Allenes as the π-Component in Electrocyclization Reactions: Transformation of 1,3,4-Pentatrienyl Azomethine Ylides into Seven-Membered Heterocycles

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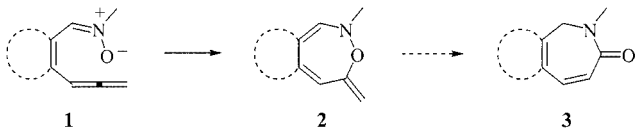
Upon treatment of the pyridinium bromides **8a–c**, obtained by quaternization of pyridines **7** with the allyl bromide **6**, with base, the annulated methylene pyridoazepines **10a–c** are formed. The reaction pathway includes base-catalysed propargyl-allene isomerization and dipole formation as the first steps followed by the ring closure of [**9**] to **10**. The latter process represents the first example of the participation of an allene unit in 1,7-electrocyclization reactions of extended azomethine ylides.

Introduction

Recent work on the high yield production of the annulated dihydroazepine-3-one derivatives **3** from the 1,3,4-pentatrienyl nitrones **1** (Scheme 1) has shown for the first time that allene units are able to participate in eight-electron dipolar cyclization reactions.[1] The ring closure represents the key step, and takes place under unusually mild conditions (room temperature) giving labile methylidene oxazepine intermediates **2** as primary products which undergo a straightforward transformation to the final heterocycles **3**.

In continuation of the above studies, investigations were performed to find out if azomethine ylides can likewise be used as a dipolar functionality for analogous ring-forming reactions. The general scope of 1,5- and 1,7-electrocyclization of conjugated azomethine ylides is less broad than for many other dipolar systems.[2,3] However, it has been shown that with appropriately structured pyridinium ylides as representatives of extended 2-aza-heptatrienyl dipoles, ring-forming reactions yielding dihydroazepine derivatives take place with high efficiency.[4,5] In these cases the high periselectivity of the reaction mode of the delocalised π-system, i.e. the exclusive 1,7- vs. 1,5-ring closure, could be further rationalized by quantum mechanical calculations. Here, both the kinetic and the thermodynamic data favour the 8π-process.[6]



Scheme 1

Here we present our results for the allenyl derivatives [**9a–c**] formed by concomitant deprotonation (e.g. ylide formation) and base-catalysed tautomerization[7] of the corresponding propargyl precursors **8**.[8]

Results and Discussion

The new cycloimmonium bromides **8a–c** were obtained in 72–87% overall yield from the aldehyde **4**[8] in three steps, namely by (i) sodium borohydride reduction to **5**, (ii) bromide substitution with PBr_3 to **6**, and (iii) quaternization of the pyridine derivatives **7** (Scheme 2). Their structures were confirmed by the spectroscopic and analytical data (see Exp Sect.).

As the base-catalyzed tautomerization of propynes has already been successfully exploited for the generation of the pentatrienyl nitrones **1**,[1] similar conditions were explored for the transformation **8**→[**9**]. The latter step requires a base for both the dipole and allene formation. Although even potassium carbonate was able to induce the desired processes, higher product yields were obtained with sodium methoxide using a small amount of methanol as solvent. In the case of the unsubstituted system **8a** the colour of the mixture immediately turned to bright yellow, indicating the formation of the ylide. The precipitation of a beige amorphous solid occurred which, after ca. 9 h, was collected in 71% yield and identified as the bisannulated methylidene pyridoazepine **10a**. Extraction of the filtrate with diethyl ether and work up delivered a further product in up to 9% yield; according to the MS (m/z = 180) and the ^{1}H NMR spectro-

