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Azobridges from Azines, XVII[1]. Intra- and Intermolecular [3+2] Cycloaddition between Nonstabilized Azomethineimines and Alkenes

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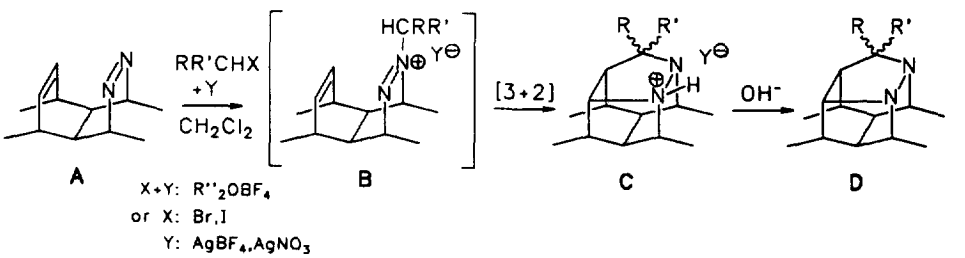
Dedicated to Emeritus Professor Hans Suschitzky on the occasion of his 80th birthday

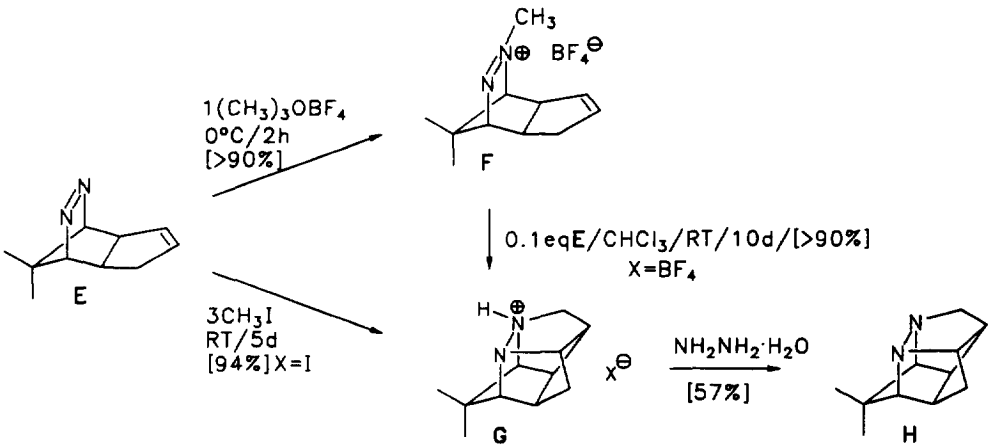
Abstract: Azo compounds **1** and **3** containing a CC-double bond in a parallel but distant position are quaternized by Me_3OBF_4 to **1,MeBF$_4$** and **3,MeBF$_4$**, whereas MeI produces the cage compounds **2,HX** and **4,HX**. These [3+2] cycloadducts also are quantitatively formed from **1,MeBF$_4$** and **3,MeBF$_4$** with catalytic amounts of azo compounds. Intermolecular [3+2] cycloadditions occur with a mixture of DBH (**5**) or DBO (**8**), MeI and a variety of alkenes (→ HI) salts of (**6**, **7**, **9** - **12**). The intermediate azomethineimines, if stabilized by a fluorenylidene group, can be isolated (**20**, **22**, **24**), but not, however, in the presence of a close parallel CC-bond (**25** → **26**).

Background and Targets

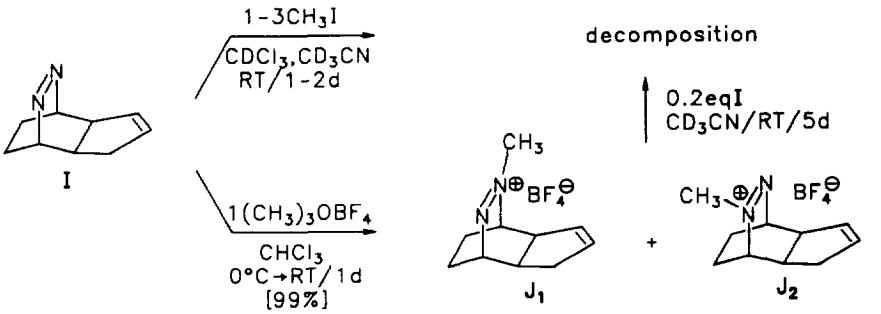
Aza alkanes are quaternized by trialkyl oxonium salts, by alkyl halides together with silver salts or by certain stable radical cations.[3-6] If, however, the azo group is flanked by an olefinic bridge in a close parallel position (**A**), the expected quaternary salt **B** cannot be isolated or even detected by NMR. Instead protonated cage compounds **C** are found.[3] This reaction has been described as an [3+2] 1,3-dipolar cycloaddition between a (protonated) azo methine formed from **B** and the CC-double bond (vide infra).[3]



A somewhat different behaviour is found if the azo group and the CC-double bond are arranged as in **E**. Here the quaternary salt **F** can easily be isolated on alkylation with trimethyloxonium tetrafluoroborate, whereas the [3+2] cycloadduct **G** is quantitatively formed if methyl iodide is employed as alkylating agent. Besides, salt **F** is smoothly converted into the protonated cage **G** on addition of some **E**.[7]



Interestingly, on switching from **E** [diazabicycloheptene (DBH) moiety] to **I** [diazabicyclooctane (DBO) moiety] still another reaction pattern on alkylation is observed. Again, Me_3OBF_4 yields the expected quaternary salts J_1 and J_2 quantitatively, but the olefinic bond acts no longer as a dipolarophile: Both alkylation of **I** with methyl iodide and reaction of $J_1 + J_2$ with some azo compound **I** yield only various decomposition products.



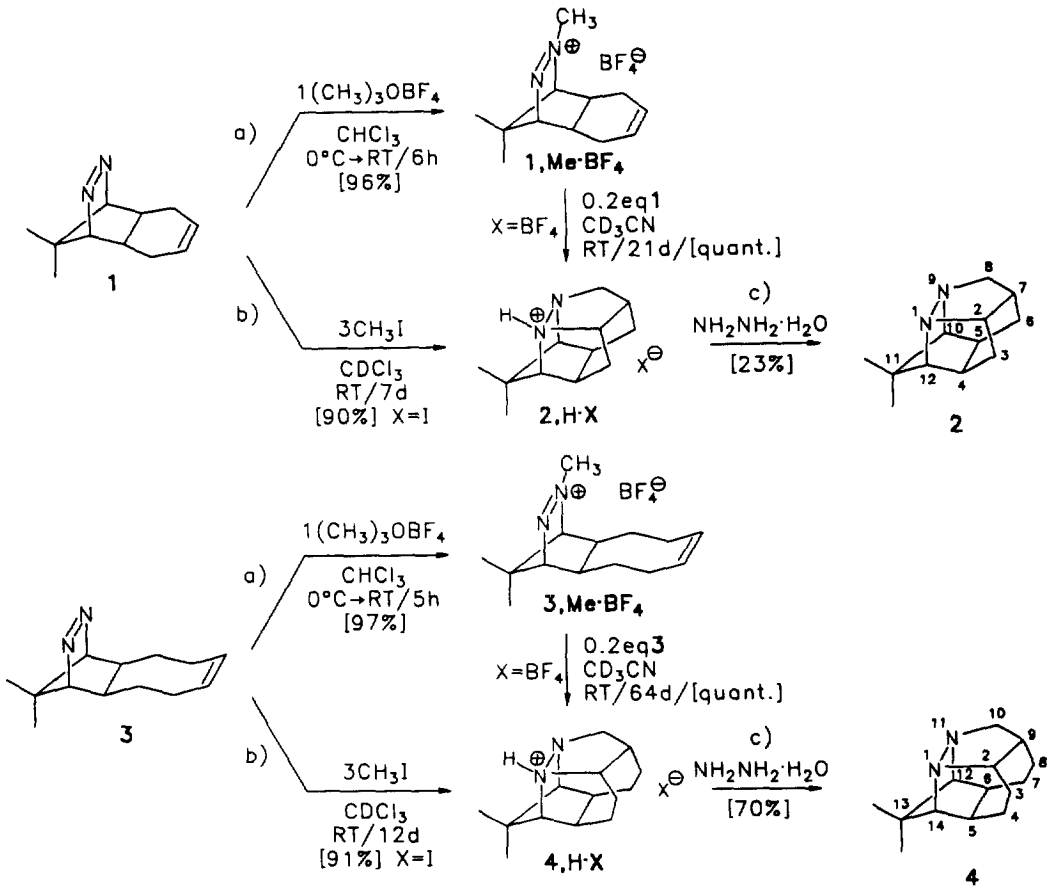
Based on these somewhat puzzling results we set out to answer the following questions:

1. Are the intramolecular [3+2] cycloadditions **B** → **C**, **E** → **F**, and **F** → **G** bound to a specific neighbouring group effect which is absent in **J** or do these cycloadditions only depend on a favourable geometry of the two partners in the transition state?
2. If the latter assumption is correct, not only should larger cages be accessible but also intermolecular [3+2] cycloaddition with these intermediate non stabilized azomethineimines. Moreover, such a synthesis of pyrazolidines might even be performed by mixing an azo compound, an olefin, and a methyl iodide.
3. Finally, it should be possible to tune the reactivity of the 1,3-dipole, the intermediate azomethineimine (eventually protonated).[5] By alkyl and aryl substituents their stabilization might be enhanced strongly enough to prevent a consecutive intramolecular [3+2] cycloaddition.

Results and Discussion

We took the pattern for more intramolecular [3+2] cycloadditions from **E** with its DBH moiety and extended the olefinic ring as in **1**[8] and **3**.[8] Both compounds show the same reactivity: On route **a** the quaternary salts **1,MeBF4** and **3,MeBF4** are formed quantitatively, whereas on route **b** only the protonated cage

compounds **2,HX** and **4,HX** are obtained. Besides, the transformation **1,MeBF$_4$** → **2,HX** and **3,MeBF$_4$** → **4,HX** in the presence of the corresponding azo compound again proceeds in quantitative yield.



Isolation of the highly sensitive bases, pyrazolidines **2** and **5**, meets with some difficulties. Hydrazine hydrate turns out to be the most reliable reagent.[7] In contrast to types **A**[5] and **E**[7] the n-π^* transition of the azo group in **1** and **3** is typical for a DBH unit[7] and excludes a specific neighbouring group effect. However, **1** and **3** are flexible enough to allow a conformation with overlapping orbitals prerequisite for a [$\pi^4_s + \pi^2_s$] 1,3-dipolar cycloaddition.

The structure of **4,HI** has been corroborated by an X-ray analysis, given in Fig. 1.

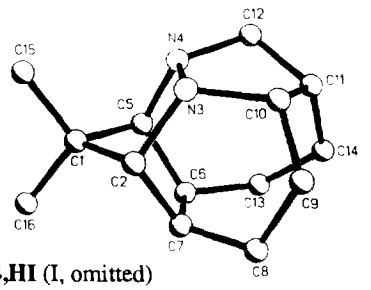
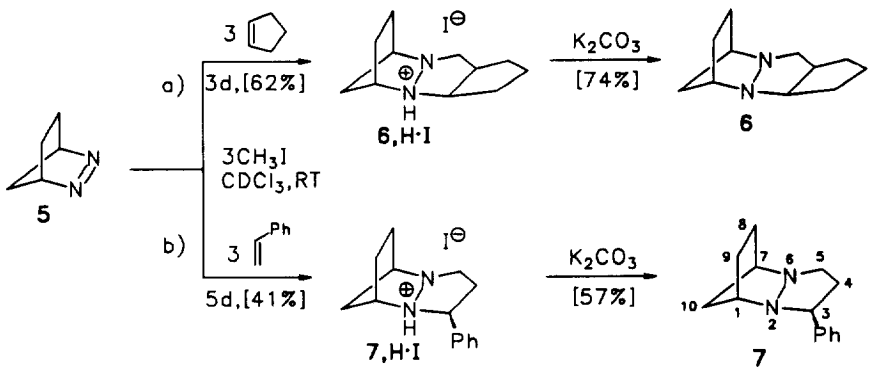


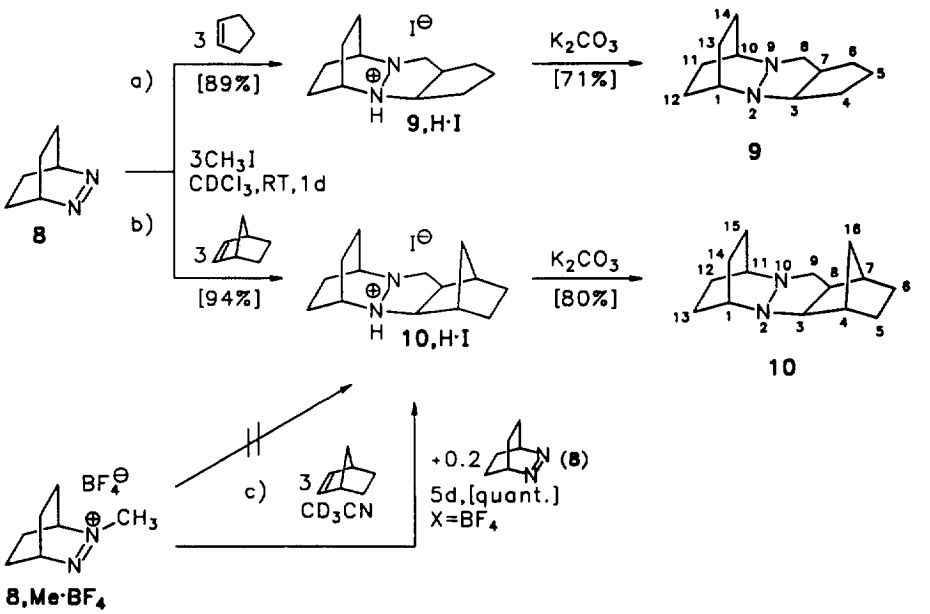
Fig. 1. Stereographic projection of **4,HI** (I, omitted)

Intermolecular [3+2] Reactions

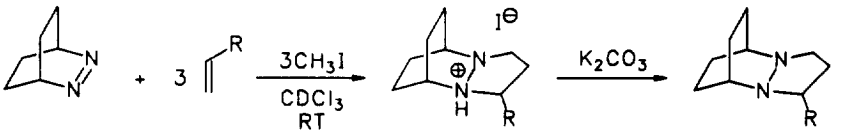
We were inspired by these encouraging results to probe an intermolecular version of these [3+2] cycloadditions by means of a three component reaction. Taking the pattern from **1** and **3** containing a DBH moiety, DBH itself was reacted with methyl iodide and cyclopentene or styrene. In both cases a rather smooth reaction took place, yielding the expected pyrazolidine salts **6,HI** and **7,HI**, respectively, from which the bases **6** and **7** could be isolated with less difficulty than with example **H**.



