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The First 1,7-Electrocyclizations of Butadienyl Pyridinium Ylides: Stereoselective Formation of 1,2-Annulated 2,3-Dihydroazepines [1]

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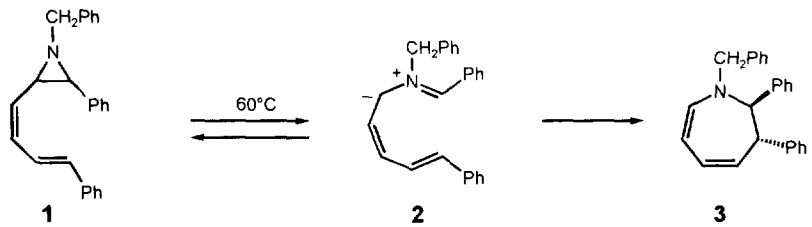
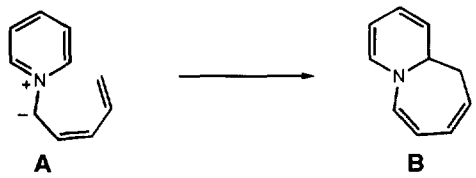
Abstract: Upon deprotonation of pentadienyl substituted pyridinium bromides **6/13,** conjugated azomethine ylide-type dipoles are formed which undergo stereoselective 8π-electrocyclization affording 10,10a-dihydropyrido[1,2-*a*]-azepines **8a-k** and **15a,b**, respectively. © 1997 Published by Elsevier Science Ltd.

Among the various methodologies for the construction of heterocycles, dipolar cyclizations belong to an especially useful and simple methodology. Although the majority of known applications, which include the use of almost every kind of 1,3-dipoles, are 6π-processes leading to five-membered heterocycles,[4-6] there is an increasing number of 8π-dipolar cyclizations resulting in seven-ring systems.[4,7-9] Surprisingly, and in contrast to the results with related carbonyl ylide analogues,[4-6,10] indications for the involvement of azomethine ylides in the latter type of reactions are extremely scarce. To the best of our knowledge only one simple example is known, namely the transformation of the diphenyl epiminohexadiene **1** into the dihydroazepine **3**.[11] In the few other reports on such ring closures, azomethine ylides are postulated as reactive species in more complex, multistep rearrangements.[12,13]



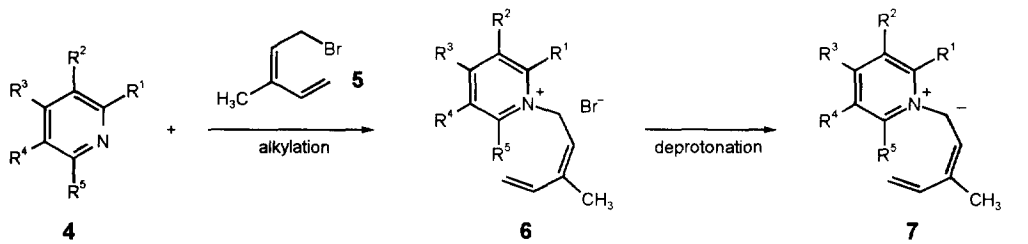
1 **2** **3**

With regard to the obvious gap for practical applications of azomethine ylides we have investigated the reactivity of conjugated pyridinium ylides which represent a special kind of this dipole; we now disclose first results on successful transformations of type **A**→**B**.[14] The generation of the dipole system **A** was accomplished by alkylation of pyridine derivatives with appropriately substituted, (*Z*)-configurated pentadienes followed by deprotonation of the corresponding pyridinium salts.



A B

The first experiments were conducted with 5-bromo-3-methyl-pentadiene (**5**) as alkylating agent, accessible in two steps from commercially available -(2*Z*)-3-methyl pentenynol.[15] After the reaction of **5** with the pyridines **4a-k**, the pyridinium bromides **6a-k** were formed and then isolated as solid compounds (**g-k**) or oils (**a-f**) in nearly quantitative yield (exceptions: **6i,j**). On treatment of the salts with potassium *tert*-butoxide in boiling THF/CH_3CN (10 : 1), the color of the suspension immediately changed to dark-red, and after completion of the reaction (tlc) a major product resulted in each case which was isolated in moderate to good yields[19] (the particular low yield for **8i,j** can be explained by steric hindrance of the cyclization step) and identified as a derivative of 10,10a-dihydropyrido[1,2-*a*]azepine (**8**). Up to now no other examples of this particular bicyclic system are described. There are only a few isomeric structures with the double bonds of the 7-ring in different positions,[20] and only one procedure, which affords pyrido[1,2-*a*]azepinones as final product, takes place with comparable efficiency.[2]

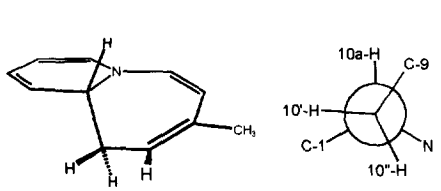


4 5 6 7 8

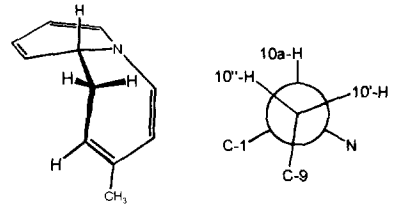
8	R^1	R^2	R^3	R^4	R^5	yield (%)
a	H	H	H	H	H	50
b	D	D	D	D	D	50
c	CH_3	H	H	H	H	52
d	Ph	H	H	H	H	26 (+34% **4c**)
e	H	H	CH_3	H	H	63
f	H	H	*t*Bu	H	H	75
g	CH_3	H	CH_3	H	H	32
h	H	CH_3	H	CH_3	H	49
i	CH_3	H	H	H	CH_3	24
j	CH_3	H	CH_3	H	CH_3	17
k	H	H	Ph	H	H	70

The structural assignments of **8a-k** were in full agreement with the HRMS analyses and the usual spectroscopical data (see Experimental Section). Inspection of simple models of the annulated

dihydroazepines **8** reveals some conformational mobility of the bicyclic system with two low energy structures (for **8a** see **C** and **D**). On the basis of geometry optimizations, performed by PM3 calculations for several derivatives of **8**, it turned out that the structure with the methylene hydrogens being approximately bisected by the (C-10a)-H bond (structure **D**) is less stable by 2-5 kcal/mol. The predominance of the **C**-geometry is confirmed by the ^{1}H NMR coupling constants of 10'-H/10''-H with 10a-H and 9-H, respectively: due to the different dihedral angles the signal of 10'-H shows, in addition to the geminal splitting $J_{10',10''}$(16.8 Hz), vicinal coupling with the vinyl proton 9-H (J = 9.0 Hz), whereas 10''-H is mainly coupled with the bridgehead hydrogen at C-10a (J = 4.5 Hz); the respective values of $J_{10'',9}$ and $J_{10',10a}$ are small (< 1 Hz).



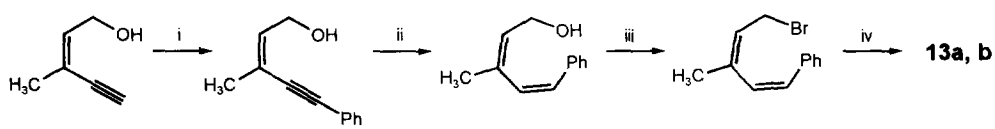
C



D

As the substitution pattern of the pyridinium ylides **7** does not permit any conclusion concerning the stereochemical mode of the ring closure step, the pyridinium bromides **13a,b** were prepared which after sequential deprotonation and cyclization should afford dihydroazepines bearing labels at C-10.

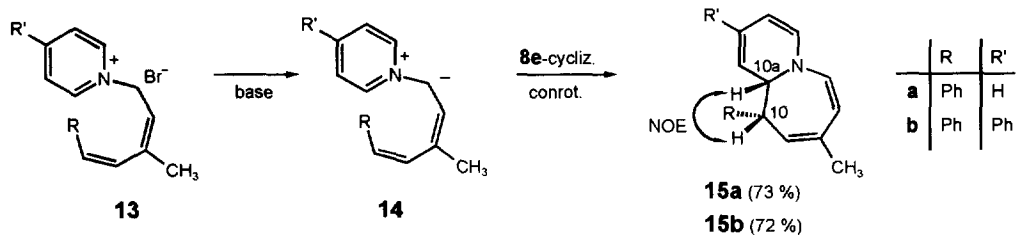
The synthesis of **13a,b** was performed according to the same general method as used for **6** by employing the bromodiene **12** as alkylating reagent.[14] Starting with (*Z*)-3-methyl-2-penten-4-yn-1-ol (**9**) Pd-catalyzed phenylation under Sonogashira conditions[21] afforded **10** in 93% yield.[22] The stereo- and chemoselective reduction of the triple bond of **10** (to **11**) was executed with activated zinc following the protocol of Boland et al.[16] Bromination of **11** was accomplished with phosphorous tribromide at -70 °C and gave a 55% yield of pure **12** after chromatographic purification. Subsequent reaction of **12** with the pyridines **4a,k** resulted in the formation of the required pyridinium salts **13a** (99%) and **13b** (86%).



9 **10** **11** **12**

i: PhI, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N; ii: Zn(Cu/Ag), $MeOH/H_2O$ (1:1); iii: PBr_3; iv: **4a**, **k**, CH_3CN

After treatment of **13a,b** with potassium *tert*-butoxide under standard conditions (see Experimental Section) the ^{1}H NMR analysis of the isolated cyclization products revealed that the starting compounds are transformed into the dihydroazepines **15a,b**, in which the bridgehead proton 10a-H and group R are trans-positioned.



13 **14**

15a (73 %)
15b (72 %)

	R	R'
a	Ph	H
b	Ph	Ph

The stereochemistry of compounds **15a/15b** was again determined by means of the ^{1}H NMR coupling parameters: $J_{9,10}$ = 8.6/8.2 Hz, $J_{10,10a}$ < 1 Hz. The cis-relation between 10a-H and 10-H was additionally confirmed by NOE experiments performed with **15b**.

