 70) on the cycloreversion of dicyclopentadiene. To the best of our knowledge a generalized view of their results has not been published.

7 K. Beck, S. Hünig, Angew. Chem. 99 (1987) 694; Angew. Chem. Int. Ed. Engl. 26 (1987) 670.

8 K. Beck, H. Burghard, G. Fischer, S. Hünig, P. Reinold, Angew. Chem. 99 (1987) 695; Angew. Chem. Int. Ed. Engl. 26 (1987) 672.

9 Protonation of one nitrogen atom is expected to catalyse [4+2] cycloaddition and [3,3] rearrangement. Cf. R.P. Lutz, Chem. Rev. 84 (1984) 205,; H. Heimgartner, H.-J. Hansen, H. Schmidt in H. Böhme, H. Viehe (Edit.): Iminium Salts in Organic Chemistry, Part II, Wiley, New York 1979, 655.

10 a) J.P. Snyder, M.L. Heymann, M. Gudestrup, J. Chem. Soc., Perkin Trans. I, 1977, 1561; b) S.F. Nelsen, R.T. Landis, J. Am. Chem. Soc. 96 (1974) 1788.

11 S.F. Nelsen, S.C. Blackstock, T.B. Frigo, J. Am. Chem. Soc. 106 (1984) 3366.