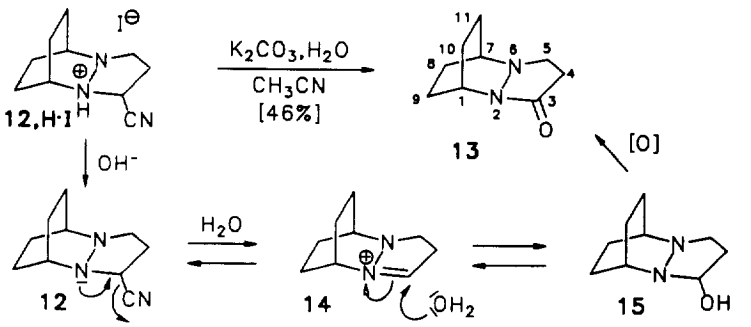
DBO (**8**) constitutes an even more suitable starting material for these three components reaction with methyl iodide and an olefin. With cyclopentene and norbornene the [3+2] cycloadducts **9,HI** and **10,HI** are formed in high yields within one day at room temperature. By sharp contrast, a mixture of **8,MeBF$_4$** and norbornene in acetonitrile remains unchanged even after 30 days at ambient temperature. Some added DBO, however, triggers a quantitative [3+2] cycloaddition to **10,HBF$_4$**.



Azomethineimines have been calculated to react by their low lying LUMOs and therefore prefer electron rich olefines such as, e.g., cyclopentene and norbornene as dipolarophiles.[9] Consequently, alkenes with HOMOs of lower energies such as styrene and acrylonitrile are expected to require longer reaction times. Indeed, cycloadducts **11,HI** and **12**,HI are isolated after 3 and 7 days, respectively, in definite lower yields than **9,HI** and **10,HI** after one day under the same conditions.



By potassium carbonate **11,HI** is smoothly transformed into pyrazoline **11**. The same procedure, however, yields pyrazolinone **13** if **12,HI** is employed. Obviously, α-cyanopyrazoline **12** equilibrates with its iminium ion **14**, a well documented reaction for α-amino nitriles.[10] Hydration of iminium ion **14** will lead to hemiaminal **15** which on autoxidation finally should yield **13**.



Mechanistic Considerations

Regio- and Stereochemistry of the Cycloaddition

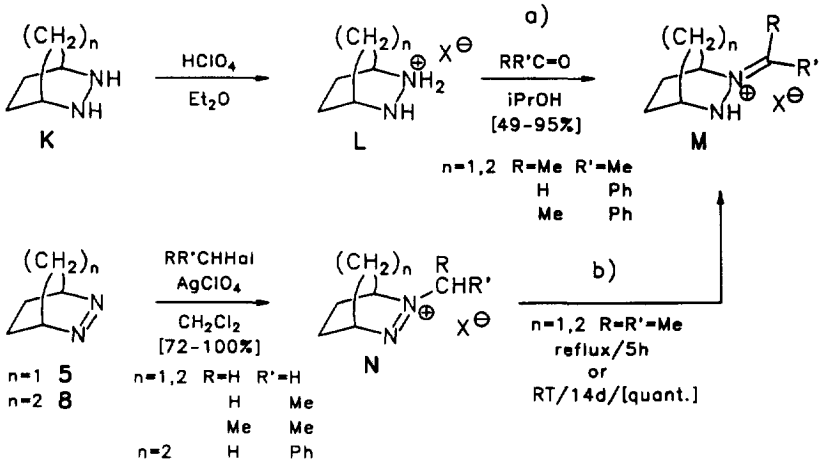
In the ^{1}H- and ^{13}C-NMR spectra of both **11,HI** and **12,HI** the possible regioisomers with R = Ph,CN in the 4-position of the pyrazolidine ring cannot be detected. The observed regioselectivity of this [3+2] cycloaddition is also predicted by MO theory. Their regioselectivity is given by the coefficients of the atomic orbitals of the dominant $LUMO_{diene}$-$HOMO_{ene}$ pair (large + large, small + small).[11] The larger coefficients are found at the C-atom (LUMO) of the azomethineimine and the less substituted olefinic C-atoms (HOMO) of styrene and acrylonitrile.

Pyrazoline **7** allows even more detailed insight into the course of the cycloaddition. With respect to the half chair of the pyrazolidine ring in **7** only one configurational isomer is found carrying the phenyl group in an equatorial position. This conclusion can be drawn from the vicinal coupling constants of proton 3-H (δ = 3.64 ppm) of 11.5 Hz ($J_{3,4ax}$) and 5.5 Hz ($J_{3,4eq}$). All other coupling constants of the pyrazoline protons are in accordance with this correlation (see experimental section). Equilibration at room temperature with $J_{3,4}$ ca. 7-8 Hz[12] can be excluded. Very probably this thermodynamically stable isomer is formed directly in the course of the 1,3-dipolar cycloaddition, which, thus, has to occur from an exo/exo arrangement of both partners.

The Role of the Counterion

Alkylations with trialkyloxonium tetrafluoroborate are fast and virtually irreversible (hard anion, weak nucleophile), whereas alkylations with alkyl iodides proceed much more slowly and are principally reversible (soft anion, strong nucleophile, weak base).[13]

The quantitative formation of the N-methyl azo cations, **F**, **J**, **1**, **3**, and **8** by alkylation with $[Me_3O]BF_4$ must be due to a very rapid reaction with the azo bridge and the absence of traces of base (in fact, the alkylating agent may contain traces of $Me_2O{\bullet}HBF_4$). Rearrangement of these salts to the corresponding hydrazonium salts obviously is base catalyzed as already demonstrated by Snyder[3] with examples **N** → **M**. The quaternary salts **N** obtained from DBH (**5**) and DBO (**8**) slowly rearrange to **M**. This reaction is catalyzed by traces of water and by the counterion in the sequence $Cl^- >> Br^- > I^- >> ClO_4^-$.[3] The hydrazonium salts **M** (protonated azomethineimines) are identical with those prepared from hydrazines **K** in the presence of strong acids (**L**) with the corresponding aldehydes and ketones.



This way, the catalytic action of non-alkylated azo compounds (weak bases) on the rearrangement of the quaternized azo compounds to hydrazonium salts and their consecutive [3+2] cycloadditions can easily be interpreted (**F** → **G**; **1,MeBF$_4$** → **2,HX**; **3,MeBF$_4$** → **4,HX**; **8,MeBF$_4$** → **10,HI**).

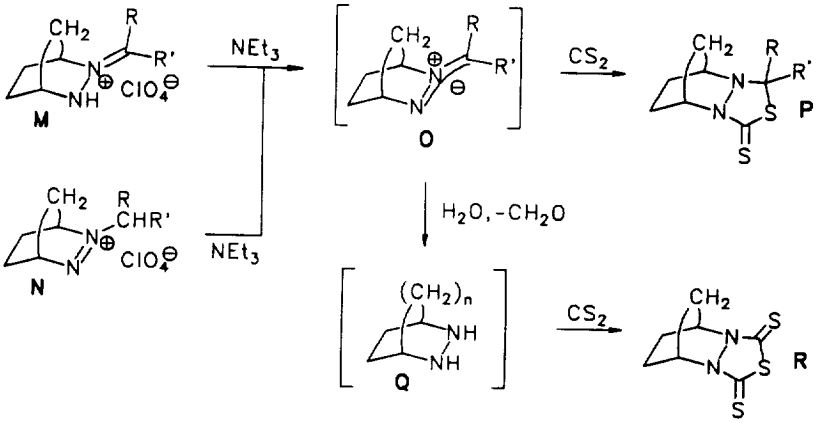
During these reactions methyl transfer from the quaternized azo bridge to the added azo compound does not occur. As probed by an NMR experiment, **3,MeBF$_4$** rearranges quantitatively to the corresponding cage compound **4,HBF$_4$** in the presence of 1 equiv. of **E** within six days at room temperature in CD_3CN. None of the quaternary salt **F** or the cage compound **G** is observed.

The catalytic action of the halide ions may be different. Formation of some azo compound by dealkylation of the quaternary azo cation. Indeed, reaction of **8,MeBF$_4$** with norbornene in the presence of tetrabutyl ammonium iodide in CD_3CN not only yields the expected cycloadduct **10,HX** (85%), but also 12% of **8** (DBO) after ten days. These results can be interpreted by slow methyl transfer from **8,MeBF$_4$** to the iodide ion and isomerization of **8,MeBF$_4$** catalyzed by azo compound **8** to the corresponding hydrazonium ion (cf. **N**→ **M**).

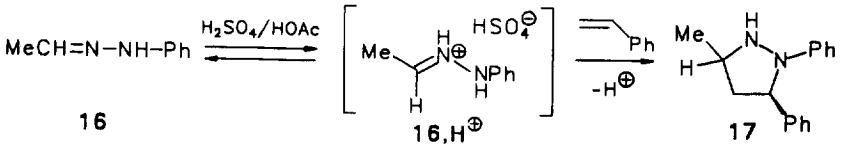
[3⁺+2] or [3+2] Cycloaddition?

From the forementioned results as well as from earlier reports[5] we cannot decide if the hydrazonium ions ['3⁺] or the corresponding azomethineimines ['3'] enter into the cycloaddition. Snyder has shown in his pioneering work[3] that azomethine-imines **O**, developed from either **M** or **N** by triethylamine can be trapped with carbondisulfide, probably in a [3+2] reaction as cycloadducts **P**. The rather low yields of **P** are explained by extreme sensitivity of **O** to moisture. Water is supposed to hydrolyze **P** to hydrazines **Q** since the heterocycles **R** were isolated as the other main products of the reaction. However, it has been demonstrated that in carbon disulfide the thiono group constitutes a much weaker dipolarophile than in its [3+2] cycloadducts. Therefore, e.g. with azomethineimines only in special cases high yields of 1:1 adducts are found,[14a] whereas with a series of other 1,3-dipoles bis-adducts or other consecutive products are observed.[14b-e]

Reaction of **O** with alkenes has not been reported so far. We have already demonstrated, however, that system **A** on reaction with dihalocarbenes yield cage compounds **D** directly, a reaction which is supposed to proceed via a [3+2] cycloaddition.[15]



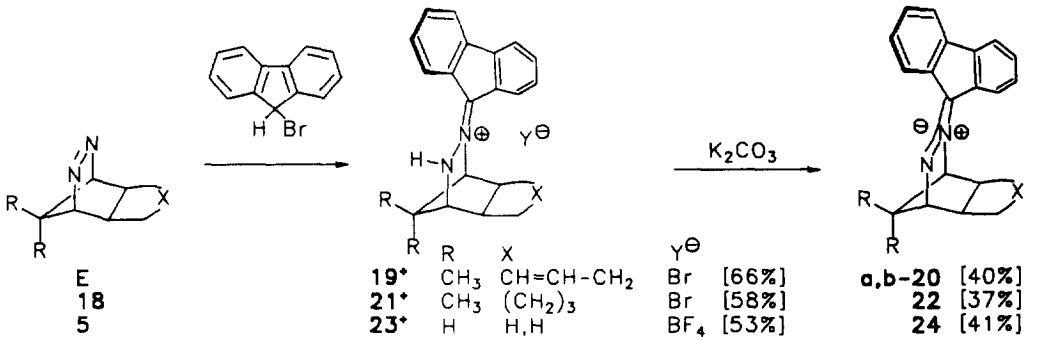
On the other hand, as exemplified by the conversion **16**,H^+ → **17** a variety of [3⁺+2] cycloadditions have been demonstrated to proceed rather smoothly.[16]