Whereas the cyclization mode of 1,7-dipolar cyclizations remained undetermined (or undeterminable) in most reported examples, the results with **13** add further experimental evidence[11,23] to the theoretical prediction that 8π-electrocyclizations take place in a conrotatory manner. As has been shown for dipolar systems[7-9,11-13,24] as well as for the isoelectronic neutral[25] and anionic species,[26] the helically twisted geometry of the π-perimeter represents an especially favorable stereoelectronic situation, ideally suited for antarafacial interaction of the terminal orbitals.

In conclusion, the synthesis of a series of dihydro-pyridoazepines has been accomplished by stereoselective 1,7-electrocyclization of butadienyl pyridinium ylides, a subclass of azomethine ylides. Further applications of this method to the preparation of specifically substituted and annulated heterocyclic compounds are currently under investigation.

EXPERIMENTAL SECTION

IR: Perkin-Elmer 257 Infracord. - ^{1}H NMR: Bruker WM 250 (250 MHz) and Bruker WM 400 (400 MHz); ^{13}C NMR: Bruker WM 400 (100.6 MHz); $CDCl_3$ as solvent and TMS as internal standard; signals marked by an asterisk are not clearly separated. - MS: Finnigan MAT 44 S (70 eV) with Datasystem MAT SS 200. - Elemental analyses: Perkin-Elmer Elemental Analyzer 240. - Flash chromatography was performed on SiO_2 (Silica 32-36, ICN Biomedicals) Al_2O_3 (Alumina N, Biomedicals). - Tlc: SiO_2 60 F-254, 0.2 mm (Merck); Al_2O_3 60 F-254, neutral type E, 0.2 mm (Merck).

General procedure for the quarternization of the N-heteroaromatic compounds 4:

A ca. 1 molar solution of compound **4** and 1 equivalent of the bromodiene [in case of dienes **5** varying mixtures of the (2*Z*/2*E*) diastereomers are used] in acetonitrile is stirred at r.t. for the given period. After addition of diethyl ether precipitation of a viscous oil or a solid takes place. Isolation is

accomplished either by filtration and washing of the amorph-solid residue with diethyl ether (in case of solids) or by a repeated solving-separation procedure (in case of oils) using acetonitrile/diethyl ether as dissolving and separating agents, respectively. The derivatives obtained by this method are characterized by ^{1}H-NMR analysis and used directly for the cyclization reactions.

1-(3'Methyl-2',4'-pentadien-1'-yl)-pyridinium bromide (6a): According to the general procedure **4a** (1.410 g, 17.8 mmol) and **5** [2.867 g, 17.8 mmol, (Z/E) = 9:2] in 20 ml of acetonitrile afforded after 2d 4.111 g (96%) of **6a** [9:2-(*Z/E*) mixture] as viscous orange oil.

^{1}H NMR (250 MHz, $CDCl_3$); **(2'*Z*)-6a**: δ = 9.43 (m_c , 2H, 2-H, 6-H), 8.58 (m_c , 1H, 4-H), 8.16 (m_c, 2H, 3-H, 5-H), 7.10 (dd, 1H, 4'-H, $^3J_{4',5'cis}$ = 10.5 Hz, $^3J_{4',5'trans}$ = 17.5 Hz), 5.84 (d, 2H, 1'-H, $^3J_{1',2'}$ = 7 Hz), 5.77 (d, 1H, 2'-H, $^3J_{2',1'}$ = 7 Hz), 5.51 (d, 1H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.5 Hz), 5.45 (d, 1H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.5 Hz), 1.95 (s, br., 3H, C<u>H</u>$_3$). - **(2'*E*)-6a**: d= 9.43 (m_C , 2H, 2-H, 6-H), 8.58 (m_C , 1H, 4-H), 8.16 (m_C, 2H, 3-H, 5-H), 6.40 (dd, 1H, 4'-H, $^3J_{4',5'cis}$ = 10.5 Hz, $^3J_{4',5'trans}$ = 18.2 Hz), 5.84 (d, 2H, 1'-H, $^3J_{1',2'}$ = 7 Hz), 5.77 (d, 1H, 2'-H, $^3J_{2',1'}$ = 7 Hz), 5.41 (d, 1H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 18.2 Hz), 5.25 (d, 1H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.5 Hz), 2.05 (s, br., 3H, C<u>H</u>$_3$).

2,3,4,5,6-Pentadeutero-1-(3'-methyl-2',4'-pentadien-1'-yl)-pyridinium bromide (6b): According to the general procedure **4b** (252 mg, 3.0 mmol) and **5** [483 mg, 3.0 mmol, (*Z/E*) = 5:2] in 4 ml of acetonitrile afforded after 2d 677 mg (92%) of **6b** [5:2-(*Z/E*) mixture] as a viscous orange-red oil.

^{1}H NMR (250 MHz, $CDCl_3$); **(2'*Z*)-6b**: δ = 7.10 (dd, 1H, 4'-H, $^3J_{4',5'cis}$ = 10.5 Hz, $^3J_{4',5'trans}$ = 17.5 Hz), 5.84 (d, 2H, 1'-H, $^3J_{1',2'}$ = 7 Hz), 5.77 (d, 1H, 2'-H, $^3J_{2',1'}$ = 7 Hz), 5.51 (d, 1H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.5 Hz), 5.45 (d, 1H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.5 Hz), 1.95 (s, 3H, C<u>H</u>$_3$). - **(2'*E*)-6b**: d= 6.40 (dd, 1H, 4'-H, $^3J_{4',5'cis}$ = 10.5 Hz, $^3J_{4',5trans}$ = 18 Hz), 5.84 (d, 2H, 1'-H, $^3J_{1',2'}$ = 7 Hz), 5.77 (d, 1H, 2'-H, $^3J_{2',1'}$ = 7 Hz), 5.41 (d, 1H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 18 Hz), 5.25 (d, 1H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.5 Hz), 2.05 (s, 3H, C<u>H</u>$_3$).

2-Methyl-1-(3'-methyl-2',4'-pentadien-1'-yl)-pyridinium bromide (6c): According to the general procedure **4c** (438 mg, 4.7 mmol) and **5** [757 mg, 4.7 mmol, (Z/E) = 6:1] in 5 ml of acetonitrile afforded after 4d 1.05 g (88%) of **6c** [6:1-(*Z/E*) mixture] as a viscous orange-red oil.

^{1}H NMR (250 MHz, $CDCl_3$); (*Z*)-**6c**: δ = 8.88 (dm, 1 H, 6-H, $^3J_{6,5}$ = 6.1 Hz), 8.46 (m_c, 1 H, 4-H), 8.05-7.90 (m, 2 H, 3-H, 5-H), 6.99 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 9.8 Hz, $^3J_{4',5'trans}$ = 17.1 Hz), 5.57 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.1 Hz), 5.56-5.39 (m, 2 H, 2'-H*, 5'*cis*-H*), 4.86 (s, 2 H, 1'-H), 2.87 (s, 3 H, 2-C<u>H</u>$_3$), 1.99 (d, 3 H, 3'-C<u>H</u>$_3$, $^4J_{CH3,2'}$ = 1.2 Hz). - (*E*)-**6c**: δ = 8.74 (dm, 1 H, 6-H, $^3J_{6,5}$ = 6.7 Hz), 8.46 (m_c, 1 H, 4-H), 8.05-7.90 (m, 2 H, 3-H, 5-H), 6.48 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.8 Hz, $^3J_{4',5'trans}$ = 17.7 Hz), 5.56-5.39 (m, 2 H, 2'-H*, 5'*trans*-H*), 5.22 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.7 Hz), 4.86 (s, 2 H, 1'-H), 2.88 (s, 3 H, 2-C<u>H</u>$_3$), 2.01 (d, 3 H, 3'-C<u>H</u>$_3$, $^4J_{CH3,2'}$ = 1.2 Hz).

2-Phenyl-1-(3'-methyl-2',4'-pentadien-1'-yl)-pyridinium bromide (6d): According to the general procedure **4c** (633 mg, 4.08 mmol) and **5** [657 mg, 4.08 mmol, (Z/E) = 6:1] in 4 ml of acetonitrile afforded after 2d 1.238 g (96%) of **6d** [6:1-(*Z/E*) mixture] as a viscous orange-red oil.

^{1}H NMR (250 MHz, $CDCl_3$); (*Z*)-**6d**: δ = 9.59 (pd, 1 H, 6-H, $^3J_{6,5}$ = 6.5 Hz), 8.61 (m_c, 1 H, 4-H, $^3J_{4,3}$ = 7.9 Hz), 8.22 (m_c, 1 H, 5-H, $^3J_{5,4}$ = 7.6 Hz, $^3J_{5,6}$ = 6.5 Hz,), 7.85 (m_c, 1 H, 3-H, $^3J_{3,4}$ = 7.9 Hz), 7.63-7.58 (m, 5 H, Ph-<u>H</u>), 6.39 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.8 Hz, $^3J_{4',5'trans}$ = 17.2 Hz), 5.60 (d, 2 H, 1'-H, $^3J_{1',2'}$ = 7.3 Hz), 5.55-5.39 (m, 2 H, 2'-H*, $^3J_{2',1'}$ = 7.3 Hz), 5.26 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.2 Hz), 5.15 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.8 Hz), 1.83 (s, 3 H, 3'-C<u>H</u>$_3$). - (*E*)-**6d**: δ = 9.67 (pd, 1 H, 6-H, $^3J_{6,5}$ = 6.5 Hz), 8.61 (m_c, 1 H, 4-H, $^3J_{4,3}$ = 7.9 Hz), 8.22 (m_c, 1 H, 5-H, $^3J_{5,4}$ = 7.6 Hz, $^3J_{5,6}$ = 6.5 Hz,), 7.85 (m_c, 1 H, 3-H, $^3J_{3,4}$ = 7.9 Hz), 7.63-7.58 (m, 5 H, Ph-<u>H</u>), 6.27 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.7 Hz, $^3J_{4',5'trans}$ = 17.2 Hz), 5.61 (d, 2 H, 1'-H, $^3J_{1',2'}$ = 7.3 Hz), 5.55-5.39 (m, 2 H, 2'-H*, $^3J_{2',1'}$ = 7.3 Hz), 5.33 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.2 Hz), 5.20 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.7 Hz), 1.56 (s, 3 H, 3'-C<u>H</u>$_3$).

4-Methyl-1-(3'-methyl-2',4'-pentadien-1'-yl)-pyridinium bromide (6e): According to the general procedure **4e** (1.060 g, 11.38 mmol) and **5** [1.833 g, 11.38 mmol, (Z/E) = 4:1) in 12 ml of acetonitrile afforded after 2d 1.238 g (96%) of **6e** (4:1-[*Z/E)* mixture] as an orange-brown oil.

^{1}H NMR (250 MHz, $CDCl_3$); **(*Z*)-6e**: δ = 8.88 (d, 2 H, 2-H, $^3J_{2,3}$ = 6.6 Hz), 8.00 (d, 2 H, 3-H, $^3J_{3,2}$ = 6.6 Hz), 7.05 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 11.0 Hz, $^3J_{4',5'trans}$ = 17.3 Hz), 5.72 (t, br., 1 H, 2'-H, $^3J_{2',1'}$ = 7.3 Hz), 5.50 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.3 Hz), 5.46-5.34 (m, 3 H, 1'-H*, 5'*cis*-H*,), 2.61 (s, 3 H, 4-C$\underline{H}_3$), 1.89 (d, 3 H, 3'-C$\underline{H}_3$, $^4J_{\underline{CH}3,2'}$ = 1.2 Hz). - **(*E*)-6e**: δ = 8.88 (d, 2 H, 2-H, $^3J_{2,3}$ = 6.6 Hz), 8.00 (d, 2 H, 3-H, $^3J_{3,2}$ = 6.6 Hz), 6.43 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.8 Hz, $^3J_{4',5'trans}$ = 17.4 Hz), 5.80 (t, br., 1 H, 2'-H, $^3J_{2',1'}$ = 7.0 Hz), 5.46-5.34 (m, 3 H, 1'-H*, 5'*trans*-H*,), 5.22 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.8 Hz), 2.61 (s, 3 H, 4-C$\underline{H}_3$), 1.93 (d, 3 H, 3'-C$\underline{H}_3$, $^4J_{\underline{CH}3,2'}$ = 1.2 Hz).

4-*tert*-Butyl-1-(3'-methyl-2',4'-pentadien-1'-yl)-pyridinium bromide (6f): According to the general procedure **4f** (419 mg, 3.10 mmol) and **5** [499 mg, 3.10 mmol, (Z/E) = 7:2] in 4 ml of acetonitrile afforded after 3d 909 mg (99%) of **6f** [7:2-(*Z/E)* mixture] as a viscous yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$); **(*Z*)-6f**: δ = 9.37 (d, 2 H, 2-H, $^3J_{2,3}$ = 7.0 Hz), 7.98 (d, 2 H, 3-H, $^3J_{3,2}$ = 7.0 Hz), 7.08 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.4 Hz, $^3J_{4',5'trans}$ = 17.1 Hz), 5.80-5.72 (m, 3 H, 1'-H*, 2'-H*), 5.50 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.1 Hz), 5.44 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.4 Hz), 1.94 (s, 3 H, 3'-C$\underline{H}_3$), 1.40 (s, 9 H, C(C$\underline{H}_3$)$_3$). - **(*E*)-6f**: δ = 9.41 (d, 2 H, 2-H, $^3J_{2,3}$ = 7.2 Hz), 7.99 (d, 2 H, 3-H, $^3J_{3,2}$ = 7.2 Hz), 6.39 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.8 Hz, $^3J_{4',5'trans}$ = 17.4 Hz), 5.80-5.72 (m, 3 H, 1'-H*, 2'-H*), 5.34 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.4 Hz), 5.22 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.8 Hz), 2.04 (s, 3 H, 3'-C$\underline{H}_3$), 1.40 (s, 9 H, C(C$\underline{H}_3$)$_3$).

2,4-Dimethyl-1-(3'-methyl-2',4'-pentadien-1'-yl)-pyridinium bromide (6g): According to the general procedure **4g** (699 mg, 6.53 mmol) and **5** [1.052 g, 6.53 mmol, (Z/E) = 11:3] in 7 ml of acetonitrile afforded after 3d 1.61 g (92%) of **6g** [7:2-(*Z/E)* mixture] as a red-brown oil.

^{1}H NMR (250 MHz, DMSO-d6); **(Z)-6g**: δ = 8.81 (d, 1 H, 6-H, $^3J_{6,5}$ = 6.2 Hz), 7.93 (s, 1 H, 3-H), 7.84 (d, 1 H, 5-H, $^3J_{5,6}$ = 6.2 Hz), 7.00 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.7 Hz, $^3J_{4',5'trans}$ = 17.1 Hz), 5.56 (pt, 1 H, 2'-H, $^3J_{2',1'}$ = 7.3 Hz, $^4J_{2',\underline{CH}3}$ = 1.2 Hz), 5.50 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.1 Hz), 5.45-5.30 (m, 3 H, 1'-H*, 5'*cis*-H*), 2.75 (s, 3 H, 2-C$\underline{H}_3$), 2.36 (s, 3 H, 4-C$\underline{H}_3$), 1.89 (d, 3 H, 3'-CH$_3$, $^4J_{\underline{CH}3,2'}$ = 1.2 Hz). - **(*E*)-6g**: δ = 8.84 (d, 1 H, 6-H, $^3J_{6,5}$ = 6.2 Hz), 7.93 (s, 1 H, 3-H), 7.84 (d, 1 H, 5-H, $^3J_{5,6}$ = 6.2 Hz), 6.42 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 11.0 Hz, $^3J_{4',5'trans}$ = 17.4 Hz), 5.66 (pt, 1 H, 2'-H, $^3J_{2',1'}$ = 6.4 Hz, $^4J_{2',\underline{CH}3}$ = 0.8 Hz), 5.45-5.30 (m, 3 H, 1'-H*, 5'*trans*-H*), 5.19 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 11.0 Hz), 2.75 (s, 3 H, 2-C$\underline{H}_3$), 2.36 (s, 3 H, 4-C$\underline{H}_3$), 1.92 (d, 3 H, 3'-CH$_3$, $^4J_{\underline{CH}3,2'}$ = 0.8 Hz).

3,5-Dimethyl-1-(3'-methyl-2',4'-pentadien-1'-yl)-pyridinium bromide (6h): According to the general procedure the solution of **4g** (666 mg, 6.22 mmol) in 6 ml of acetonitrile was treated with **5** [1.002 g, 6.22 mmol, (Z/E) = 4:1]. Shortly after the addition the slightly exothermic reaction was accompanied by beginning precipitation of a solid. After continued stirring for 2d at r.t. 1.52 g (91%) of **6g** [4:1-(*Z/E)* mixture] was collected as a yellow solid.

^{1}H NMR (250 MHz, $CDCl_3$); **(*Z*)-6h**: δ = 9.08 (s, 2 H, 2-H), 8.02 (s, 1 H, 4-H), 7.08 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 11.1 Hz, $^3J_{4',5'trans}$ = 17.0 Hz), 5.72 (ps, 3 H, 1'-H, 2'-H), 5.50 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.0 Hz), 5.44 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 11.1 Hz), 2.58 (s, 6 H, 3-C$\underline{H}_3$), 1.94 (s, 3 H, 3'-C$\underline{H}_3$). - **(*E*)-6h**: δ = 9.11 (s, 2 H, 2-H), 8.02 (s, 1 H, 4-H), 6.40 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.9 Hz, $^3J_{4',5'trans}$ = 17.1 Hz), 5.72 (ps, 3 H, 1'-H, 2'-H), 5.39 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.1 Hz), 5.23 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.9 Hz), 2.58 (s, 6 H, 3-C$\underline{H}_3$), 2.04 (s, 3 H, 3'-C$\underline{H}_3$).

2,6-Dimethyl-1-(3'-methyl-2',4'-pentadien-1'-yl)-pyridinium bromide (6i): According to the general procedure **4i** (532 mg, 4.96 mmol) and **5** [799 mg, 4.96 mmol, (Z/E) = 2:3] in 5 ml of acetonitrile afforded after 2d 831 mg (62%) of **6i** [2:3-(*Z/E)* mixture] as a slightly beige solid.

^{1}H NMR (250 MHz, $CDCl_3$): (*Z*)-**26**: δ = 8.36-8.21 (m, 1 H, 4-H), 7.57 (dm, 2 H, 3-H = 5-H, $^3J_{3,4}$ = 7.9 Hz), 6.92 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.2 Hz, $^3J_{4',5'trans}$ = 17.1 Hz), 5.55 (d, 2 H, 1'-H, $^3J_{1',2'}$ = 6.4 Hz), 5.51 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.1 Hz), 5.45 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.2 Hz), 5.14 (pt, 1 H, 2'-H, $^3J_{2',1'}$ = 6.4), 3.00 (s, br., 6 H, 2-C$\underline{H}_3$ = 6-C$\underline{H}_3$), 1.91 (d, 3 H, 3'-CH_3, $^4J_{\underline{CH}3,2'}$ = 1.5 Hz). - (*E*)-**26**: δ = 8.36-8.21 (m, 1 H, 4-H), 7.89 (dm, 2 H, 3-H = 5-H, $^3J_{3,4}$ = 9.8 Hz), 6.32 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.7 Hz, $^3J_{4',5'trans}$ = 17.4 Hz), 5.55 (d, 2 H, 1'-H, $^3J_{1',2'}$ = 6.4 Hz), 5.37 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.4 Hz), 5.25 (pt, 1 H, 2'-H, $^3J_{2',1'}$ = 6.4), 5.19 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.7 Hz), 3.00 (s, br., 6 H, 2-C$\underline{H}_3$ = 6-C$\underline{H}_3$), 2.02 (d, 3 H, 3'-CH_3, $^4J_{\underline{CH}3,2'}$ = 1.2 Hz).