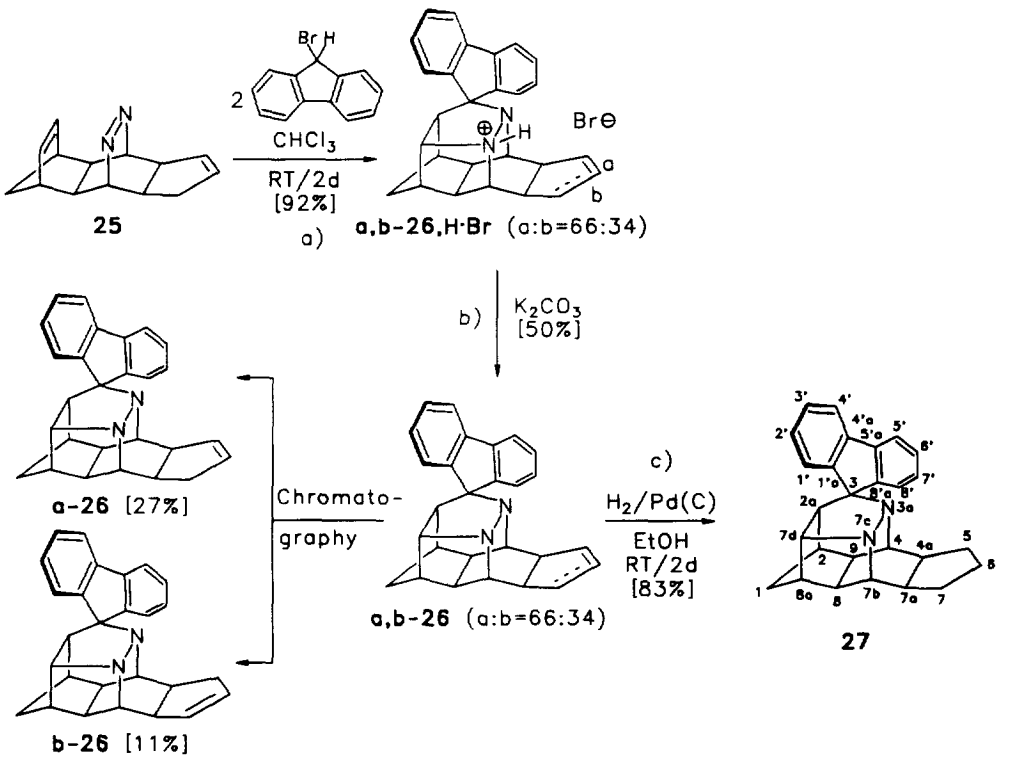
As already mentioned by Snyder, both the persistence of hydrazonium ions **M** and azomethineimines **N** is increased by alkyl and especially phenyl substituents.[3,17]

We assumed that the thermodynamic stability and persistence of the isolated[3] hydrazonium salts **M** and azomethineimine **O** (n = 1, R,R' = Ph) should be enhanced by introducing the planar fluorenyl group instead of

the phenyl substituents. Indeed, 9-bromofluorene reacts with the azo bridge of **E** much faster than isopropyl iodide (6 days) and the reaction stops cleanly at the hydrazonium salt **19**$^+$ without any sign of cycloaddition. On addition of potassium carbonate, the intense yellow azomethineimine **20** is isolated as a stable compound. The similar products **22** and **24** are obtained correspondingly starting from **18** and **5**, respectively.



The strong stabilization of the hydrazonium ions by the fluorenylidene group is still not efficient enough to



prevent cycloaddition with a CC-double bond in the optimal close and parallel position of type **A** as exemplified with **25**. Monitoring the reaction with 9-bromofluorene by ^{1}H-NMR reveals only the cage product **a,b-26,HBr** without signals for any intermediate. The two isomers of **26** are caused by the differing positions of the residual CC-double bond as shown by hydrogenation to a single product (**27**) and separation into **a-26** and **b-26**.

Conclusion

The already described intramolecular [3$^+$+2] and/or [3+2] cycloaddition between an olefinic bond and an azo group on alkylation does not depend on a neighbouring group effect. As demonstrated with examples **1** and **3**, hard alkylation agents (Me_3OBF_4) produce methyl diazenium salts (**1,MeBF$_4$**, **3,MeBF$_4$**), whereas soft alkylating agents (MeI) yield cage compounds (**2,HX**; **4,HX**). The latter can also be obtained from the methyl diazenium salts via catalysis by azo compounds (e.g. **1**, **3**). Besides, these cycloadditions can easily be performed in an intermolecular version between azo compound, alkene, and methyl iodide (e.g. **5** → **6, HI**; **8** → **11,HI**). Intermediate hydrazonium salts (type **N**) and azomethineimines (type **O**) can be isolated as stable compounds if stabilized by a fluorenylidene group (e.g. **19**$^+$ and **20**).

Acknowledgement

Financial support by *Fonds der Chemischen Industrie*, Frankfurt/Main, is greatly acknowledged.

Experimental Section

Melting points were detemined using a Kofler instrument and are corrected. IR: Perkin-Elmer 1420, UV: Perkin-Elmer 330, ^{1}H- and ^{13}C-NMR: Bruker WM 200 200 MHz (^{1}H)/50 MHz (^{13}C) or Bruker WM 400 400 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.

X-Ray analysis of ***4,HI***

Crystallographic Section		**Data Collection**	
empirical formula	$C_{14}H_{23}N_2I$	diffractometer	Huber
molecular mass	346.26	radiation	Mo $K\alpha$
a [pm]	2423.9(8)	monochromator	graphite
b [pm]	1013.1(4)	crystal size [mm]	0.4 x 0.5 x 0.3
c [pm]	1364.5(5)	data collection mode	Ø/Ø-scan
β [deg]	125.03(1)	theta range [deg]	1.75 → 25.0
V [pm^3]	2743.8•10^6	recip. latt. segment	h = 0 → 28
Z	8		k = 0 → 11
d(calcd) [g•cm^{-3}]	1.676		l = -16 → 13
crystal system	monoclinic	no. refl. measd.	2708
space group	C2/c	no. unique refl.	2440
		no. refl. $F > 3\,\sigma(F)$	2240
		lin. abs. coeff. [mm^{-1}]	2.29

Further crystallographic data have been deposited with Cambridge Crystallographic Data Centre.

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 into 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.

(1α,4α,4aα,8aα)-1,4,4a,5,8,8a-Hexahydro-2,9,9-trimethyl-1,4-methanophthalazinium tetrafluoroborate (**1,MeBF$_4$**). **1**[8] (80.0 mg, 0.454 mmol) in $CHCl_3$ (10 ml), $(CH_3)_3OBF_4$ 67.1 mg, 0.454 mmol, 6 h. **1,MeBF$_4$** (121 mg, 96%), colourless viscous oil; UV (CH_3CN) λ_{max} (log ε) 297 nm (2.38); IR ν 3040 (=C-H), 2970, 2940, 2890, 2850 (C-H), 1640 (C=C), 1465, 1450, 1385, 1285, 1265, 1225, 1200-950 (BF_4^-), 890, 845, 755, 690; ^{1}H NMR (CD_3CN, 200.1 MHz,) δ 0.81 (s, 1H,)$_{en}$-CH_3), 1.21 (s, 3H, 9_{ex}-CH_3), 2.06-2.41 (m, 4H, 5-8H), 3.30-3.59 (m, 2H, 4a-,8a-H), 4.47 (s, 3H, N(2)-CH_3), 5.10 (s, 1H, 1-H), 5.56-5.64 (m, 2H, 4-,6#-H), 74 (m, 1H, 7#-H), #exchangeable; ^{13}C NMR (CD_3CN, 50.3 MHz) δ 18.09 and 19.33 (2q, 9-CH_3), 22.62 and 22.89 (2t, C-5,-8), 36.25 (d, C-8a), 38.74 (d, C-4a), 53.50 (q, N(2)-CH_3), 63.90 (s, C-9), 94.29 (d, C-4), 95.22 (d, C-1), 124.6 and 128.8 (2d, C-6,-7); MS m/z (assignment, %) 190 (25, M^+-H), 175 (100, M^+-H-CH_3), 109 (35), 94 (55), 79 (87, $C_6H_7^+$), 55 (30), 49 (50), 41 (57); 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.

11,11-Dimethyl-1-azonia-9-azapentacyclo[7.3.0.0^{2,7}.0^{5,10}]dodecane iodide (2,HI).a) Compound **1**[8] (227 mg, 1.29 mmol), $CDCl_3$ (1.5 ml) MeI (548 mg, 3.86 mmol). After 7 d at r.t. **1** is consumed (^{1}H-NMR monitoring). Treatment at 0.01 Torr (60 °C) for 1 h left **2,HI**, yellow crystals (368 mg, 90%), m.p. 200-203 °C. b) In the ^{1}H-NMR spectra of **1,MeBF$_4$** (21.0 mg, 0.076 mmol) and **1** (2.75 mg, 0.015 mmol) in CD_3CN (0.50 ml) the signals for **1,MeBF$_4$** are replaced by those for **2,H$^+$** after 21 d at r.t. IR ν 2930, 2870 (C-H), 2700, 2620, 2530 (N^+-H), 1465 (C-H), def.), 1395, 1375 [C-H, def. symm., >$C(CH_3)_2$], 1355, 1325, 1300, 1275, 1220, 1180, 1150, 1095, 1070, 1050, 925, 905, 870, 860, 830, 770, 740; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.20 and 1.44 (2s,2x3H, 11-CH_3), 1.68 (d, $J_{6',6''}$=14.0 Hz, 1H, 6'-H), 1.92 (dd, $J_{3',3''}$=13.0 Hz, $J_{3',2}$=5.5 Hz, 1H, 3'-H), 2.08 (d, 1H, 3"-H), 2.73 (ps.br.d, 1H, 5-H), 2.84 (br.s, 1H, 7-H), 2.98 (br.d, $J_{4,5}$=9.0 Hz, 1H, 4-H), 3.07, br.s, 1H, 10-H), 3.35 (d, $J_{8',8''}$=12.5 Hz, 1H, 8'-H), 3.53 (dm, 1H, 8"-H), 3.77 (br.s, 1H, 12-H), 4.61 (ps.t, $J_{2,7}$=5.5 Hz, 1H, 2-H), 11.70 (very br.s, 1H, N(1)-H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.13 and 19.73 (2q, 11-CH_3), 23.46 and 24.53 (2t, C-3,-6), 34.57, 37.03, 39.48 (3d, C-4,-5,-7), 48.21 (s, C-11), 56.03 (t, C-8), 68.94 (d, C-2), 69.17 (d, C-10), 77.53 (d, C-12); MS m/z (assignment, %) 190 (28, M^+-H), 175 (100, M^+-H-CH_3), 128 (37), 127 (18), 93 (22), 83 (17), 55 (6), 41 (12); calcd. for $C_{12}H_{19}IN_2$ (318.29) C 45.30, H 6.02, N 8.80; found C 45.10, H 6.21, N 9.15.

Cage compound 2. Salt **2,HI** (220 mg, 0.691 mmol) is treated with hydrazine hydrate (100%, 5 drops) and filtered through silica gel. **2** (30.0 mg, 23%) is obtained as colourless solid (m.p.35 °C) after removal of the solvent and distillation (110 °C, 0.01 Torr, Kugelrohr). IR ($CDCl_3$) ν 2970, 2880 (C-H), 1450, 1420 (C-H, def.), 1370 [C-H), def. symm. >$C(CH_3)_2$], 1270, 1215, 1075, 995; ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ 1.10 and

1.36 (2s. 2x3H, 11-CH_3), 1.38 (br.d, J=12.0 Hz, 1H), 1.56-1.61 (m, 2H) and 1.81 (br.d, J=12.0 Hz, 1H, 3-,6-H), 2.25-2.37 (m, 2H,5-,7-H), 2,55-2.59 [br.s + br.d (partly obscured), 2H, 4-,12-H], 2.85 (br.s, 1H, 10-H), 2.92 (d, $J_{8',8''}$=12.0 Hz, 1H, 8'-H), 3.07 (dm, 1H, 8"-H), 3.69 (ps.t, $J_{2,3}$=5.8 Hz, 1H, 2-H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 20.09 and 20.33 (2q, 11-CH_3), 24.78 and 25.39 (2t, C-3,-6), 35.13, 37.21 and 40.17 (3d, C-4,-5,-7), 47.92 (s, C-11), 54.83 (t, C-8), 65.59 (d, C-2), 68.76 (d, C-10), 75.67 (d, C-12); MS m/z (assignment, %) 190 (M^+), 175 (100, M^+-CH_3), 111 (6), 93 (30), , 83 (23), 68 (7), 55 (7), 41 (16); calcd. for $C_{12}H_{18}N_2$ 190.1470; found 190.1466.

(1α,4α,4aα,10aα)-1,4,4a,5,6,9,10,10a-Octahydro-2,11,11-trimethyl-1,4-methanocycloocta[d]pyridazinium tetrafluoroborate (3,MeBF$_4$). Compound **3**[8] (100 mg, 0.489 mmol), $CHCl_3$ (10 ml), $(CH_3)_3OBF_4$ (72.3 mg, 0.489 mmol), 5 h ,colourless viscous oil (146 mg, 97%) **3,MeBF$_4$**. UV (CH_3CN) λ_{max} (log ε) 292 nm (246); IR ν 3020 (=C-H), 2940, 2880 (C-H), 1640, 1625 (C=C), 1465, 1450, 1430, 1400, 1385, 1285, 1255, 1240, 1205, 1200-900 (BFT_4^-); ^1H NMR (CD_3CN, 200.1 MHz) 0.82 (s, 3H, 11_{en}-CH_3), 1.18 (s, 3H, 11_{ex}-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, 4a-,10a-H), 4.51 (s, 3H, N(2)-CH_3), 5.17 (br.s, 1H, 1-H), 5.55 (br.s, 1H, 4-H), 5.75 (m, 2H, 7-,8-H); ^{13}C NMR (CD_3CN, 50.3 MHz) δ 18.50 and 19.35 (2q, 11-CH_3), 25.38, 25.68 and 27.50 (2) (3t, C-5,-6,-9-,-10), 42.88 (d, C-10a), 44.41 (d, C-4a), 53.85 (q, N(2)-CH_3), 63.30 (s, C-11), 95.00 (d, C-4), 96.47 (d, C-1), 132.11 and 132.45 (2d, C-7,-8); MS m/z (assignment, %) 218 (1, M^+-H), 203 (1, M^+-H-CH_3), 177 (1, M^+-CH_3-N_2+1), 109 (14, $C_8H_{13}^+$), 83 (100), 67 (22), 54 (17), 49 (69), 41 (24); 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.