2,4,6-Trimethyl-(3'-methyl-2',4'-pentadien-1'-yl)pyridinium bromide (6j): According to the general procedure **4i** 978 mg, 8.07 mmol) and **5** [1.300 g, 8.07 mmol, (Z/E) = 5:2] in 8 ml of acetonitrile afforded after 4d 320 mg (14%) of **6j** [5:2-(*Z/E)* mixture] as a colorless solid.

^{1}H NMR (250 MHz, $CDCl_3$): (*2'Z*)-**6j**: δ = 7.58 (s, 2H, 3-/5-H), 6.91 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.4 Hz, $^3J_{4',5'trans}$ = 16.8), 5.51 (d, 2H, 1'-H, $^3J_{1',2'}$ = 7.1 Hz), 5.49 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 16.8 Hz), 5.32 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.4 Hz), 5.11 (t, 1H, 2'-H, $^3J_{2',1'}$ = 7.1 Hz), 2.56 (s, 9H, 2-/4-/6-C$\underline{H}_3$), 1.91 (s, 3H, C$\underline{H}_3$). - (*2'E*)-**6j**: δ = 7.58 (s, 2H, 3-/5-H), 6.31 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.7 Hz, $^3J_{4',5'trans}$ = 17.2), 5.51 (d, 2H, 1'-H, $^3J_{1',2'}$ = 7.1 Hz), 5.36 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 17.2 Hz), 5.21 (t, 1H, 2'-H, $^3J_{2',1'}$ = 7.1 Hz), 5.19 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.7 Hz), 2.56 (s, 9H, 2-/4-/6-C$\underline{H}_3$), 2.02 (s, 3H, C$\underline{H}_3$).

4-Phenyl-1-(3'-methyl-2',4'pentadien-1'-yl)-pyridinium bromide (6k): According to the general procedure **4i** (954 mg, 6.15 mmol) and **5** [990 mg, 6.15 mmol, (Z/E) = 11:1] in 6 ml of acetonitrile afforded after 2d 1.674 g mg (86%) of **6k** [11:1-(*Z/E)* mixtur] as a colorless solid.

^{1}H NMR (250 MHz, CD_3OD); (*Z*)-**6k**: δ = 8.91 (d, 2 H, 2-H, $^3J_{2,3}$ = 7.0 Hz), 8.41 (d, 2 H, 3-H, $^3J_{3,2}$ = 7.0 Hz), 8.04-7.97 (m, 2 H, 2''-H), 7.68-7.58 (m, 3 H, 3''-H, 4''-H), 7.07 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.7 Hz, $^3J_{4',5'trans}$ = 16.7 Hz), 5.78 (t, 1 H, 2'-H, $^3J_{2',1'}$ = 7.3 Hz), 5.59 (d, 1 H, 5'*trans*-H, $^3J_{5'trans,4'}$ = 16.7 Hz), 5.52-5.42 (m, 3 H, 1'-H*, 5'*cis*-H *), 2.02 (s, 3 H, 3'-C$\underline{H}_3$); (**E**)-**6k**: δ = 8.91 (d, 2 H, 2-H, $^3J_{2,3}$ = 7.0 Hz), 8.41 (d, 2 H, 3-H, $^3J_{3,2}$ = 7.0 Hz), 8.04-7.97 (m, 2 H, 2''-H), 7.68-7.58 (m, 3 H, 3''-H, 4''-H), 6.52 (dd, 1 H, 4'-H, $^3J_{4',5'cis}$ = 10.7 Hz, $^3J_{4',5'trans}$ = 17.7 Hz), 5.85 (t, 1 H, 2'-H, $^3J_{2',1'}$ = 7.9 Hz), 5.52-5.42 (m, 3 H, 1'-H*, 5'*trans*-H *), 5.27 (d, 1 H, 5'*cis*-H, $^3J_{5'cis,4'}$ = 10.7 Hz), 2.05 (s, 3 H, 3'-C$\underline{H}_3$).

General procedure for the transformation of the pyridinium salts 6/13 into the dihydroazepines 8/15:

To a solution of the pyridinium bromide **6/13** (1.5-2.5 mmol) in 3-5 ml of acetonitrile (and, if necessary, 1 ml of dry ethanol) 20 ml of dry THF are added under argon. The resulting suspension is heated to reflux and is then treated with 1.1 equivalent of potassium *tert*-butoxide. Refluxing of the dark brown-violet mixture is continued until completion of the reaction (tlc, 2-4 h). After cooling down to r.t. 50 ml of diethyl ether are added, the mixture is filtrated and then washed with satd. aqueous sodium chloride solution (4 x 20 ml). The combined organic fractions are dried ($MgSO_4$), concentrated in vacuo and then purified by flash chromatography. The indicated yields of compounds **8** are related to the respective pentadienyl pyridinium salts with Z-configuration of the double bond at 2'-C. The dihydroazepines **8/15** are relatively unstable compounds which tend to undergo decomposition reactions during workup and on longer standing; therefore, as shown by the ^{1}H NMR analysis of the raw mixtures, the amount of **8** formed during the deprotonation-cyclization process is usually significantly higher than indicated.

8-Methyl-10,10a-dihydropyrido[1,2-*a*]azepine (8a): According to the general procedure the reaction of **6a** [370 mg, 1.54 mmol; (*Z/E*= 9:2)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ ethyl acetate 2:1) 100 mg of **8a** [50%, related to (*Z*)-**6a**] as a red oil; R_f = 0.64 (cyclohexane/ethyl acetate 1:1).

IR (CCl_4): 3030 (br.) (=CH– st), 2960, 2910 (br.), 2850, 2820, 1640 (C=C st), 1595 (C=C st), 1560 (br.), 1455, 1440, 1385, 1370, 1315, 1250, 1195, 1180, 1080, 1035, 990, 920, 895, 855, 690 (=CH–), 610 cm^{-1}. - **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.23 (d, 1H, 6-H, $^3J_{6,7}$ = 9.7 Hz), 6.19 (d, 1H, 4-H, $^3J_{4,3}$ = 7.5 Hz), 5.85 (ddm, 1H, 2-H, $^3J_{2,1}$ = 9.5 Hz, $^3J_{2,3}$ = 6 Hz), 5.64 (dm, 1H, 9-H, $^3J_{9,10'}$ = 9 Hz), 5.43 (ddd, 1H, 1-H, $^3J_{1,2}$ = 9.5 Hz, $^3J_{1,10a}$ = 5.8 Hz, $^3J_{1,3}$ = 1.5 Hz), 4.88 (d, 1H, 7-H, $^3J_{7,6}$ = 9.7 Hz), 4.81 (ddm , 1H, 3-H, $^3J_{3,2}$ = 6 Hz, $^3J_{3,4}$ = 7.5 Hz), 3.74 (pdd, 1H, 10a-H, $^3J_{10a,1}$ = 5.8 Hz, $^3J_{10a,10''}$ = 4.5 Hz), 2.49 (dd, 1H, 10'-H, $^2J_{10',10''}$ = 16.8 Hz, $^3J_{10',9}$ = 9 Hz), 2.19 (ddm, 1H, 10''-H, $^2J_{10'',10'}$ = 16.8 Hz, $^3J_{10'',10a}$ = 4.5 Hz), 1.90 (pdd, 1H, C$\underline{H}_3$, $^4J_{CH3,9}$ = 1.5 Hz, $^5J_{CH3,10''}$ = 2.3 Hz). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ= 132.9 (C-8), 132.7 (C-6), 131.4 (C-4), 126.4 (C-9), 121.6 (C-2), 120.2 (C-1), 105.6 (C-7), 96.0 (C-3), 59.5 (C-10a), 43.7 (C-10), 25.2 (C$\underline{H}_3$). - **MS** (170 eV, CI, *i*-butane), m/z (%): 216 (19) [M^+ + *i*-Butyl], 162 (6), 161 (15), 160 (16), 159 (17) [M^+], 158 (5). - $C_{11}H_{13}N$: calcd.159.1048, found 159.1047 (HRMS).

1,2,3,4,10a-Pentadeutero-8-methyl-10,10a-dihydropyrido[1,2-*a*]azepine (8b): According to the general procedure the reaction of **6b** [267 mg, 1.09 mmol; (*Z*/*E*= 5:2)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 1:1) 64 mg of **8b** [50%, related to (*Z*)-**6b**] as a yellow-red oil; R_f = 0.64 (cyclohexane/ethyl acetate 1:1).

IR (CH_2Cl_2): 2930, 2880, 1640 (C=C st), 1595 (C=C st), 1550, 1325, 1200, 1105, 1040, 920, 855 cm^{-1}. - **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 6.25 (d, 1H, 6-H, $^3J_{6,7}$ = 9.5 Hz) 5.66 (dq, 1H, 9-H, $^3J_{9,10'}$ = 9 Hz), 4.89 (d, 1H, 7-H, $^3J_{7,6}$ = 9.5 Hz), 2.49 (dd, 1H, 10'-H, $^2J_{10',10''}$ = 16.8 Hz, $^3J_{10',9}$ = 9 Hz), 2.19 (dq, 1H, 10''-H, $^2J_{10'',10'}$ = 16.8), 1.90 (dd, 1H, C$\underline{H}_3$, $^4J_{CH3,9}$ = 1.5 Hz, $^5J_{CH3,10''}$ = 2.3 Hz). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ= 132.9 (C-8), 132.7 (C-6), 126.4 (C-9), 105.6 (C-7), 43.6 (C-10), 25.2 (C$\underline{H}_3$). - **MS** (170 eV, CI, iC_4H_9), m/z (%): 221 (19) [M^+ + iC_4H_9], 180 (6), 179 (13), 166 (16), 65 (100), 164 (29) [M^+], 163 (8), 162 (6), 160 (8), 85 (8). - $C_{12}H_8D_5N$: calcd. 164.1362, found 164.1369 (HRMS).