13,13-Dimethyl-1-azonia-11-azapentacyclo[9.3.0.0^{2,9}.0^{5,14}.0^{6,12}]tetradecane iodide (4,HI). a) Procedure cf. **2,HI**. Compound **3**[8] (200 mg, 0.98 mmol), $CDCl_3$ (1.50 ml), MeI (417 mg, 294 mmol), 12 d, pale yellow crystals of **4,HI** (308 mg, 91%, m.p. 262-264 °C). b) Compound **3,MeBF$_4$**. **3** (25.0 mg, 0.122 mmol), 0.50 ml CD_3CN. After 64 d **3,Me$^+$** is completely converted into **4,H$^+$** (^1H NMR). IR ν 2950, 2930, 2900, 2880, 2860 (C-H), 2790, 2640, 2610 (N^+-H), 1475, 1460 (C-H, def.), 1405, 1390 (C-H, def. symm., >C(CH_3)$_2$), 1310, 1210, 1090, 1010, 965; ^1H NMR ($CDCl_3$, 400.1 MHz) δ 1.19 and 1.54 (2s, 2x3H, 13-CH_3), 1.78-2.13 (m, 8H, 3-,4-,7-,8-H), 2.63-2.68 (m, 1H, 6-H), 2.76 (ddd, $J_{5,6}$=12.5 Hz, $J_{5,4'}$=9.0 Hz, $J_{5,14}$=2.0 Hz, 1H, 5-H), 2.84 (ps.q, $J_{9,2}$=6.0 Hz, 1H, 9-H), 2.95 (br.s, 1H, 12-H), 3.30-3.34 (d, 1H, $J_{10',10''}$=13.0 Hz, 1H, 1o'-H), 3.44-3.49 (dd, 1H, $J_{10'',9}$=6.0 Hz, 1H, 1o"-H), 3.59 (br.s, 1H, 14-H), 4.39 (m, 1H, 2-H), 11.29 (very br.s., 1H, N(1)-H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 15.43, 17.09, 20.77 and 23.98 (4t, C-3,-4-7,-8), 21.85 (2q, 13-CH_3), 29.65, 36.21 and 42.76 (3d, C-5,-6-9), 50.34 (s, C-13, 52.89 (t, C-10), 60.47 (d, C-2), 68.25 (d, C-12), 74.15 (d, C-14); MS m/z (assignment %) 218 (66, M^+-H), 203 (100, H^+-H-CH_3), 138 (11), 128 (41), 127 (21), 121 (10), 93 (22), 83 (32), 67 (19), 55 (16), 41 (19); 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.

Cage Compound 4: Procedure cf. **2**. Salt **4,HI** (400 mg, 1.16 mmol) $CHCl_3$ (2 ml), NH_2NH_2•H_2O (10 drops), colorless viscous oil of **4** (176 mg, 70%, 100 °C/0.01 Torr, Kugelrohr). IR ν 2920, 2870 (C-H), 1480, 1470, 1460, 1440 (C-H, def.), 1390, 1380 (C-H), def. symm., >C(CH_3)$_2$), 1365, 1320, 1255, 1205, 1190, 1180, 1120, 1090, 1075, 1060, 1040, 790, 735, 660; ^1H NMR ($CDCl_3$, 200.1 MHz) δ 1.09 and 1.46 (2s, 2x3H, 13-CH_3), 1.62-2.10 (m, 8H, 3-,34-,7-,8-H), 2.43-2.58 (m, 3H, 5-,6-,9-H), 2.60 (d, 1H, $J_{14,5}$=2.5 Hz, 14-H), 2.93 (br.s, 1H, 12-H), 3.09 (d, 1H, $J_{10',10''}$=13.0 Hz, 10'-H), 3.26 (ddd, 1H, $J_{10'',9}$=6.0 Hz, 10"-H), 3.74 (mc, 1H, 2-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 17.22 and 18.12 (2t, C-4,-7), 21.41 and 21.95 (2q, 13-CH_3), 22.95 and 25.45 (2t, C-3,-8), 32.19, 37.17 and 44.12 (3d, C-5,-6,-9), 49.52 (s, C-13), 51.75 (t, C-10), 58.70

(d, C-2), 65.92 (d, C-12), 73.52 (d, C-14); MS m/z (assignment %) 218 (61, M^+), 203 (100, M^+-CH_3), 175 (2), 162 (2), 138 (12), 121 (12), 93 (25), 83 (39, 79 (31), 67 (22), 55 (21), 41 (33); calcd. for $C_{14}H_{22}N_2$ (218.3) C 77.01, H 10.16, N 12.83; found C 76.63, H 10.42, N 13.19.

(1α,3α,7α,10α)-2,9-Diazatetracyclo[8.2.1.0^{2,9}.0^{3,7}]tridecane hydroiodide (6,HI). DBH (5) (150 mg, 1.56 mmol), cyclopentene (319 mg, 4.68 mmol), $CDCl_3$ (1 ml), MeI (664 mg, 4.58 mmol). The mixture slowly becomes dark brown. On evaporation after 3 d (^{1}H NMR monitoring) the remaining brown oil is dissolved in some CH_2Cl_2. This solution is slowly added to PE/EE (1:1, 30 ml), yellow brownish crystals of **6,HI** (296 mg, 62%, m.p. 145-147 °C). IR ν 2880 (C-H), 2790, 2680, 2620 (N^+-H), 1460, 1435, 1420 (CH_2, def.), 1350, 1310, 1280, 1250, 1175, 1145, 1125, 1050, 1000, 985, 970, 930, 890, 685; ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ 1.62-2.16 (m, 11H) and 2.65 (m, 1H, 4-,5-,6-,11-,13-H),2.91 (m, 1H, 7-H), 3.02 (dd, $J_{8A,8B}$=11.0 Hz, $J_{8A,7}$=7.0 Hz, 1H, 8_A-H), 3.54 (ps.t, $J_{3,7}$ and $J_{3,4A}$=5.2 Hz, 1H, 3-H), 3.72 (br.s, 1H, 10$^{\#}$-H), 4.13 [m (br.d + br.s), 2H, 1$^{\#}$-8_B-H], 10.50 (very br.s, 1H, N^+-H), $^{\#}$exchangeable; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 24.38, 25.03, 27.77, 29.33, 32.51 and 33.23 (5t, C-4,-5,-6,-11,-12,-13), 44.98 (d, C-7), 58.43 (t, C-8), 64.37 and 67.44 (2d, C-1,-10), 73.46 (d, C-3); MS m/z (assignment %) 178 (42, M^+-H), 163 (4, M^+-H-CH_2-1), 149 (59, M^+-H-C_2H_4-1), 137 (100, M^+-C_3H_6), 111 (54), 95 (10), 81 (32), 67 (40), 55 (34), 41 (49); calcd. for $C_{11}H_{19}IN_2$ (306.2) C 43.15, H 6.25, N 9.15; found C 42.91, H 6.20, N 9.34

Cycloadduct 6. Treatment of **6,HI** in CH_2Cl_2 with conc. aqueous K_2CO_3 yields **6** (73.0 mg, 74%, colorless viscous oil, b.p. 120 °C/0.01 Torr, Kugelrohr). IR δ 2960, 2860 (C-H), 1465, 1435 (CH_2, def.), 1340, 1300, 1275, 1240, 1210, 1170, 1120, 1100, 1055, 1030, 1010, 930, 895, 735; ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ 1.05 (d, $J_{13A,13B}$=10.0 Hz, 1H, 13_A-H), 1.37-1.90 (m, 11H, 4-,5-,6-,11-,12-,13_B-H), 2.53 (m, 1H, 7-H), 2.67 (dd, $J_{8A,8B}$=10.0 Hz, $J_{8A,7}$=7.8 HZ, 1H, 8_A-H), 3.01-3.08 (m, 3H, 3-,8_B-,10$^{\#}$-H), 3.18 (br.s, 1H, 1$^{\#}$-H), $^{\#}$exchangeable; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 24.66, 29.18, 29.27, 30.28, 31.08 and 33.94 (6t, C-4,-5,-6,-11,-12,-13) 46.01 (d, C-7), 60.26 (t, C-8), 64.04 and 64.50 (2d, C-1,-10), 71.98 (d, C-3); MS m/z (assignment, %) 178 (47, M^+), 163 (5, M^+-CH_2-1), 149 (57, M^+-C_2H_4-1), 137 (100, M^+-C_3H_6+1), 111 (55), 95 (9), 81 (27), 67 (32), 55 (25), 41 (35); calcd. for $C_{11}H_{18}N_2$ (178.3) C 74.11, H 10.18, N 15,71; found C 73.77, H 10.56, N 15.66.

(1α,3α,7α)-5-Phenyl-2,6-diazatricyclo[5.2.1.0^{2,6}]decane hydroiodide (7,HI). DBH (5) (100 mg, 1.04 mmol), styrene (325 mg, 3.12 mmol), $CDCl_3$ (0.5 ml), MeI (443 mg, 3.12 mmol). The mixture turns slowly to dark brown. On evaporation after 5 d (^{1}H-NMR monitoring) the remaining oil is dissolved in $CHCl_3$, filtered through a pad of silica gel and eluted with CH_3CN. After removal of the solvent a yellowish solid of **7,HI** (146 mg, 41 %, m.p. 187-189 °C) is isolated. (IR ν 3030 (=C-H), 2980, 2935, 2880 (C-H), 2790, 2680, 2620 (N^+-H), 1595 (C=C), 1485, 1450 (CH_2, def.), 1350, 1310, 1290, 1220, 1160, 1050, 1030, 1015, 830, 815, 750, 700 (=C-H, def.); ^{1}H NMR (CD_3CN, 250.1 MHz) δ 1.53 (m, 2H), 1.77 (m, 3H) and 2.27 (dm, J=11.0 Hz, 1H, 8-,9-,10-H), 2.00 (m, 1H, 4_{ax}-H), 2.47 (dt, $J_{4eq,4ax}$=12.0 Hz, 1H, 4_{eq}-H), 3.09 (ddd, $J_{5ax,4ax}$=13.0 Hz, $J_{5ax,4eq}$=5.5 Hz, 1H, 5_{ax}-H), 3.59 (br.s, 1H, 7$^{\#}$-H), 3.96 (dd, $J_{5eq,5ax}$=11.0 Hz, $J_{5eq,4ax}$=7.0 Hz, 1H, 5_{eq}-H), 4.17 (dd, $J_{3,4ax}$=11.3 Hz, $J_{3,4eq}$=5.5 Hz, 1H, $3_{(ax)}$-H), 4.26 (br.s, 1H, 1$^{\#}$-H), 7.26.-7.38 (m, 3H, 3'-,4'-,5'-H), 7.46 (br.d, $J_{2',3'}$ and $J_{6',5'}$=7.3 Hz, 2H, 2'-,6'-H), 11.15 (very br.s, 1H, N^+.H), $^{\#}$exchangeable; ^{13}C NMR (CD_3CN, 62.9 MHz) δ 25.41, 25.58 and 33.35 (3t, C-8,-9,-10), 35.85 (t, C-4), 53.73 (t, C-5), 62.75 and 67.39 (2d, C-1,-7), 68.73 (d, C-3), 128.37 (2) and 129 (3) (2d, C-2',-3',-4',-5',-6'), 139.63 (s, C-1'); MS m/z (assignment, %) 214 (43, M^+-H), 185 (15, M^+-2H-C_2H_4), 158 (20), 144 (46), 125 (14, M^+-CH_2-C_6H_5+1),

117 (26), 104 (16), 97 (25), 82 (65), 77 (32, $C_6H_5^+$), 71 (54), 69 (37), 57 (100), 41 (53); calcd. for $C_{14}H_{19}IN_2$ (342.2) C 49.14, H 5.60, N 8.19; found C 48.72, H 5.31, N 7.81.

Cycloadduct 7. On treatment with conc. aqueous K_2CO_3 **7,HI** (146 mg, 0.427 mmol) in CH_2Cl_2 yields **7** (52.0 mg, 57%), viscous colorless oil (b.p. 140 °C, 0.01 Torr, Kugelrohr). IR ν 3075, 3040 (=C-H), 2990, 2950, 2850 (C-H), 1600 (C=C), 1490, 1445 (CH_2, def.), 1360, 1300, 1280, 1215, 1155, 1060, 1025, 1005, 835, 810; ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ 1.25 (ps.t, J=6.8 Hz, 2H), 1.58 (m, 3H) and 1.87 (dm, J=10.8 Hz, 1H, 8-,9-,10-H), 2.11 (dddd, 1 H, 4_{ax}-H), 2.24 (dt, $J_{4eq,4ax}$=11.0 Hz, 1H, 4_{eq}-H), 2.63 (ddd, $J_{5ax,4ax}$=12.5 Hz, $J_{5ax,4eq}$=5.5 Hz, 1H, 5_{ax}-H), 3.30 (br.s, 1 H, 7#-H), 3.43 (br.s, 1H, 1#-H), 3.50 (dd, $J_{5eq,5ax}$=9.0 Hz, $J_{5eq,4ax}$=6.3 Hz, 1H, 5_{eq}.H), 3.64 (dd, $J_{3,4ax}$=11.5 Hz, $J_{3,4eq}$=5.5 Hz, 1H. $3_{(ax)}$-H, 7.24-7.36 (m, 3'-,4'-,5'-H), 7.47 (dd, $J_{2',3'}$ and $J_{6',5'}$=7.5 Hz, $J_{2',4'}$ and $J_{6',4'}$=1.8 Hz, 2'-,6'-H), #exchangeable; ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 28.49, 28.97 and 29.15 (3t, C-8,-9,-10), 36.34 (t, C-4), 53.35 (t, C-5), 61.23 and 63.67 (2d, C-1,-7), 68.05 (d, C-3), 127.36 (3) and 128.29 (2) (2d, C-2',-3',-4',-5',-6'), 141.29 (s, C-1'); MS m/z (assignment, %)214 (45, M^+), 185 (10, M^+-C_2H_4-1), 157 (12), 144 (61), 125 (11, M^+-CH_2-C_6H_5+2), 117 (35), 104 (24), 97 (32), 82 (70), 77 (29,$C_6H_5^+$), 71 (64), 69 (46), 57 (100), 41 (65); calcd. for $C_{14}H_{18}N_2$ (214.3) C 78.46, H 8.47, N 13.07; found C 77.92, H 8.63, N 13.23.

(3α,7α)-2,9-Diazatetracyclo[8.2.2.0^{3,7}]tetradecane hydroiodiodide (8,HI). DBO (**8**) (70.0 mg, 0.635 mmol), cyclopentene (130 mg, 1.91 mmol), $CDCl_3$ (0.50 ml), MeI (270 mg, 1.91 mmol) are reacted for 1 d (^{1}H NMR monitoring). After evaporation of the mixture the yellow residue is dissolved in some MeCN/$CHCl_3$ (2:1) and the mixture slowly added to PE/EE (1:1, 20 ml), colourless crystals of **9,HI** (181 mg, 89%, m.p. 194-195 °C). IR ν 2940, 2870, 2820 (C-H), 2740, 2720, 2660, 2620 (N^+-H), 1460, 1450, 1430 (CH_2, def.), 1390, 1370, 1350, 1335, 1320, 1300, 1155, 1130, 1110, 1090 1070, 1060, 1015, 965, 880, 860; ^{1}H NMR ($CDCl_3$, 2001. MHz) δ 1.48-2.19 (m, 13H) and 2.57 (m, 1H, 4-,5-,6-,11-,12-,13-,14-H), 2.96 (m, 1H, 7-H), 3.07 (br.s, 1H, 10#-H), 3.43 (br.s, 1H, 1#-H), 3.50 (dd, $J_{8A,8B}$=11.0 Hz, $J_{8A,7}$=7.0 Hz, 1H, 8_A-H), 3.65 (br.d, 1H, 8_B-H), 3.87 (m, 1H, 3-H), 10.71 (very br.s, 1H, N^+-H), #exchangeable; ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 16.96, 17.53, 22.18 and 24.19 (4t, C-11,-12,-13,-14), 25.18, 29.30 and 31.79 (3t, C-4,-5,-6), 43.08 (d, C-7), 49.19 and 52.76 (2d, C-1,-10), 54.80 (t, C-8), 68.23 (d, C-3); MS m/z (assignment, %) 192 (M^+-H), 163 (100, M^+-H-C_2H_4-1), 149 (13, M^+-H-C_3H_8-1), 138 (29), 123 (27), 108 (13), 97 (30), 81 (35), 68 (46), 54 (25), 41 (61); calcd. for $C_{12}H_{21}IN_2$ (320.2) C 45.01, H 6.61, N 8.75; found C 45.25, H 6.77, N 8.62.

Cycloadduct 9. Procedure cf. **7**. Salt **9,HI** (338 mg, 1.06 mmol) yields **9** (144 mg, 71%), colourless viscous oil (b.p. 120 °C/0.01 Torr, Kugelrohr). IR ν 2960, 2880 (C-H), 1475, 1450 (CH_2, def.), 1330, 1300, 1255, 1215, 1150, 1125, 1110, 1070, 1025, 930, 880, 860, 810, 780, 720; ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ 1.15-2.00 (m, 14H, 4-,5-,6-,11-,12-,13-,14-H), 2.50 (br.s, 1H, 10#-H), 2.61-2.76 (m, 3H, 1#-,7-,8_A-H), 3.10 (dd, 1H, $J_{8B,8A}$=11.5 Hz, $J_{8B,7}$=10.0 Hz, 1H 8_B-H), 3.55 (m, 1H, 3-H), # exchangeable; ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 18.89, 19.65, 24.22 and 26.62 (4t, C-11,-12,-13,-14), 27.27, 31.26 and 33.32 (3t, C-4,-5,-6), 44.59 (d, C-7), 49.54 and 51.21 (2d, C-1,-10), 56.79 (t, C-8), 66.25 (d, C-3); MS (m/z (assignment, %) 192 (65, M^+), 163 (100, M^+-C_2H_4-1), 149 (14, M^+-C_3H_8-1), 138 (30), 123 (27), 109 (16), 97 (30), 81 (37), 68 (47), 54 (30), 41 (71); calcd. for $C_{12}H_{20}N_2$ (192.3) C 74.95, H 10.48, N 14.57; found C 74.39, H 10.42, N 14.21.

(3α,4β,7β,8α)-2,10-Diazapentacyclo[9.2.2.1^{4,7}.0^{2,10}.0^{3,8}]hexadecane hydroiodide (10,HI). a) Procedure cf. **9,HI**. DBO (**8**) (72.0 mg, 0.653 mmol), norbornene (185 mg, 1.96 mmol), $CDCl_3$ (0.50 ml), MeI (278 mg, 1.96 mmol), 1 d. The slowly crystallizing oil is washed with PE/EE 1:1 to remove norbornene (TLC)

and dried, colourless crystals of **10,HI**, m.p. 230-231 °C (213 mg, 94 %). b) Salt **8,MeBF$_4$**[5] (100 mg, 0.472 mmol) in 0.50 ml CD_3CN and norbornene (133 mg, 1.42 mmol) does not react within 30 d (^{1}H NMR monitoring). After addition of **8** (10.4 mg, 0.0944 mmol) the NMR signals for **8,MeBF$_4$** are completely replaced by those for **10,HI** after 5 d. IR ν 2950, 2870, 2820 (C-H). 2780, 2750, 2660, 2620 (N^+-H), 1465, 1450, 1440 (CH_2, def.), 1395, 1370, 1345, 1340, 1300, 1130, 1110, 1085, 1045, 1005, 970, 880, 860, 750, 665; ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ 0.98-1.15 (m, 2H, 1.24 (dm, J=11.3 Hz, 1H), 1.50-1.65 (m, 5H), 1.68-1.86 (m, 3H), 1.94 (dm, J=11.3 Hz, 1H), 2.13 (m, 1H), 2.24 (br.s, 1H), 2.30 (m, 1H) and 2.80 (m, 1H, 4-,5-,6-,7-,12-,13-,14-,15-,16-H), 2.60 (m, 1H, 8-H), 3.21 (br.s, 1H, 11$^{\#}$-H), 3.42 (m, dd, $J_{9A,9B}$=12.5 Hz, $J_{9A,8}$=10.3 Hz, 1H, 9_A-H and br.d, $J_{3,8}$=8.0 Hz, 1H, 3-H), 3.55 (br.s, 1H, 1$^{\#}$-H), 3.80 (ddm, $J_{9B,8}$=4.0 Hz, 1H, 9_B-H), 11.20 (very br.s, 1H, N^+-H), $^{\#}$exchangeable; ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 17.55, 17.89, 21.86 and 24.13 (4t, C-12,-13,-14,-15), 25.14 and 27.23 (2t, C-5,-6), 33.39 (t, C-16), 40.87 and 42.05 (2d, C-4,-7), 47.17 (d, C-8), 51.25 and 54.60 (2d, C-1,-11), 56.14 (t, C-9), 71.95 (d, C-3); MS m/z (assignment, %) 218 (61, M^+-H), 189 (100, M^+-H-C_2H_4-1), 175 (8, M^+-H-C_3H_8-1), 164 (30), 149 (18), 137 (12), 123 (31), 95 (30), 81 (31), 69 (37), 54 (20), 41 (55); calcd. for $C_{14}H_{23}IN_2$ (346.3) C 48.56, H 6.70, N 8.09; found C 48.13, H 6.53, N, 7.71.

Cycloadduct 10. Procedure cf. **7**. Salt **10,HI** (193 mg, 0.557 mmol) yields **10** (98.0 mg, 80%), colourless crystals, m.p. 34 °C. IR ν 2850 (C-H), 1465, 1440 (CH_2, def.), 1325, 1290, 1280, 1245, 1210, 1195, 1160, 1105, 1080, 1060, 1010, 955, 875, 855, 785, 775, 725, 710, 700; ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ 0.87-1.00 (m, 2H) and 1.20-2.07 (m, 14H, 4-,5-,6-,7-,12-,13-,14-,15-,16-H), 2.30 (m, 1H, 8-H), 2.52$^{\#}$ (br.s (m), 1H, 11-H), 2.65 (dd, $J_{9A,9B}$=12.0 Hz, $J_{9A,8}$=5.8 Hz, 1H, 9_A-H), 2.77$^{\#}$ (br.s (m), 1H, 1-H), 3.07 (dd, $J_{9B,8}$=10.0 Hz, 1H, 9_B-H), 3.13 (br.d, $J_{3,8}$=8.0 Hz, 1H, 3-H), $^{\#}$exchangeable; ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 19.31, 20.67, 25.01 and 26.50 (4t, C-12,-13,-14,-15), 27.11 and 27.72 (2t, C-5,-6), 32.29 (t, C-16), 20.62 and 41.65 (2d, C-4,-7), 49.39 (d, C-8), 50.45 and 52.49 (2d, C-1,-11), 56.83 (t, C-9), 70.05 (d, C-3); MS m/z (assignment, %) 218 (74, M^+), 189 (100, M^+-C_2H_4-1), 175 (7, M^+-C_3H_8-1), 164 (31), 149 (17), 137 (12), 123 (29), 95 (24), 81 (25), 69 (29), 54 (15), 41 (40); calcd. for C 77.01, H 10.15, N 12.83; found C 76.63, H 10.57, N 12.88.

*3-Phenyl-2,6-diazatricyclo[5.2.2.0^{2,6}]undecane hydroiodide (**11,HI**)*. Procedure cf. **6,HI**. DBO (**8**) (67.0 mg, 0.608 mmol), styrene (90 mg, 1.82 mmol), $CDCl_3$ (0.5 ml), MeI (205 mg, 1.82 mmol), 3 d, colourless crystals of **11,HI** (127 mg, 59%, m.p. 197-198 °C). IR ν 3030 (=C-H), 2930, 2870 (C-H), 2800, 2700, 2650, 2590 (N^+-H), 1600 (C=C), 1490, 1470, 1450, 1430 (CH_2, def.), 1385, 1335, 1305, 1290, 1250, 1215, 1125, 1105, 1035, 1025, 1005, 995, 965, 875, 840, 770, 735, 700 (=C-H, def.); ^{1}H NMR (CD_3CN, 200.1 MHz) δ 1.49-2.61 (m, 10H, 4-,8-,9-,10-,11-H), 2.88 (br.s, 1H, 7$^{\#}$-H), 3.59 (m (br.s + m), 2H, 1$^{\#}$-,5_{ax}-H), 3.77 (dd, $J_{5eq,5ax}$=10.0 Hz, $J_{5eq,4ax}$=6.5 Hz, 1H, 5_{eq}-H), 4.61 (dd, $J_{3,4ax}$=11.0 Hz, $J_{3,4eq}$=5.5 Hz, 1H, $3_{(ax)}$-H, 7.32 (m, 3H, 3'-,4'-,5'-H), 7.48 (dd, $J_{2',3'}$ and $J_{6',5'}$=7.3 Hz, $J_{2',4'}$ and $J_{6',4'}$=1.8 Hz, 2H, 2'-,6'-H), 10.67 (very br.s, 1H, N^+-H), $^{\#}$exchangeable; ^{13}C NMR (CD_3CN, 50.3 MHz) δ 17.55, 18.30, 23.32 and 26.68 (3t, C-8,-9,-10,-11), 35.08 (t, C-4), 48.77 (d, C-7$^{\#}$), 50.99 (t, C-5), 54.03 (d, C-1$^{\#}$), 65.16 (d, C-3), 128.77 (2) and 129.94 (2, each d, C-2',-3',-5',-6'), 129.55 (d, C-4'), 134.20 (s, C-1'), $^{\#}$exchangeable; MS m/z (assignment, %) 228 (85 (M^+-H), 199 (34, M^+-H-C_2H_4-1), 172 (39), 145 (27), 124 (100, M^+-C_2H_4-C_6H_5), 117 (37), 104 (44), 96 (55); 77 (29, $C_6H_5^+$), 68 (57), 55 (28), 41 (64); calcd. for $C_{15}H_{21}IN_2$ (356.3) C 50.57, H 5.94, N 7.86; found C 50.67, H 6.02, N 7.85.