4,8-Dimethyl-10,10a-dihydropyrido[1,2-*a*]azepine (8c): According to the general procedure the reaction of **6c** [956 mg, 3.76 mmol; (*Z*/*E*= 6:1)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 1:1) 292 mg of **8c** [52%, related to (*Z*)-**6c**] as a dark-red oil; R_f = 0.70 (cyclohexane/ ethyl acetate 1:1).

IR (CCl_4): 2920 (br.), 1635 (C=C st), 1575 (br.), 1410, 1310, 1247, 1390, 920, 875, 695 (=CH–) cm^{-1}. - **^{1}H NMR** (400 Mhz, $CDCl_3$): δ = 6.52 (d, 1 H, 6-H, $^3J_{6,7}$ = 9.2 Hz), 5.87 (dd, 1 H, 2-H, $^3J_{2,1}$ = 9.5 Hz, $^3J_{2,3}$ = 5.8 Hz), 5.82 (dm, 1 H, 9-H, $^3J_{9,10'}$ = 8.5 Hz), 5.48 (dd, 1 H, 1-H, $^3J_{1,2}$ = 9.5 Hz, $^3J_{1,10a}$ = 4.8 Hz), 5.05 (d, 1 H, 7-H, $^3J_{7,6}$ = 9.2 Hz), 4.85 (dt, 1 H, 3-H, $^3J_{3,2}$ = 5.8 Hz, $^3J_{3,4\text{-}C\underline{H}3}$ = 1.3 Hz), 3.42 (pt, 1 H, 10a-H, $^3J_{10a,1}$ = 4.8 Hz, $^3J_{10a,10''}$ = 3.4 Hz), 2.39 (dd, 1 H, 10'-H, $^3J_{10',10''}$ = 17.6 Hz, $^3J_{10',9}$ = 8.5 Hz), 2.08 (dm, 1 H, 10''-H, $^3J_{10'',10'}$ = 17.6 Hz), 1.97 (s, br., 3 H, 4-C$\underline{H}_3$), 1.94 (s, br., 3 H, 8-C$\underline{H}_3$). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 136.6 (C-4), 131.8 (C-8), 129.4 (C-6), 128.4 (C-9), 120.6 (C-1), 120.2 (C-2), 108.0 (C-7), 96.6 (C-3), 59.0 (C-10a), 42.7 (C-10), 25.8 (8-C$\underline{H}_3$), 20.8 (4-C$\underline{H}_3$). - **MS** (70 eV, EI), m/z (%): 173 (29) [M^+], 172 (7), 170 (5), 158 (7), 157 (5), 156 (5), 144 (5), 143 (5), 130 (6), 118 (11), 117 (5), 115 (5), 94 (100) [H_3C-py-H^+], 93 (20), 92 (5), 80 (50) [(py-H^+)], 79 (57) [py], 78 (14), 77 (22), 66 (7), 65 (13). - $C_{12}H_{15}N$: calcd. 173.1204, found 173.1209 (HRMS).

8-Methyl-4-phenyl-10,10a-dihydropyrido[1,2-*a*]azepine (8d): According to the general procedure the reaction of **6d** [571 mg, 1.81 mmol; (*Z*/*E*= 6:1)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 2:1) 95 mg of **8d** [26%, related to (*Z*)-**6d**] as a dark-red oil; R_f = 0.68 (cyclohexane/ ethyl acetate 1:1). In addition, 96 mg (34%) of 2-phenyl pyridine (**4d**) is isolated.

IR (CCl_4): 3030 (br.) (=CH– st), 2890 (br.), 1637 (C=C st), 1510 (br.), 1488, 1443, 1410, 1315, 1305, 1275, 1183, 700 (=CH–) cm^{-1}. - **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.34 (m_c, 5 H, Ph-H), 6.20 (d, 1 H, 6-H, $^3J_{6,7}$ = 8.8 Hz), 6.01 (ddd, 1 H, 2-H, $^3J_{2,1}$ = 9.6 Hz, $^3J_{2,3}$ = 6.0 Hz, $^4J_{2,10a}$ = 1.5 Hz), 5.82 (m_c, 1 H, 9-H, $^3J_{9,10}$ = 6.4 Hz), 5.53 (ddd, 1 H, 1-H, $^3J_{1,2}$ = 9.6 Hz, $^3J_{1,10a}$ = 5.1 Hz, $^4J_{1,3}$ = 1.1 Hz), 5.03 (dd, 1 H, 3-H, $^3J_{3,2}$ = 6.0 Hz, $^4J_{3,1}$ = 1.1 Hz), 4.86 (dd, 1 H, 7-H, $^3J_{7,6}$ = 8.8 Hz, $^4J_{7,9}$ = 1.3 Hz), 3.77 (m_c, 1 H,

10a-H, $^3J_{10a,1}$ = 5.1 Hz), 2.45 (m_c, 2 H, 10-H, $^3J_{10,9}$ = 6.4 Hz), 1.93 (pd, 3 H, C$\underline{H}_3$, $^4J_{8\text{-}C\underline{H}3,9}$ = 1.6 Hz). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 138.0 (C-4), 133.3 (C-8), 132.1 (C-1'), 128.6(C-6), 128.4 (C-2'), 128.4 (C-3'), 128.2 (C-4'), 127.6 (C-9), 121.3 (C-1), 121.0 (C-2), 107.8 (C-7), 100.1 (C-3), 59.5 (C-10a), 42.2 (C-10), 26.4 (8-$\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%): 235(26) [M^+], 234(15), 233(15), 232(15), 220(7), 219(5), 218(10), 217(5), 206(5), 204(9), 180(10), 167(9), 157(6), 156(100) [$C_{10}H_{11}N^+$], 155(32), 154(25), 129(6), 128(11), 127(9), 126(3), 117(3), 116(5), 115(15), 109(5), 105(5), 104(5), 103(9), 102(11), 96(5), 91(5), 89(7), 81(8), 80(56) [$C_5H_6N^+$], 79(37) [py], 78(18), 77(31), 76(9), 75(5), 65(8). - $C_{17}H_{17}N$: calcd. 235.1361, found 235.1358 (HRMS).

2,8-Dimethyl-10,10a-dihydropyrido[1,2-*a*]azepine (8e): According to the general procedure the reaction of **6e** [478 mg, 1.88 mmol; (*Z*/*E*= 4:1)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 2:1) 166 mg of **8e** [63%, related to (*Z*)-**6e**] as an orange-brown oil; R_f = 0.70 (cyclohexane/ ethyl acetate 1:1).

IR (CCl_4): 3035 (=CH– st), 2910 (br.), 1667, 1642 (C=C st), 1580 (br.), 1460, 1440 (br.), 1375, 1255, 1170, 1135, 862 (=CH– oop) cm^{-1}. - **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.22 (d, 1 H, 6-H, $^3J_{6,7}$ = 9.4 Hz), 6.16 (d, 1 H, 4-H, $^3J_{4,3}$ = 7.5 Hz), 5.60 (dm, 1 H, 9-H, $^3J_{9,10'}$ = 8.8 Hz), 5.14 (s, br., 1 H, 1-H), 4.85 (d, 1 H, 7-H, $^3J_{7,6}$ = 9.4 Hz), 4.68 (dd, 1 H, 3-H, $^3J_{3,4}$ = 7.5 Hz, $^3J_{3,2\text{-}C\underline{H}3}$ = 1.9 Hz), 3.70 (m_c, 1 H, 10a-H, $^3J_{10a,10''}$ = 4.8 Hz), 2.45 (dd, 1 H, 10'-H, $^3J_{10',10''}$ = 16.6 Hz, $^3J_{10',9}$ = 8.8 Hz), 2.16 (dm, 1 H, 10''-H, $^3J_{10'',10'}$ = 16.6 Hz), 1.88 (s, br., 3 H, 8-C$\underline{H}_3$), 1.74 (s, br., 3 H, 2-C$\underline{H}_3$). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 132.8 (C-8), 132.7 (C-6), 131.0 (C-4), 128.2 (C-2), 126.1 (C-9), 117.1 (C-1), 105.3 (C-7), 99.50 (C-3), 59.5 (C-10a), 43.7 (C-10), 3.17 (8-$\underline{C}H_3$), 21.0 (2-$\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%):174 (11) [M^+ + 1], 173 (30) [M^+], 172 (10), 158 (9), 157 (7), 156 (8), 144 (9), 132 (7), 131 (6), 130 (7), 107 (6), 97 (7), 95 (14), 94 (100) [$C_6H_9N^+$], 93 (11), 83 (7), 82 (6), 81 (9), 80 (35) [$C_5H_6N^+$], 79 (34) [py], 78 (7), 77 (16), 71 (8), 69 (8), 67 (7), 65 (10), 55 (11). - $C_{12}H_{15}N$: calcd. 173.1204, found 173.1203 (HRMS).

2-*tert*-Butyl-8-methyl-10,10a-dihydropyrido[1,2-*a*]azepine (8f): According to the general procedure the reaction of **6f** [720 mg, 2.43 mmol; (*Z*/*E*= 7:2)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 1:1) 305 mg of **8f** [75%, related to (*Z*)-**6f**] as an oil; R_f = 0.72 (cyclohexane/ ethyl acetate 1:1).