Cycloadduct 11. Procedure cf. 7. Salt **11,HI** (217 mg, 0.609 mmol) yields **11** (87.5 mg, 63%), colourless highly viscous oil (b.p. 140 °C/0.01 Torr, Kugelrohr). IR ν 3070, 3040 (=C-H), 2960, 2870 (C-H), 1605 (C=C), 1495, 1485, 1470, 1455 (CH_2, def.), 1365, 1355, 1305, 1250, 1230, 1215, 1200, 1175, 1155, 1115, 1085, 1070, 1025, 880, 770, 725, 705 (=C-H, def.); ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ 1.42 (m, 2H), 1.71 (m, 2H) and 1.96-2.38 (m, 6H, 4-,8-,9-,10-,11-H), 2.64 (br.s, 1H, 7#-H), 2.79 (br.s, 1H, 1#-H), 3.19 (ddd, $J_{5ax,4ax}$=11.0 Hz, $J_{5ax,5eq}$=8.5 Hz, $J_{5ax,4eq}$=5.5 Hz, 1H, 5_{ax}-H), 3.28 (ps.t, $J_{5eq,4ax}$=8.5 Hz, 1H, 5_{eq}-H), 4.24 (dd, $J_{3,4ax}$=11.0 Hz, $J_{3,4eq}$=5.5 Hz, 1H, $3_{(ax)}$-H), 7.17-7.33 (m, 3H, 3'-,4'-,5'-H), 7.38-7.44 (m, 2H, 2'-,6'-H), #exchangeable; ^{13}C NMR (CD_3CN, 50.3 MHz) δ 17.90, 26.24 and 27.36 (2) (3t, C-8,-9,-10,-11), 36.18 (t, C-4), 46.29 (d, C-7#), 49.28 (t, C-5), 51.07 (d, C-1#), 63.36 (d, C-3), 127.25 (d, C-4'), 127.30 (2) and 128.21 (2) (2d, C-2',-3',-5',-6'), 141.50 (s, C-1'), #exchangeable; MS m/z (assignment, %) 228 (87, M^+), 199 (23, M^+-C_2H_4-1), 174 (7), 144 (6), 124 (100, M^+-C_2H_4-C_6H_5-1), 117 (26), 104 (28), 97 (39), 81 (16), 77 (14, $C_6H_5^+$), 69 (47), 55 (19), 41 (46); calcd. for. $C_{15}H_{20}N_2$ (228.3) C 78.90, H 8.83, N 12.27; found C 78.43, H 8.84, N 11.78.

3-Cyano-2,6-diazatricyclo[5.2.2.0^{2,6}]undecane hydroiodide (12,HI). Procedure cf. **10,HI**- DBO (**8**) (72.0 mg, 0.653 mmol), acrylo nitrile (104 mg, 1.96 mmol), $CDCl_3$ (0.50 ml), MeI (278 mg, 1.96 mmol). After 7 d a solid was desposited. Yellowish crystals of **12,HI** (145 mg, 73%, m.p. 139-141 °C). IR ν 2920, 2870, 2860 (C-H), 2820, 2710, 2660, 2620, 2580, 2520 (N^+-H), 2250 (CN), 1475, 1470, 1455, 1445, 1425 (CH_2, def.), 1360, 1340, 1300, 1265, 1250, 1230, 1215, 1180, 1090, 1045, 1020, 1000, 970, 875, 825; ^{1}H NMR (CD_3CN, 200.1 MHz) δ 1.57-2.57 (m, 9H, 4'-,8-,9-,10-,11-H), 2.78 (m, 1H, 4"-H), 3.40, br.s, 1H, 7#-H), 3.48 (td, $J_{5ax,4ax}$=10.5 Hz, $J_{5ax,4eq}$=6.0 Hz, 1H, 5_{ax}-H), 3.64 (br.s, 1H, 1#-H), 3.79 (dd, $J_{5eq,5ax}$=10.5 Hz, $J_{5eq,4ax}$=7.0 Hz, 1H, 5_{eq}-H), 4.48 (dd, $J_{3,4ax}$=11.0 Hz, $J_{3,4eq}$=6.0 Hz, 1H, $3_{(ax)}$-H), 11.09 (very br.s, 1H, N^+-H), #exchangeable; ^{13}C NMR (CD_3CN, 50.3 MHz) δ 17.62, 17.87, 23.10, 26.06 (4t, C-8,-9,-10,-11), 30.44 (t, C-4), 50.63 (t, C-5), 51.12 (d, C-7#), 52.05 (d, C-3), 54.45 (d, C-1#), #exchangeable (^{13}C NMR in CD_3OD δ =112.00 (s, CN); MS m/z (assignment, %) 177 (24, M^+-H), 149 (39, M^+-H-C_2H_4), 123 (30, M^+-H-C_2H_4-CN), 96 (14), 81 (32), 69 (65), 54 (18), 41 (43); calcd. for $C_{10}H_{16}IN_3$ (305.2) C 39.36, H 5.28, N 13.77; found C 39.61, H 4.99, N 13.56.

2,6-Diazatricyclo[5.2.2.0^{2,6}]undecane-3-one (13). To a solution of salt **12,HI** (160 mg, 0.524 mmol) in MeCN (15 ml) are added K_2CO_3 (ca. 3 g) and water (0.5 ml). After 2 h more K_2CO_3 is added. The filtered solution is evaporated and the residue destilled, colourless oil of **13** (47.0 mg, 46%, b.p. 120 °C/0.01 Torr, Kugelrohr). IR ν 2960, 2870 (C-H), 1670 (C=O), 1445, 1420 (CH_2, def.), 1335, 1305, 1270, 1235, 1205, 1170, 1100, 1085, 1030, 990, 855, 805; ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ 1.62 (m, 4H) and 1.85-2.20 (m, 4H, 8-,9-,10-,11-H), 2.54 (t, 2H, 4-H), 2.85 (br.s, 1H, 7-H), 3.15 (t, $J_{5,4}$=8.0 Hz, 2H, 5-H), 4.10 (br.s, 1H, 1-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.37 and 25.22 (3) (2t, C-8,-9,-10,-11), 32.35 (t, C-4), 44.12 (d, C-7), 48.36 (t, C-5), 53.15 (d, C-1), 165.91 (s, C-3); MS m/z (assignment, %) 166 (100, M^+), 137 (34, M^+-C_2H_5), 110 (35, M^+-C_2H_4CO), 95 (44), 82 (27), 67 (53), 54 (30), 42 (13); calcd. for $C_9H_{14}N_2O$ (166.2) 166.1106; found 166.1109.

(1α,4α,4aα,7aα)-3-(9'-Fluorenidene)-1,2,4,4a,7,7a-hexahydro-8,8-dimethyl-1,4-methano-cyclo-penta[d]-pyridazinium bromide (a-19,Br) and (1α,4α,4aα,7aα)-2-(9'-Fluorenidene)-1,3,4,4a,7,7a-hexahydro-8,8-dimethyl-1,4-methano-cyclopenta[d]pyridazinium bromide (b-19,Br). Compound **E**[7] (150 mg, 0.924 mmol), 9-bromofluorene (680 mg, 2.77 mmol) and $CHCl_3$ (2 ml) are stirred under exclusion of light for 6 d at r.t. (^{1}H NMR monitoring). The mixture is slowly added to PE/EE (1:1, 30 ml) and the latter treated with PE/EE (6:3,

40 ml). This procedure is repeated twice. The product is dissolved in some $CHCl_3$ and pourred on a plug of silica gel. After washing with PE/EE (6:4) and CH_2Cl_2 the product is eluted with MeOH. Yellow powder of **a/b-19;Br** (ratio 3:1 according to the 8'-H ^1H NMR signals, 250 mg (66%), dec. >160 °C. UV (CH_3CN) λ_{max} (log ε) 220 (4.38), 257 (sh, 4.46), 264 (4.53), 360 (4.02); IR ν 3450 (N-H), 3070, 3020 (=C-H), 2990, 2950, 2810 (C-H), 1625, 1605, 1590 (C=C), 1460, 1380, 1340, 1285, 1240, 1205, 1105, 1050, 790, 740 (=C-H, def.), 700, 650, 620; ^1H NMR ($CDCl_3$, 250.1 MHz) : **a-19$^+$** δ 1.40 and 1.44 (2s, 2x3H. 8-CH_3, 2.38 and 2.79 (2m, 2x1H, 7-H), 3.31 (tm, $J_{4a,7a}$=9.8 Hz, $J_{7a,7}$=9.8 Hz, 1H, 7a-H), 4.02 (m, 2H, 1-,4a-H), 5.22 (m, 2H, 4-6$^{\#}$-H), 5.70 (m, 1H, 5$^{\#}$-H), 7.27-7.56 (m, 5H, 2'-,3'-,5'$^{\#}$-,6'-,7'-H), 7.62 (d, $J_{4',3'}$=7.5 Hz, 1H, 4'$^{\#}$-H), 7.77 (d, $J_{8',7'}$=7-9 Hz, 1H, 8'-H), 8.89 (d, $J_{1',2'}$=7.8 Hz, 1H, 1'-H), 10.16 (br.s, 1H, N(2)-H). - **b-19$^+$** δ 1.40 and 1.44 (2s, 2x3H, 8-CH_3), 2.04 and 2.53 (2m, 2x1H, 7-H), 3.59 (tm, $J_{7a,7}$=10.0 Hz, 1H, 7a-H), 3.83 (dm, $J_{4a,7a}$=10.0 Hz, 1H, 4a-H), 4.14 (ps.d, $J_{4,4a}$=3.0 Hz, 1H, 4-H), 5.22 (m, 1H, 1-H), 5.58 (m, 1H, 5$^{\#}$-H), 5.97 (m, 1H, 6$^{\#}$-H), 7.27-7.56 (m, 5H, 2'-,3'-,5'$^{\#}$-,6'-,7'-H), 7.64 (d, $J_{4',3'}$=7.5 Hz, 1H, 4'$^{\#}$-H), 7.84 (d, $J_{8',7'}$=8.0 Hz, 1H, 8'-H), 8.89 (d, $J_{1',2'}$=7.8 Hz, 1H, 1'-H), 9.18 (br.s, 1H, N(3)-H), $^{\#}$exchangeable. ^{13}C NMR ($CDCl_3$, 50.3 MHz) **a-19$^+$** δ 19.11 and 21.02 (2q, 8-CH_3), 32.57 (t, C-7), 41.83 (d, C-7a), 54.05 (s, C-8), 54.13 (d,C-4a), 67.02 (d, C-1), 78.94 (d, C-4), 120.54, 121.61, 126.06, 129.03, 130.33, 131.64. 134.09 and 135.06 (8d, C-1',-2',-3',-4',-5',-6',-7',-8'), 124.75 and 137.91 (2d, C-5,-6), 128.08 and 129.45 (2s, C-1'a$^{\#}$,-8'a$^{\#}$), 141.43 and 142.98 (2s, C-4'a$^{\#}$,-5a$^{\#}$), 151.65, $^{\#}$exchangeable. - **b-19$^+$** δ 19.11 and 20.70 (2q, 8-CH_3), 31.58 (t, C-7), 41.35 (d, C-7a), 53.51 (s, C-8), 53.70 (d, C-4a), 65.13 (d, C-4), 80.05 (d, C-1), 120.78, 121.72, 126.52, 129.03, 129.29, 130.58, 132.22 and 135.37 (8d, C-1',-2',-3',-4',-5',-6',-7',-8), 130.10 and 134.42 (2d, C-5,-6), 128.26 and 128.73 (2s, C-1'a$^{\#}$,-8'a$^{\#}$), 141.58 and 142.98 (2s, C-4'a$^{\#}$,-5'a$^{\#}$), 152.29 (C-9'), $^{\#}$exchangeable; MS m/z (assignment, %) 326 (26, M^+-H), 260 (7, M^+-H-C_5H_6), 233 (100, $C_{16}H_{13}N_2H^+$), 218 (25), 191 (12), 180 (11), 164 (31, $C_{13}H_8^+$), 147 (13), 80 (16), 43 (56); calcd. for $C_{23}H_{23}BrN_2$ (407.4) 326.1783; found 326.1781.

*Azomethineimines **a,b-20***. A solution of **19,Br** (200 mg, 490 mmol) in CH_2Cl_2 (15 ml) is treated with sat. K_2CO_3 (30 ml). The separated aqueous phase is extracted with CH_2Cl_2 (2 x 4 ml) and the combined organic phases are dried over K_2CO_3. After evaporation of the solvent a black oil is obtained that is dissolved in CH_2Cl_2 (2 ml), added on silica gel, and eluted with PE/EE 1:1). After removal of the solvent the remaining oil is crystallized by treating with PE (5 ml), intense yellow crystals of **a,b-20** (65.0 mg, 40%, m.p. 170-171 °C). UV (CH_3CN) λ_{max} (log ε) 255 (4.67), 376 (sh, 3.85), 432 (4.48); IR ν 3050 (=C-H), 2990, 2970, 2940, 2910, 2900, 2840 (C-H), 1590, 1565 (C=C), 1530 (C=N), 1470, 1440, 1430, 1390, 1375, 1355, 1335, 1320, 1310, 1295, 1265, 1250, 1220, 1205, 1170, 1155, 1135, 1120, 1105, 1040, 1030, 1000, 935, 930, 760, 740, 720 (=C-H, def.), 635; ^1H NMR ($CDCl_3$, 200.1 MHz) : **a-20** δ 1.13 and 1.35 (2s, 2x3H, 8-CH_3) 2.24-243 and 2.66 (2m, 2H, 7-H), 3.37 (m, 1H, 7a-H), 3.86 (ps.dm, $J_{4a,7a}$=7.0 Hz), 4.09 (ps. d, $J_{1,7a}$=2.5 Hz, 1H, 1-H), 5.24 (ps.d $J_{4,4a}$=2.9 Hz, 1H, 4-H), 5.40 (m, 1H, 6$^{\#}$-H), 5.51 (m, 1H, 5$^{\#}$--H), 7.20-7.45 (m, 4H, 2'-,3'-,6'-,7'-H), 7.62 (br.d, $J_{8',7'}$=7.8 Hz, 1H, 8'-H), 7.90 (m, 2H, 4'-,5'-H), 8.61 (br.d, $J_{1',2'}$=7.8 Hz, 1H, 1'-H). - **b-20** δ 1.10 and 1.31 (2s, 2x3H, 8-CH_3), 2.24-2.43 and 2.66 (2m, 2H, 7-H), 3.37 (m, 1H, 7a-H), 3.86 (ps.dm, $J_{4a,7a}$=7.0 Hz, 1H, 4a.H), 4.23 (ps.d $J_{4.4a}$=2.5 Hz, 1H, 4-H), 5.20 (ps.d, $J_{1,7a}$=2.8 Hz, 1H, 1-H), 5.40 (m, 6$^{\#}$-H), 5.66 (m, 1H, 5$^{\#}$-H), 7.20-7.45 (m, 4H, 2'-,3'-,6'-,7'-H), 7.62 (br.d, $J_{8',7'}$=7.8 Hz), 1H, 8'-H), 7.90 (m, 2H, 4'-,5-H), 8.58 (br.d, $J_{1',2'}$=7.8 Hz), 1'-H), $^{\#}$exchangeable; ^{13}C NMR ($CDCl_3$, 50.3 MHz) **a-20** δ 19.18 and 20.60 (2q, 8-CHJ_3), 32.42 (t, C-7), 42.89 (d, C-7a), 53.20 (d, C-4a), 54.60 (s, C-8), 74.67 (d, C-1), 79.70 (d, C-4), 118.90, 119.40, 120.27, 123.43 (2), 123.64, 126.13, 126.30, 127.19 and 135.15 (9d, C-5,-6,-1',-2',-3',-4',-5',-6',-7',-8'), 131.80 (2), 134.63 and 135.62 (3s, C-1'a,-4'a,-5'a-,-8'a). - **b-20** δ 19.39 and 20.60 (2q, 8-CH_3), 31.50 (t, C-7),

40.40 (d, C-7a), 54.77 (d, C-4a), 56.13 (s, C-8), 74.04 (d, C-4), 80.85 (d, C-1), 118.90, 120.27, 123.73, 125.10, 125.22, 126.13, 127.30, 129.18, 131.49 and 134.63 (10d, C-5,-6,-1',-2',-3',-4',-5',-6',-7',-8'), 132.70 (2), 134.63 and 135.42 (3s, C-1'a,-4'a,-5'a,-8'a); MS m/z (assignment, %) 326 (16, M^+), 260 (6, M^+-C_5H_6), 233 (100, $C_{16}H_{13}N_2^+$), 218 (26), 191 (7), 180 (10), 164 (26, $C_{13}H_8^+$), 149 (10), 132 (6), 120 (6), 105 (7), 97 (13), 91 (7), 77 (7), 66 (7), 57 (6), 41 (10); calcd. for $C_{23}H_{22}N_2$ (326.4) C 84.63, H 6.79, N 8.58; found C 84.35, H 6.73, N 8.34.

(1α,4α,4aα,7aα)-2-(9'-Fluorenidene)-1,3,4,4a,5,6,7,7a-octahydro-8,8-dimethyl-1,4-methano-cyclopen-ta[d]-pyridazinium bromide (21,Br). Procedure cf. **19,Br**. Azo compound **18**[18] (100 mg, 0.609 mmol), $CHCl_3$ (1.5) ml, 9-bromofluorene (448 mg, 1.83 mmol), yellow powder of **21,Br** (144 mg, 58%, dec. > 155 °C). UV (CH_3CN) λ_{max} (log ε) 195 (4.54), 223 (4.41, 258 (sh, 4.58), 265 (4.64), 362 (4.15; IR ν 3470 (N-H), 3080, 3030, 3020 (=C-H), 2980, 2890, 2820 (C-H), 1610, 1590, 1535 (C=C), 1460, 1385, 1340, 1200, 1145, 1120, 790, 740 (=C-H), def.), 705, 635; ^1H NMR ($CDCl_3$, 200.1 MHz) δ 1.08-1.90 (m, 6H, 5-,6-,7-H), 1.23 and 1.41 (2s, 2x3H, 8-CH_3), 3.15 (m, 1H, 4a-H), 3.37 (m, 1H, 7a-H), 3.78 (ps.d J=2.3 Hz, 1H, 4-H), 5.27 (ps.d, J=2.3 Hz, 1H, 1-H), 7.42 (m, 2H) and 7.59 (br.t, J=7.9 Hz, 2H, 2'-,3'-,6'-,7'-H), 7.80 (ps.br.t, $J_{4',3'}$ and $J_{5',6'}$=7.9 Hz, 4'-5'-H), 7.94 (br.d, $J_{8',7'}$)=7.9 Hz, 1H, 8'-H), 8.71 (br.d, $J_{1',2'}$=7.9 Hz, 1H, 1'-H), 9.38 (very br.s, 1H, N(3)-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 19.57 and 20.72 (2q, 8-CH_3) 25.94, 26.10 and 28.81 (3t, C-5,-6,-7), 45.14 and 45.59 (d, C-4a,-7a), 56.57 (s, C-8), 67.04 (d, C-4), 79.90 (d, C-1), 120.64, 121.56, 126.55, 129.28, 130.13, 131.56, 134.18 and 135.12 (8d, C-1',-2',-3',-4',-5',-6',-7',-8'), 129.01# and 129.16# (2s, C-1'a#,-8'a#), 141.55 and 142.68 (2s, C-4'a#,-5'a'#), 152.16 (s, C-9), #exchangeable; MS m/z (assignment, %) 328 (39, M^+-H), 260 (3, M^+-H-C_5H_8), 233 (100, $C_{18}H_{13}N_2^+$), 218 (25), 206 (13), 191 (7), 179 (23), 165 (44, $C_{13}H_9^+$), 151 (10), 107 (8), 83 (14), 41 (9); calcd for. $C_{23}H_{25}BrN_2$ (409.4) C 67.48, H 6.16, N 6.84; found C 67.19, H 6.54, N 6.69.

Azomethineimine 22. Procedure cf. **20**. Salt **21,Br** (52.8 mg, 0.129 mmol) yields **22** (15.7 mg, 37%), intense yellow crystals with m.p. 169-171 °C. UV (CH_3CN) λ_{max} (log ε) 198 (4.16), 258 (4.55), 375 (sh, 3.74), 434 (4.37); IR ν 3060 (=C-H), 2960, 2930, 2860 (C-H), 1530 (C=N), 1465, 1455, 1430, 1335, 1295, 1265, 1240, 1220, 1195, 1140, 1130, 1120, 1040, 935, 765, 725 (=C-H, def.); ^1H NMR ($CDCl_3$, 200.1 MHz) δ 1.07 and 1.33 (2s, 2x3H, 8-CH_3), 1.38-1.82 (m, 6H, 5-,6-,7-H), 3.17 (m, 2H, 4a-,7a-H), 4.03 (br.s, 1H, 4-H), 5.10 (br.s, 1H, 1-H), 7.18-7.46 (m, 4H, 2#-,3'-,6'-,7'-H), 7.62 (br.d, $J_{8',7'}$=7.9 Hz, 1H, 8'-H), 7.90 (dm, $J_{4',3'}$, $J_{5',6'}$=7.9 Hz, 2H, 4'-,5'-H), 8.64 (dm, $J_{1',2'}$=7.9 Hz, 1H, 1'-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 19.70 and 20.42 (2q, 8-CH_3), 26.34 (2) and 29.14 (2t, C-5,-6,-7), 44.56 (d, C-4a), 46.89 (d, C-7a), 57.48 (s, C-8), 75.18 (d, C-4), 80.73 (d, C-1), 118.97, 119.50, 120.27, 123.26, 123.51, 125.05, 126.14 and 127.24 (8d, C-1',-2',-3',-4',-5',-6',-7',-8'), 131.85, 132.00, 134.73 and 135.50 (4s, C-1'a,-4,-5'a,-8'a); MS m/z (assignment, %) 328 (50, M^+), 260 (3, M^+-C_5H_8), 233 (100, $C_{16}H_{13}N_2^+$), 218 (20), 206 (15), 191 (7), 179 (23), 164 (28, $C_{13}H_8N_2^+$), 151 (10), 107 (11), 57 (11), 41 (13); calcd. for $C_{23}H_{24}N_2$ (328.5) 328.1939; found 328.1940.

2-(9'-Fluorenidene)-2-azonia-3-azabicyclo[2.2.1]heptane-tetrafluoroborate (23,BF_4). A solution of 9-bromofluorene (191 mg, 0.780 mmol) in CH_2Cl_2 (3 ml) is slowly added to DBH (**5**) (50.0 mg, 0.520 mmol) and $AgBF_4$ (253 mg, 1.30 mmol) in CH_2Cl_2 (6 ml). A pale yellow precipitate is formed immediately. The mixture is stirred for 3 h under exclusion of light, filtered and the solvent evaporated. The crude product is treated with CH_3CN whereby a grey material remains undissolved. On evaporation of the solvent **23,BF_4** (99.0 mg, 55%) is obtained as yellow powder with m.p. 169-172 °C. UV (CH_3CN) λ_{max} (log ε) 224 (4.28), 256 (sh, 4.54), 263 (4.63), 346 (4.16); IR ν 3420 (N-H), 3020 (=C-H), 2940, 2820 (C-H), 1610 (C=C), 1460,

1325, 1200, 1170, 1085, 1040, 990, 935, 880, 815, 780, 745, 730 (=C-H, def.), 680, 650, 625; ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ 2.03-2.45 (m, 6H, 5-,6-,7-H), 4.41 (br.s, 1H, 4-H), 5.73 (br.s (m), 1H, 1-H), 6.97 (ps.d, $J_{NH,4}$=2.0 Hz, n(3)-H), 7.46 (td, $J_{3',4'}$, $J_{6',5'}$=7.8 Hz, $J_{3',2'}$, $J_{6',7'}$=7.8 HZ, $J_{3',1'}$, $J_{6',8'}$=1.3 Hz, 2H, 3'-,6'-H), 7.64 (td, $J_{7',8'}$=7.8 Hz, $J_{7',5'}$=1.2 Hz, 1H, 7'-H), 7.66 (td, $J_{2',1'}$=7.8 Hz, $J_{2',4'}$=1.2 Hz, 1H, 2'-H), 7.81 (ddd, $J_{4',1'}$, $J_{5',8'}$=0.8 Hz, 2H, 4'-,5'-H), 7.92 (br.d, 1H, 8'-H), 8.12 (br.d, 1H, 1'-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 27.52 (t, C-5), 29.01 (t, C-6), 40.09 (t, C-7), 60.18 (d, C-4), 71.23 (d, C-1), 122.90, 123.19, 128.31, 130.57, 130.88 (2), 136.08 and 136.75 (2d, C-1',-2',-3',-4',-5',-6',-7',-8'), 131.32 (2), s (C-1'a$^{\#}$,-8'a$^{\#}$), 143.66 (2), s, C-4'a$^{\#}$,-5'a$^{\#}$), 152.60 (s, C-9'), $^{\#}$exchangeable; MS m/z (assignment, %) 260 (71, M^+-H), 232 (11, M^+-H-C_2H_4), 205 (80), 192 (10), 178 (100), 163 (39, $C_{13}H_7^+$), 151 (19), 116 (27), 102 (20), 76 (11), 67 (12), 49 (43); calcd. for $C_{18}H_{17}BF_4N_2$ (348.2) C 62.10, H 4.49, N 8.05; found C 62.05, H 4.95, N 7.88.

Azomethineimine 24. Procedure cf. **20**. Salt **23,BF$_4$** (220 mg, 0.632 mmol) yields a crude product that is purified by chromatography (PE/EE first, 8:2, then 1:1), yellow orange crystals of **24** (67.0 mg, 41%), m.p. 133-135 °C. UV (CH_3CN) λ_{max} (log ε) 197 (4.28), 258 (4.68), 377 (sh, 3.85), 429 (442); IR ν 3060 (=C-H), 3010, 2950, 2870 (C-H), 1595, 1570 (C=C), 1535 (C=N), 1470, 1455, 1440, 1365, 1350, 1330, 1310, 1290, 1240, 1220, 1210, 1190, 1155, 1130, 1045, 1025, 1000, 950, 910, 890, 785, 740 (=C-H, def.); ^{1}H NMR (CD_3CN, 200.1 MHz) δ 1.46-2.20 (m, 6H, 5-,6-,7-H), 4.64 (br.s, 1H, 4-H), 5.86 (br.s, 1H, 1-H), 7.16-7.41 (m, 4H, 2'-,3'-,6'-,7'-H), 7.81 (d, $J_{8',7'}$=7.8 Hz, 1H, 8'-H), 7.89 (dm, $J_{4',3'}$, $J_{5',6'}$=7.8 Hz, 1H, 4'-,5'-H), 8.47 (dm, $J_{1',2'}$=7.8 Hz, 1H, 1'-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 26.36 (t, C-5), 27.53 (t, C-6), 41.36 (t, C-7), 65.58 (d, C-4), 69.67 (d, C-1), 119.16, 119.48, 120.41, 123.76 (2), 125.43, 126.50 and 127.34 (7d, C-1',-2',-3',-4',-5',-6',-7',-8'), 131.60, 132.48, 135.16 and 135.58 (4d, C-1'a,-4'a,-5'a); MS m/z (assignment, %) 260 (69, M^+), 232 (11, M^+-C_2H_4), 205 (79), 178 (100), 163 (40. $C_{13}H_7H^+$), 151 (20), 116 (23), 102 (17), 81 (10), 76 (11), 67 (9), 54 (9), 41(16); calcd. for $C_{18}H_{16}N_2$ (260.3) C 83.05, H 6.19, N 10.76; found C 82.67, H 6.16, N 10.48.