IR (CCl_4): 3030 (=CH– st), 2970 (br.), 2910, 1660, 1640 (C=C st), 1575 (br.), 1460, 1362, 1310, 1270, 1250, 1195, 1142, 1080, 1055, 865 (=CH–), 665, 605 cm^{-1}.-.**^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.21 (d, 1 H, 6-H, $^3J_{6,7}$ = 9.5 Hz), 6.19 (d, 1 H, 4-H, $^3J_{4,3}$ = 7.7 Hz), 5.60 (dm, 1 H, 9-H, $^3J_{9,10'}$ = 8.8 Hz, $^4J_{9,\,C\underline{H}3}$ = 1.3 Hz), 5.18 (dd, 1 H, 1-H, $^3J_{1,10a}$ = 4.7 Hz, $^4J_{1,3}$ = 2.0 Hz), 4.89 (dd, 1 H, 3-H, $^3J_{3,4}$ = 7.7 Hz, $^4J_{3,1}$ = 2.0 Hz), 4.84 (d, 1 H, 7-H, $^3J_{7,6}$ = 9.5 Hz), 3.72 (pt, br., 1 H, 10a-H, $^3J_{10a,1}$ = 4.7 Hz), 2.46 (dd, 1 H, 10'-H, $^3J_{10',10''}$ = 16.8 Hz, $^3J_{10',9}$ = 8.8 Hz), 2.41 (dm, 1 H, 10''-H, $^3J_{10'',10'}$ = 16.8 Hz, $^5J_{10'',C\underline{H}3}$ = 2.4 Hz), 1.89 (dd, 3 H, 8-C$\underline{H}_3$, $^4J_{C\underline{H}3,9}$ = 1.3 Hz, $^5J_{C\underline{H}3,10''}$ = 2.4 Hz), 1.07 (s, 9 H, C(C$\underline{H}_3$)$_3$). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 140.5 (C-2), 132.8 (C-4), 132.5 (C-6), 131.1 (C-8), 125.9 (C-9), 113.5 (C-1), 105.1 (C-7), 96.5 (C-3), 59.5 (C-10a), 43.7 (C-10), 33.6 ($\underline{C}(CH_3)_3$), 29.0 (C($\underline{C}H_3$)$_3$), 25.2 ($\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%): 216 (5) [M^+ + 1], 215 (23) [M^+], 137 (10), 136 (100) [*tert*-Bu-py-H^+], 121 (19), 120 (11), 92 (7), 81 (6), 80 (51) [py-H^+], 79 (21) [py], 77 (9). - $C_{15}H_{21}N$: calcd. 215.1674, found 215.1675 (HRMS).

2,4,8-Trimethyl-10,10a-dihydropyrido[1,2-*a*]azepine (8g): According to the general procedure the reaction of **6g** [467 mg, 1.74 mmol; (*Z*/*E*= 4:1)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 2:1) 81 mg of **8g** [32%, related to (*Z*)-**6g**] as an oil; R_f = 0.72 (cyclohexane/ ethyl acetate 1:1).

IR (CCl_4): 2920 (br.), 1670, 1640 (C=C st), 1580 (br.), 1415, 1308, 1240, 1210, 1195, 925, 875 (=CH–) cm^{-1}. - **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.50 (d, 1 H, 6-H, $^3J_{6,7}$ = 9.3 Hz), 5.71 (dm, 1 H, 9-H, $^3J_{9,10'}$ = 8.4 Hz, $^3J_{9,8\text{-}C\underline{H}3}$ = 1.8 Hz), 5.19 (d, 1 H, 1-H, $^3J_{1,10a}$ = 5.0 Hz), 5.02 (d, 1 H, 7-H, $^3J_{7,6}$ = 9.3 Hz), 4.74 (s, 1 H, 3-H), 3.39 (pt, br., 1 H, 10a-H, $^3J_{10a,1}$ = 5.0 Hz), 2.36 (dd, 1 H, 10'-H, $^2J_{10',10''}$ = 17.6 Hz, $^3J_{10',9}$ = 8.4 Hz), 2.05 (ddm, 1 H, 10''-H, $^2J_{10'',10'}$ = 17.6 Hz, $^3J_{10'',10a}$ = 5.9 Hz), 1.96 (s, 3 H, 2-C$\underline{H}_3$), 1.93 (t, 3 H, 8-C$\underline{H}_3$, $^3J_{8\text{-}C\underline{H}3,9}$ = 1.8 Hz), 1.75 (s, 1 H, 4-C$\underline{H}_3$). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 136.2 (C-4), 131.8 (C-8), 129.4 (C-2), 128.7 (C-6), 128.0 (C-9), 115.9 (C-1), 107.6 (C-3), 100.3 (C-7), 59.2 (C-10a), 42.9 (C-10), 25.8 (8-$\underline{C}H_3$), 20.9 (4-$\underline{C}H_3$), 20.7 (2-$\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%): 188 (15) [M^+ + 1], 187 (69) [M^+], 186 (14) [M^+ - 1], 172 (25), 171 (8), 158 (10), 157 (8), 144 (11), 132 (34), 109 (38), 108 (100) [$(CH_3)_2$-py-H^+], 107 (39), 106 (10), 92 (7), 91 (8), 81 (15), 80 (82) [py-H^+], 79 (73) [py], 78 (10), 77 (38), 65 (20), 63 (7). - $C_{13}H_{17}N$: calcd. 187.1361, found 187.1360 (HRMS).

1,3,8-Trimethyl-10,10a-dihydropyrido[1,2-*a*]azepine (8h): According to the general procedure the reaction of **6h** [370 mg, 1.38 mmol; (*Z*/*E*= 4:1)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 2:1) 102 mg of **8h** [49%, related to (*Z*)-**6h**] as a dark-red oil; R_f = 0.68 (cyclohexane/ethyl acetate 1:1).

IR (CCl_4): 3020 (br.) (=CH– st), 2920 (br.), 1675, 1637 (C=C st), 1585 (br.), 1460, 1440 (br.), 1365 (br.), 1297, 1260, 1230, 1170, 1147, 915 cm^{-1}. - **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.23 (d, 1 H, 6-H, $^3J_{6,7}$ = 9.1 Hz), 5.91 (s, 1 H, 4-H), 5.67 (ddm, 1 H, 9-H, $^3J_{9,10'}$ = 8.8 Hz, $^3J_{9,8\text{-}C\underline{H}3}$ = 1.3 Hz), 5.59 (s, 1 H, 2-H), 4.88 (d, 1 H, 7-H, $^3J_{7,6}$ = 9.1 Hz), 3.31 (d, 1 H, 10a-H, $^3J_{10a,10''}$ = 5.6 Hz), 2.70 (dd, 1 H, 10'-H, $^2J_{10',10''}$ = 17.5 Hz, $^3J_{10',9}$ = 8.8 Hz), 1.92 (dd, 3 H, 8-C$\underline{H}_3$, $^4J_{8\text{-}C\underline{H}3,9}$ = 1.8 Hz, $^5J_{8\text{-}C\underline{H}3,10''}$ = 2.4), 1.81 (s, 3 H, 3-C$\underline{H}_3$), 1.80 (dm, 1 H, 10''-H, $^2J_{10'',10'}$ = 17.5 Hz, $^3J_{10'',10a}$ = 5.6 Hz), 1.69 (s, 1 H, 1-C$\underline{H}_3$). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 132.9 (C-8), 132.3 (C-6), 129.9 (C-4), 126.0 (C-9), 124.5 (C-1), 121.2 (C-2), 105.6 (C-3), 104.9 (C-7), 63.1 (C-10a), 38.6 (C-10), 25.4 (8-$\underline{C}H_3$), 20.6 (3-$\underline{C}H_3$), 17.7 (1-$\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%): 188 (5), 187 (33) [M^+], 186 (4), 109 (9), 108 (100) [$C_7H_{10}N^+$], 107 (7), 80 (25) [$C_5H_6N^+$], 79 (18) [py], 77 (8). - $C_{13}H_{17}N$: calcd. 187.1361, found 187.1356 (HRMS).

4,8,10a-Trimethyl-10,10a-dihydropyrido[1,2-*a*]azepine (8i): According to the general procedure the reaction of **6i** [452 mg, 1.69 mmol; (*Z*/*E*= 2:3)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 2:1) 30 mg of **8i** [24%, related to (*Z*)-**6i**] as a dark-red oil; R_f = 0.68 (cyclohexane/ ethyl acetate 1:1).

IR (CCl_4): 2927 (br.), 1650 (C=C st), 1574, 1440, 1348, 1265, 1095 (br.), 1014 (br.) cm^{-1}. - **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 6.49 (d, 1 H, 6-H, $^3J_{6,7}$ = 10.3 Hz), 5.76 (dd, 1 H, 2-H, $^3J_{2,1}$ = 9.7 Hz, $^3J_{2,3}$ = 5.8 Hz), 5.44 (m_c, 1 H, 9-H, $^3J_{9,10}$ = 7.9 Hz), 5.17 (d, 1 H, 1-H, $^3J_{1,2}$ = 9.7), 4.86 (d, br., 1 H, 3-H, $^3J_{3,2}$ = 5.8 Hz), 4.83 (d, 1 H, 7-H, $^3J_{7,6}$ = 10.3 Hz), 2.26 (d, br., 1 H, 10-H, $^3J_{10,9}$ = 7.9 Hz), 2.01 (s, br., 3 H, 4-C$\underline{H}_3$), 1.89 (s, br., 3 H, 8-C$\underline{H}_3$), 0.91 (s, br., 3 H, 10a-C$\underline{H}_3$). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 136.8 (C-4), 135.0 (C-8), 128.9 (C-6), 127.1 (C-9), 120.2 (C-1), 119.5 (C-2), 105.3 (C-7), 99.0 (C-3), 63.3 (C-10a), 44.9 (C-10), 24.1 (8-$\underline{C}H_3$), 23.2 (10a-$\underline{C}H_3$), 22.1 (4-$\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%): 188 (15), 187 (100) [M^+], 186 (21), 173 (11), 172 (81) [$M^+ - CH_3$], 170 (12), 158 (13), 157 (28), 144 (16), 133 (11), 132 (95), 131 (15), 116 (8), 108 (35), 107 (43) [C_7H_9N], 81 (12), 80 (22), 79 (35) [C_5H_5N], 77 (19), 65 (12). - $C_{13}H_{17}N$: calcd. 187.1361, found 187.1361 (HRMS).

2,4,8,10a-Tetramethyl-10,10a-dihydropyrido[1,2-*a*]azepine (8j): According to the general procedure the reaction of **6j** [218 mg, 0.77 mmol; (*Z*/*E*= 5:2)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 2:1) 19 mg of **8j** [17%, related to (*Z*)-**6j**] as a dark-red oil; R_f = 0.68 (cyclohexane/ ethyl acetate 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.47 (d, 1H, 6-H, $^3J_{6,7}$ = 10.2 Hz), 5.42 (m_c, 1H, 9-H, $^3J_{9,10}$ = 7.6 Hz), 4.89 (s, 1H, 1-H), 4.80 (dd, 1H, 7-H, $^3J_{7,6}$ = 10.2 Hz, $^3J_{7,C\underline{H}3}$ = 1.3 Hz), 4.76 (s, 1H, 3-H), 2.22 (d, 2H, 10-H, $^3J_{10,9}$ = 7.6 Hz), 2.00 (s, 3H, 4-C$\underline{H}_3$), 1.87 (s, 3H, 2-C$\underline{H}_3$), 1.70 (d, 3H, C$\underline{H}_3$, $^3J_{C\underline{H}3,7}$ = 1.3 Hz),

0.89 (s, 3H, 10a-C$\underline{H}_3$). - **MS** (70 eV, EI), m/z (%): 202 (33), 201 (86) [M^+], 200 (38), 186 (82) [$M^+ - CH_3$], 146 (98), 122 (62) [$C_7H_{12}N^+$], 121 (67) [$C_7H_{11}N$], 111 (33), 110 (69), 108 (31), 107 (53), 106 (38), 95 (41), 91 (39), 81 (38), 80 (58), 79 (73) [C_5H_5N], 77 (53), 56 (32). - $C_{14}H_{19}N$: calcd. 201.1517, found 201.1517 (HRMS).

8-Methyl-2-phenyl-10,10a-dihydropyrido[1,2-*a*]azepine (8k): According to the general procedure the reaction of **6k** [500 mg, 1.58 mmol; (*Z*/*E*= 11:1)] gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 2:1) 241 mg of **8k** [70%, related to (*Z*)-**6k**] as an oil; R_f = 0.89 (cyclohexane/ ethyl acetate 1:1).

IR (CCl_4): 2030 (br.), 2005 (br.), 1640, 1597, 1577, 1445 (br.), 1275, 1245, 1192, 1138, 860, 695 cm^{-1}. - **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.45-7.41 (m, 2 H, *ortho*-Ph-H), 7.37-7.30 (m, 2 H, *meta*-Ph-H), 7.29-7.23 (m, 1 H, *para*-Ph-H), 6.34 (d, 1 H, 4-H, $^3J_{4,3}$ = 7.6 Hz), 6.29 (d, 1 H, 6-H, $^3J_{6,7}$ = 9.1 Hz), 5.91 (s, 1 H, 4-H), 5.68 (dm, 1 H, 9-H, $^3J_{9,10'}$ = 8.6 Hz), 5.65 (dm, 1 H, 1-H, $^3J_{1,10a}$ = 4.6 Hz), 5.18 (dd, 1 H, 3-H, $^3J_{3,4}$ = 7.6 Hz, $^4J_{3,1}$ = 1.9 Hz), 4.93 (d, 1 H, 7-H, $^3J_{7,6}$ = 9.3 Hz), 3.89 (dd, 1 H, 10a-H, $^3J_{10a,10''}$ = 5.1 Hz, $^3J_{10a,1}$ = 4.6 Hz), 2.59 (dd, 1 H, 10'-H, $^2J_{10',10''}$ = 16.9 Hz, $^3J_{10',9}$ = 8.6 Hz), 2.25 (dm, 1 H, 10''-H, $^2J_{10'',10'}$ = 16.9 Hz),1.91 (dd, 3 H, C$\underline{H}_3$, $^4J_{8\text{-}C\underline{H}3,9}$ = 1.9 Hz). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 139.7 (C-1'), 132.9 (C-2), 132.4 (C-8), 132.3 (C-6), 132.1 (C-4), 128.5 (C-4'), 127.4 (C-2'), 126.4 (C-3'), 125.57 (C-9), 117.9 (C-1), 106.0 (C-7), 96.8 (C-3), 59.6 (C-10a), 43.6 (C-10), 25.2 (8-$\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%): 235 (16) [M^+], 157 (13), 156 (100) [$C_{11}H_{10}N^+$], 155 (6), 154 (6), 128 (8), 127 (6), 118 (5), 102 (6), 81 (7), 80 (83) [$C_5H_6N^+$], 79 (57) [py], 78 (23), 77 (30), 76 (6), 65 (13), 64 (5), 63 (9), 57 (5). - $C_{17}H_{17}N$: calcd. 235.1361, found 235.1364 (HRMS).

(2*Z*)-3-Methyl-5-phenyl-2-penten-4-yn-ol (10): To the stirred solution of iodobenzene (19.29 g, 94.6 mmol) and (*Z*)-3-methyl-2-penten-4-yn-1-ol (**9**) (10.0 g, 104.0 mmol) at r.t. was added first 1.825 g of $PdCl_2(PPh_3)_2$ (2.5 mol %, 2.6 mmol), and after 10 min 190.5 mg of CuI (1 mol %, 1.04 mmol). After continued stirring for 2 h the mixture was filtrated over Al_2O_3 (N, III), and the solution was concentrated in vacuo. Flash chromatography of the dark red-brown residue (SiO_2, cyclohexane/ethyl acetate 10:1) afforded 15.1 g (93%) of **10** as an orange liquid.

IR (CCl_4): 3615 (OH st), 3470 (br., OH), 2920, 2880, 2210 (w., C≡C st), 1595, 1490, 1442, 1350, 1068, 1000 (br., C=C δ oop), 942, 690 cm^{-1}. - **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 7.50-7.39 (m, 2H, *ortho*-Ph-H), 7.38-7.28 (m, 3H, *para*/*meta*-Ph-H), 5.93 (tq, 1H, 2-H, $^3J_{2,1}$ = 6.8 Hz, $^4J_{2,C\underline{H}3}$ = 1.4 Hz), 4.41 (dd, 1H, 1-H, $^3J_{1,2}$ = 6.8 Hz, $^5J_{1,C\underline{H}3}$ = 0.9 Hz), 1.98 (dt, 3H, C$\underline{H}_3$, $^4J_{C\underline{H}3,2}$ = 1.4 Hz, $^5J_{C\underline{H}3,1}$ = 0.9 Hz), 1.68 (s, br., 1H, O$\underline{H}$). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 135.8 (C-2'), 131.6 (C-2), 128.4 (C-4'), 128.4 (C-3'), 123.2 (C-1'), 121.0 (C-3), 94.5 (C-5), 87.5 (C-4), 61.6 (C-1), 23.2 ($\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%): 173 (7) [M^+ +1], 172 (52) [M^+], 171 (33), 157 (36) [$M^+ - CH_3$], 143 (13), 141 (11), 130 (9), 129 (80), 128 (100), 127 (31), 126 (9), 115 (29), 105 (9), 103 (10), 102 (28), 91 (8), 78 (9), 77 (27). - $C_{12}H_{12}O$: calcd. 172.0888, found 172.0887 (HRMS).

(2Z,4Z)-3-Methyl-5-phenyl-2,4-pentadien-1-ol (11):To the suspension of activated zinc[16] (freshly prepared from 30 g of Zn-powder) in 180 ml of methanol/water (1:1) was added **9** (7.00 g, 40.6 mmol), and the mixture was refluxed until completion of the reaction (^{1}H-NMR, ca. 22 h). After filtration the residue was washed with methanol (50 ml) and water (50 ml). The organic solvents were then removed in *vacuo*, and the resulting aqueous solution was extracted with diethyl ether (4 x 50 ml), The combined organic phase was dried ($MgSO_4$) and then concentrated. Purification of the residue by flash chromatography (SiO_2, cyclohexane/ethyl acetate 10:1) gave 6.23 g (88%) **11** as a yellow liquid.

IR (CCl_4): 3620 (OH st), 3585, 3460 (br.), 3005, 2930, 1495, 1450, 1375, 1075, 995 (br), 695 cm^{-1}.- **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.34-7.24 (m, 4H, *ortho*/*meta*-Ph-H), 7.23-7.17 (m, 1H, *para*-Ph-H), 6.49 (d, 1 H, 5*cis*-H, $^3J_{5cis,4}$ = 11.8 Hz), 6.04 (d, 1 H, 4-H, $^3J_{4,5cis}$ = 11.8 Hz), 5.44 (tq, 1H, 2-H, $^3J_{2,1}$ = 6.7 Hz, $^4J_{2,C\underline{H}3}$ = 1.3 Hz), 3.89 (d, 1H, 1-H, $^3J_{1,2}$ = 6.7 Hz), 1.87 (d, 3H, C$\underline{H}_3$, $^4J_{C\underline{H}3,2}$ = 1.3 Hz), 0.96 (s, br.,

1H, OH). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 137.3 (C-3), 135.7 (C-1'), 130.7 (C-5), 129.3 (C-2), 128.5 (C-4), 128.4 (C-3'), 127.4 (C-4'), 126.7 (C-2'), 60.7 (C-1), 23.0 ($\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%): 174 (70) [M^+], 159 (38) [M^+ - CH_3], 157 (13), 156 (78) [M^+ - H_2O], 155 (11), 145 (14), 144 (16), 143 (100) [M^+ - CH_3O], 142 (19), 141 (69), 131 (53), 130 (12), 129 (49), 128 (92), 127 (25), 118 (12), 117 (23), 116 (13), 115 (53), 105 (23), 104 (49), 103 (14), 91 (82), 77 (19). - $C_{12}H_{14}O$: calcd. 174.1045, found 174.1045 (HRMS).