(c-4a,c-7a)-Δ5-Dodecahydro-r-2,c-4,c-8-metheno-3a-aza-7c-azonia-spiro[fluorene-3,9'-pentaleno]6,1,2-bcd]-as-indacene]bromide (a-26,HBr) and (c-4a,c-7a)-Δ6-Dodecahydo-r-2,c-4,c-8metheno-3a-aza-7c-azonia-spiro-[fluorene-3,9'-pentaleno[6,1,2-bed]-as-indacene]bromide. Azo compound **25** (100 mg, 0.471 mmol) in $CDCl_3$ (1 ml) and 9-bromofluorene (231 mg, 0.942 mmol) are reacted for 2 d at r.t. (^{1}H NMR monitoring). The yellow solution is slowly added to PE/EE (7:3) and the isolated precipitate washed with PE/EE until excess of the fluorene is removed (TLC). The salt **a,b-26,HBr** (197 mg, 92%) contains the two isomers in the ratio 2:1 according to the ^{1}H NMR spectrum (4-H signal). UV (CH_3CN) λ_{max} (log ε) 208 (4.57), 224 (sh, 4.28), 270 (4.05), 280 (sh, 3.99); IR ν 3060 (=C-H), 3000, 2980, 2930, 2900 C-H), 2870, 2700, 2610 (N^+-H), 1620, 1605, 1580 (C=C), 1480, 1440, 1370, 1230, 1210, 1120, 955, 790, 780, 760, 745, 710 (=C-H, def.); ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ 1.85 (ps.br.d, 2x1H, (**a** + **b**), 1-H_B), 2.16 (d, J_{AB}=11.0 Hz, 1H (**b**), 1-H_A), 2.19 (d, J_{AB}=10.8 Hz, 1H (**a**), 1-H_A), 2.71-3.46 (m, 9H (**a+b**), 2-,2a-,4a-,7/5-,7a-,8-,8a-,9-H), 4.20 (br.s, 1H (**b**), 4-H), 4.32 (br.s, 1H (**a**), 7b-H), 5.00 (br.s, 1H (**b**), 7b-H), 5.46 (br.s, 1H (**a**)), 5.70-5.80 (m, 1H (**a** + **b**)), 5.82-5.92 (m, 1H (**a** + **b**)) and 6.18 (br.s, 1 H (**b**), 5/7-,6-,7d-H), 7.54-7.76 (m, 4H (**a** + **b**), 2'-,3'-;6'-,7'-H), 7.82-8.00 (m, 3H (**a** + **b**), 4'-,5'-,8'-H), 8.77 (br.d, $J_{1',2'}$=8.0 Hz, 1H (**b**), 1'-H), 8.78 (br.d, $J_{1',2'}$= 7.0 Hz, 1H (**a**), 1'-H), 10.70 (br.s, 1H (**a**), N(7c)-H), 10.88 (br.s, 1H (**b**), N(7c)-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) **a-26,H$^+$** δ 31.22, 36.68, 38.19, 43.67, 44.55 and 46.61 (6d, C-2,-4a,-7a-,8-,8a,-9). 35-62 (t, C-7), 38.04 (t, C-1), 54.10 (d, C-2a), 54.25 (d, C-4), 62.04 (d, C-7b), 75.90 (d, C-7d), 78.85 (s, C-3(9')), 119.65, 120.42, 125.75, 126.86, 127.51, 129.13 and 129.48 (2) (7d, C-1',-2',-3',-4',-5',-6',-7',-8'), 129.94 and 133.53 2d, C-5,-6), 137.80,

138.95, 142.94 and 143.65 (4s, C-1a',-4a',-5a',-8a'). - **b-26,H$^+$** δ 35.02, 35.62, 38.19, 41.37, 43.80 and 44.55 (6d, C-2,-4a,-7a,-8,-8a,-9), 37.38 (t, C-5), 37.82 (t, C-1), 54.25 (d, C-2a), 56.52 (d, C-4), 61.55 (d, C-7b), 76.36 (d, C-7d), 79.11 (s, C-3(9')), 119.65, 120.42, 125.60, 126.86, 128.01, 129.13 and 129.48 (2) (7d, C-1',-2',-3',-4',-5',-6',-7',-8'), 129.94 and 133.88 (2d, C-6,-7), 137.40, 140.32, 141.21 and 145.73 (4s, C-1a',-4a',-5a',-8a'); MS m/z (assignment, %) 376 (100, M^+-H), 349 (4), 256 (20), 243 (18), 218 (18), 204 (15), 165 (29, $C_{13}H_9^+$), 132 (19), 119 (15), 106 (8), 91 (10) 80 (18), 56 (6), 43 (10); calcd. for $C_{27}H_{25}BrN_2$ (457.4) C 70.90, H 5.51, N 6.12; found C 71.12, H 5.58, N 6.04.

Pyrazolines ***a,b-26***. Solutions of **a,b-26,HBr** in CH_2Cl_2 (15 ml) and sat. K_2CO_3 (20 ml) are shaken and separated. The aqueous phase is extracted with CH_2Cl_2 (2 x 4 ml). After drying (K_2CO_3) the combined organic phases the solvent is evaporated. The residue yields **a,b-26** (120 mg, 50%) as pale yellow crystals (m.p. 228 - 230 °C) after sublimation (190 °C/0.01 Torr). The isomers are separated by flash chromatography (silica gel, PE/EE (1:1)). Fraction 1: **a-26** (65.1 mg, 27%); fraction 2: **b-26** (27.2 mg, 11%), colorless solids. UV (CH_3CN) λ_{max} (log ε) 210 (4.47), 224 (sh, 4.12), 232 (sh, 3.90), 269 (4.04), 278 (sh, 3.95); IR ν 3060, 3040 (=C-H), 2980, 2920, 2860 (C-H), 1610, 1580 (C=C), 1475, 1440, 1360, 1330, 1310, 1295, 1290, 1260, 1245, 1215, 1090, 1020, 1010, 990, 975, 840, 755, 730, 720, 700 (=C-H, def.); ^{1}H NMR ($CDCl_3$, 200.1 MHz) **a-26** δ 1.42 (br.d, J_{AB}=10.5 Hz, 1H, 1-H_A), 1.79 (br.d, 1H,. 1-H_B), 2.16 (dd, $J_{8,9}$=6.5 Hz, $J_{8,7b}$=2.5 Hz, 1H, 8-H), 2.28-2.94 (m, 8H, 3-,2a-,4a-,7-,7a-,8a-,9-H), 3.28 (br.s, 1H, 4-H), 3.67 (br.s, 1H, 7b-H), 4.22 (br.t, 1H, $J_{7d,2a}$=5.8 Hz, $J_{7d,8a}$=5.8 Hz, 7d-H), 5.35 (m, 1H, 5-H), 5.76 (m, 1H, 6-H), 7.20-7.42 (m, 4H, 2'-,3'-,5'-,7'-H), 7.57# (br.d, $J_{5',6'}$=7.5 Hz, 1H, 5'-H), 7.62 (dd, $J_{8',7'}$=7.5 Hz, $J_{8',6'}$=1.8 Hz, 1H, 8'-H), 7.70# (dd, $J_{4',3'}$=7.5 Hz, $J_{4',2'}$=1.3 Hz, 1H, 4'-H), 8.30 ($J_{1',2'}$=7.5 Hz, $J_{1',3'}$=1.8 Hz, 1H, 1'-H), #exchangeable. - **b-26** δ 1.42 (br.d, J_{AB}=10.5 Hz, 1H, 1-H_A), 1.77 (br.d, 1H, 1-H_B), 2.23 (dm, $J_{8,9}$=7.5 Hz, 1H, 8-H), 2.20-3.10 (m, 8H, 2-,2a-,4a-,5-,7a-,8-,8a-,9-H), 3.39 (br.s, 1H, 4-H), 3.62 (br.s, 1H, 7b-H), 4.35 (br.t, $J_{7d,2a}$=5.8 Hz, $J_{7d,8a}$=5.8 Hz, 7d-H), 5.62 (m, 1H, 7-H), 5.76 (m, 1H, 6-H), 7.20-7.42 (m, 4H, 2'-,3'-,6'-,7'-H), 7.56 (br.d, $J_{5',6'}$=7.5 Hz, 1H, 5'-H), 7.65 (dd, $J_{8',7'}$=7.5 Hz, $J_{8',6'}$=1.8 Hz, 1H, 8'-H), 7.74 (br.d, $J_{4',3'}$=7.5 Hz, 1H, 4'-H), 8.21 (dd, $J_{1',2'}$=7.5 Hz, $J_{1',3'}$=1.8 Hz, 1H, 1'-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) **a-26** δ 34.40, 37.64, 38.53, 46.04, 47.01 and 48.13 (6d, C-2,-4a-,7a-,8-,8a-9), 35.64 (t, C-7), 38.27 (t, C-1), 52.75 (d, C-2a), 55.65 (d, C-4), 59.72 (d, C-7b), 71.70 (d, C-7d), 77.51 (s, C-3(9')), 118.90, 119.93, 126.00, 127.76 (2), 127.85, 128.33 and 129.30 (C-1',-2',-3',-4',-5',-6',-7',-8'), 129.77 and 133.53 (2d, C-5,-6). - **b-26** δ 36.00, 36.36, 38.46, 43.37, 45.08 and 46.89 (6d, C-2,-4a,-7a,-8,-8a,-9), 37.79 (t-C-5), 38.03 (t, C-1), 55.21 (d, C-2a), 56.04 (d, C-4), 60.03 (d, C-7b), 73.64 (d, C-7d), 77.19 (s, C-3(9')), 119.08, 120.05, 126.18, 127.15, 128.35 (2), 128.79 and 129.46 (C-1',-2',-3',-4',-5',-6',-7',-8'), 130.14 and 132.62 (2d, C-6,7); MS m/z (assignment, %) 376 (100, M^+), 349 (4), 256 (27), 243 (35), 217 (27), 202 (29), 189 (32), 165 (63, $C_{13}H_9^+$), 132 (22), 118 (21), 106 (12), 91 (33), 80 (37), 66 (39); calcd. for $C_{27}H_{24}N_2$ (376.5) C 86.14, H 6.42, N 7.44; found C 86.38, H 6.67, N 7.51.

(c-4a,c-7a)Perhydro-r-2,c-4,c-8-metheno-3a,7c-diaza-spiro[fluorene-3,9'-pentaleno[6.1.2-bed]as-indacene (27). Hydrogenation of **a,b-26** (134 mg, 0.355 mmol) in 15 ml ethanol over Pd-C (60 mg, 10%) yields 124 mg of the product. On sublimation (170 °C/0.01 Torr) colorless crystals of **27** (112 mg, 83%, m.p. 208-210 °C) are obtained. UV (CH_3CN) λ_{max} (log ε) 209 (4.55), 222 (sh, 4.20), 230 (sh, 3.99), 266 (4.12), 278 (sh, 4.01); IR ν 3060 (=C-H), 2960, 2870 (C-H), 1620, 1605, 1585 (C=C), 1480, 1450, 1325, 1290, 1275, 1255, 1240, 1220 1155, 965, 945, 785, 770, 760, 745 (=C-H, def.); ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ 1.20-2.30 (m, 13H, 1-,4a-,5-,6-,7-,7a-,8-,8a-,9-H), 2.72 (br.s, 1H, 2-H), 2.79 (br.s, 1H, 2a-H), 3.45 (br.s, 1H, 4-H), 3.59 (br.s, 1H, 7b-H),, 4.49 (ps.t, $J_{7d,2a}$=5.8 Hz, 1H, 7d-H), 7.21-7.43 (m, 4H, 2'-,3'-,6'-,7'-H), 7.56# (d, $J_{5',6'}$=7.5

Hz, 1H, 5'-H), 7.65 (m, 1H, 8'-H), 7.71# (d, $J_{4',3'}$=7.5 Hz, 1H, 4'-H), 8.33 (m, 1H, 1'-H), #exchangeable; ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 26.93 (t, C-6), 28.48 and 29.98 (2t, C-5,-7), 36.87, 37.49, 38.45, 49.02, 45.41 and 46.80 (6d, C-2,-4a-,-7s,-8,-8a,-9), 38.34 (t, C-1), 54.83, (d, C-2a), 55.60 (d, C-4), 60.06 (d, C-7b), 72.54 (d, C-7d), 77.70 (s, C-3(9')), 119.00, 119.91, 126.14, 127.37, 128.07, 128.19, 128.58 and 129.52 (8d, C-1',-2',-3',-4',-5',-6',-7',-8'), 138.95, 141.52, 142.93 and 148.21 (4s, C-1a'.4a',-5a'-,8a'); MS m/z (assignment, %) 378 (82, M^+), 351 (3), 213 (100), 204 (13), 188 (19), 165 (26, $C_{13}H_9^+$), 121 (30), 106 (7), 91 (12), 80 (18); 67 (9), 56 (8), 41 (10); calcd. for $C_{27}H_{26}N_2$ (378.5) C 85.68, H 6.92, N 7.40; found C 85.03, H 7.31, N 6.99.

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