(1*Z*, 3*Z*)-5-Bromo-3-methyl-1-phenyl-1,3-pentadiene (12): To the stirred solution of **11** (4.7 g, 27.0 diethyl ether mmol) in 70 ml of dry and 0.15 ml of pyridine under N_2 at -70 °C is added dropwise the solution of phosphorus tribromide (3.16 g, 11.7 mmol) in 6 ml of dry diethyl ether (T< -60 °C). Stirring is continued until complete conversion. (tlc, ca. 3 h). The mixture was then warmed up to -20 °C, hydrolyzed with 30 ml of ice/water and extracted with diethyl ether. After washing with saturated aqueous $NaHCO_3$ (4 x 20 ml) and NaCl solutions (3 x 20 ml) the combined oragnic phases were dried ($MgSO_4$) and concentrated. Purification of the residue by flash chromatography (Al_2O_3, neutral, activity I) gave 3.9 g (55%) of **12** as a bright-yellow, lachrymatory liquid.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.38-7.16 (m, 5H, Ph-H), 6.54 (d, 1H, 2-H, $^3J_{x,y}$ = 11.9 Hz), 6.13 (d, 1H, 1-H, $^3J_{x,y}$ = 11.9 Hz), 5.58 (tq, 1H, 4-H, $^3J_{4,5}$ = 8.1 Hz, $^4J_{4,C\underline{H}3}$ = 1.3 Hz), 3.86 (d, 2H, 5-H, $^3J_{5,4}$ = 8.1 Hz), 1.87 (d, 3H, $C\underline{H}_3$, $^4J_{C\underline{H}3,4}$ = 1.3 Hz).

1-[(*2'Z*, *4'Z*)-3'-Methyl-5'-phenyl-pentadien-1'-yl] pyridinium bromide (13a): According to the general procedure for quarternization of pyridines (see above) **4a** (400 mg, 5.06 mmol) and **12** (1.200 g, 5.06 mmol) in 5 ml of acetonitrile afforded after 2d at r.t. 1.52 g (99%) of **13a** as a colorless solid.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.82 (pd, 2 H, 2-H, $^3J_{2,3}$ = 5.8 Hz), 8.40 (pt, 1 H, 4-H, $^3J_{4,3}$ = 7.3 Hz), 7.89 (pdd, 2 H, 3-H, $^3J_{3,2}$ = 5.8 Hz, $^3J_{3,4}$ = 7.3 Hz), 7.29-7.20 (m, 5 H, Ph-H), 6.64 (d, 1 H, 4'-H, $^3J_{4',5'}$ = 12.2 Hz), 6.19 (d, 1 H, 5'-H, $^3J_{5',4'}$ = 12.2 Hz), 5.72 (t, 1 H, 2'-H, $^3J_{2',1'}$ = 7.3 Hz), 5.30 (d, 2 H, 1'-H, $^3J_{1',2'}$ = 7.3 Hz), 2.04 (s, 3 H, $C\underline{H}_3$).

1-[(*2'Z*, *4'Z*)-3'-Methyl-5'-phenyl-pentadien-1'-yl]-4-phenylpyridinium bromide (13b): According to the general procedure for quarternization of pyridines (see above) **4k** (654 mg, 4.21 mmol) and **12** (998 mg, 4.21 mmol) in 5 ml of acetonitrile afforded after 2d at r.t. 1.43 g (86%) of **13b** as a beige solid.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.86 (d, 2H, 2-/6-H, $^3J_{2,3}$ = 6.9 Hz), 8.00 (d, 2H, 3-/5-H, $^3J_{2,3}$ = 6.9 Hz), 7.76-7.68 (m, 2H, *o*-4-Ph-H), 7.60-7.51 (m, 3H, *p*-4-Ph-H, *m*-4-Ph-H), 7.28-7.16 (m, 5H, 5'-Ph-H), 6.64 (d, 1H, 5'-H, $^3J_{5',4'}$ = 12.6 Hz), 6.21 (d, 1H, 4'-H, $^3J_{4',5'}$ = 12.6 Hz), 5.76 (t, 1H, 2'-H, $^3J_{2',1'}$ = 7.3 Hz), 5.23 (d, 2H, 1'-H, $^3J_{1',2'}$ = 7.3 Hz), 2.03 (s, 3H, $C\underline{H}_3$).

8-Methyl-10-phenyl-10,10a-dihydropyrido[1,2-*a*]azepine (15a): According to the general procedure for the cyclization of pyridinium bromides (see above) the reaction of **13a** (330 mg, 1.04 mmol) gave after flash chromatography of the raw material (SiO_2, cyclohexane/ ethyl acetate 3:1) 179 mg of **15a** (73%) as a dark orange-red oil; R_f = 0.71 (cyclohexane/ethyl acetate 1:1).

IR (CCl_4): 3025 (=CH– st), 2455, 1640 (C=C st), 1600 (C=C st), 1568 (br.), 1490, 1450, 1255, 1200, 1135, 920, 895, 695 (=CH–) cm^{-1}. - **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.17-7.07 (m, 3 H, *ortho*-Ph-H, *para*-Ph-H), 6,97 (dm, 2 H, *meta*-Ph-H, ^3J = 7.4 Hz), 6.28 (d, 1 H, 6-H, $^3J_{6,7}$ = 8.9 Hz), 5.98 (d, 1 H, 9-H, $^3J_{9,10'}$ = 8.2 Hz), 5.91 (d, 1 H, 4-H, $^3J_{4,3}$ = 6.9 Hz), 5.86 (dd, 1 H, 2-H, $^3J_{2,1}$ = 9.5 Hz, $^3J_{2,3}$ = 6.1 Hz), 5.48 (dd, 1 H, 1-H, $^3J_{1,2}$ = 9.5 Hz, $^3J_{1,10a}$ = 4.4 Hz), 5.00 (d, 1 H, 7-H, $^3J_{7,6}$ = 8.9 Hz), 4.36 (dd, 1 H, 3-H, $^3J_{3,2}$ = 6.1 Hz, $^3J_{3,4}$ = 6.9 Hz), 4.01 (d, 1 H, 10a-H, $^3J_{10a,1}$ = 4.4 Hz), 3.73 (d, 1 H, 10'-H, $^3J_{10',9}$ = 8.2 Hz), 2.01 (s, 3 H, $C\underline{H}_3$). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 139.6 (C-1'), 133.9 (C-8), 133.1 (C-6), 132.0 (C-4), 130.7 (C-2'), 129.4 (C-3'), 127.2 (C-4'), 126.3 (C-9), 122.0 (C-1), 119.8 (C-2), 105.9 (C-7), 96.5 (C-3), 62.2 (C-10a), 59.4 (C-10), 26.3 ($\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%): 235 (23) [M^+], 157 (13), 156 (100) [M^+ – C_5H_5N], 155 (35), 154 (5), 153 (7), 142 (6), 141 (43), 129 (10), 128 (17), 127 (6),

115 (27), 91 (22), 80 (54) [C_5H_5N-H^+], 79 (7) [$C_5H_5N^+$], 78 (13), 77 (10). - $C_{17}H_{17}N$: calcd. 235.1361, found 235.1360 (HRMS).

8-Methyl-2,10-diphenyl-10,10a-dihydropyrido[1,2-*a*]azepine (15b): According to the general procedure for the cyclization of pyridinium bromides **6** (see above) the reaction of **13b** (359 mg, 0.92 mmol) gave after flash chromatography of the raw material (SiO_2, cyclohexane/ethyl acetate 3:1) 215 mg of **15b** (75%) as a dark red-yellow wax; R_f = 0.71 (cyclohexane/ethyl acetate 1:1).

IR (CCl_4): 3030 (=CH– st), 2860, 1640 (C=C st), 1575, 1455, 1280, 1250, 1200, 900, 700 (=CH–) cm^{-1}.- **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.39-7.23 (m, 5H, (C-2)-Ph-H), 7.15-7.04 (m, 3H, (C-10)-*o*/*p*-Ph-H), 6.98-6.94 (m, 2H, (C-10)-*m*-Ph-H), 6.34 (d, 1H, 6-H, $^3J_{6,7}$ = 9.5 Hz), 6.04 (d, 1H, 9-H, $^3J_{9,10}$ = 8.4 Hz), 6.03 (d, 1H, 4-H, $^3J_{4,3}$ = 7.8 Hz), 5.69 (dm, 1H, 1-H, $^3J_{1,10a}$ = 4.8 Hz), 5.06 (dd, 1H, 7-H, $^3J_{7,6}$ = 9.5 Hz, $^3J_{7,CH3}$ = 1.1 Hz), 4.69 (dd, 1H, 3-H, $^3J_{3,4}$ = 7.8 Hz, $^3J_{3,1}$ = 2.0 Hz), 4.13 (d, 1H, 10a-H, $^3J_{10a,1}$ = 4.8 Hz), 3.86 (d, 1H, 10-H, $^3J_{10,9}$ = 8.4 Hz), 2.04 (d, 3H, C$\underline{H}_3$, $^3J_{CH3,7}$ = 1.1 Hz). - **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 140.1 (C-1''), 139.4 (C-1'), 134.4 (C-2), 133.4 (C-8), 133.3 (C-6), 132.5 (C-4), 130.77 (C-Ph), 129.3 (C-Ph), 128.5 (C-Ph), 127.4 (C-Ph), 127.2 (C-Ph), 126.4 (C-Ph), 125.6 (C-9), 116.1 (C-1), 106.5 (C-7), 97.4 (C-3), 62.2 (C-10a), 59.6 (C-10), 26.3 ($\underline{C}H_3$). - **MS** (70 eV, EI), m/z (%): 311 (9) [M^+], 158 (17), 157 (100) [M^+ – 2 C_6H_5], 156 (32) [M^+ – (C_6H_5)-C_5H_5N], 155 (16), 143 (27), 129 (8), 128 (18), 127 (9), 115 (25), 104 (5), 94 (20), 80 (17) [C_5H_5N-H^+], 79 (15) [$C_5H_5N^+$], 63 (6). - $C_{23}H_{21}N$: calcd. 311.1674, found 311.1674 (HRMS).

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