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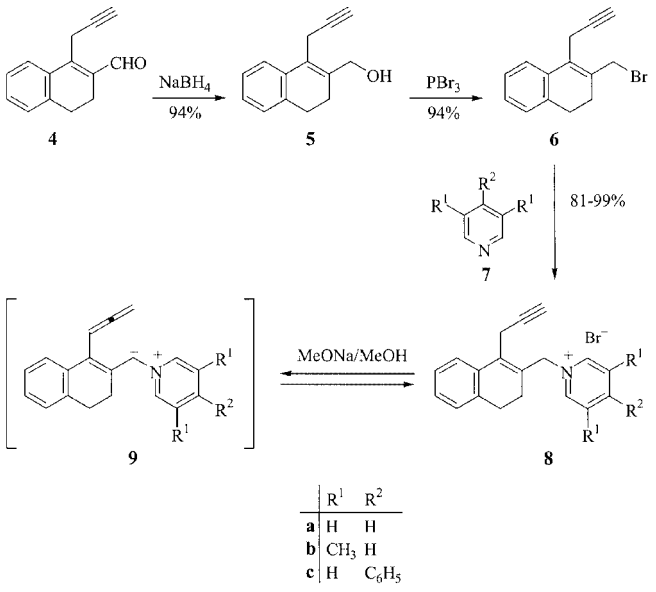
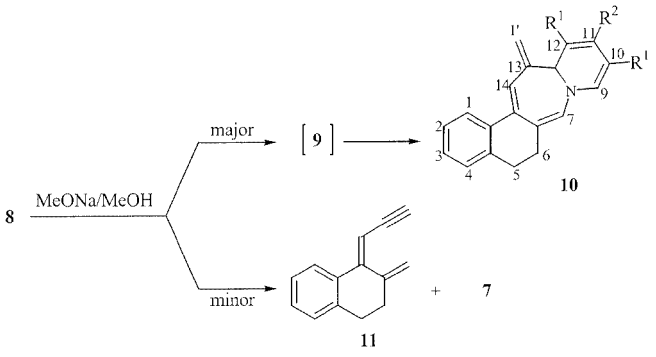


Scheme 2



Scheme 3

scopic data, it was identified as the bismethylidene dihydronaphthaline **11** (Scheme 3). Similar 1,4-eliminations are known for some other quaternary ammonium salts.[9]

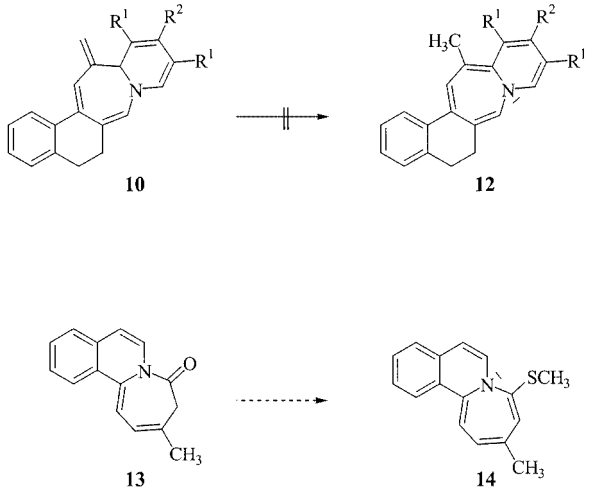
The structural characterization of **10a** is mainly based on the ^{1}H and ^{13}C NMR spectroscopic data, including extensive decoupling and NOE experiments which allow the unambiguous assignment of the aliphatic and olefinic protons. Of special importance are the doublets of the methylene protons at C-1′ with the typically small geminal coupling constant of J = 1.5 Hz. The significant difference of the δ-values ($\delta_{1'\text{-Ha}/1'\text{-Hb}}$ = 4.45/6.02) is due to the fact that the proton 1′-H_b suffers a paramagnetic shift caused by the in-plane 14-C double bond arrangement. Additional confirmation of this particular =CH_2 unit comes from the ^{13}C signal at δ = 120.9 ppm identified as a secondary carbon atom. Characteristic low field values are found for H-7 [δ = 6.65 ppm (s)], H-9 [δ = 6.28 ppm (dd, $J_{9,10}$ = 7.0 Hz, $J_{9,11}$ = 0.9 Hz)] and H-12a [δ = 3.96 ppm (d, $J_{12a,12}$ = 5.2 Hz)], which are all α to the bridgehead nitrogen. The chemical shift and the coupling constants of the dihydropyridine protons at C-9, C-10 and C-11 are in perfect agreement with related structures[4,6] (see Exp. Sect.).

The structure of the minor component **11** is likewise deduced from spectroscopic investigations. Evidence for the alkyne moiety comes from both the IR ($\nu_{\equiv C\text{-}H}$ = 3155, $\nu_{C\equiv C}$ = 2255 cm^{-1}) and the ^{1}H NMR spectra [δ = 3.35 ppm (d, $J_{3',1'}$ = 2.7 Hz)]. According to the NOE results the alkyne group has a *cis* geometry with respect to the double bond at C-1; there is no indication for the formation of the other isomer.

Under the conditions described above, the methyl and phenyl derivatives **8b**, **c** underwent the same overall transformation, yielding the pyridoazepines **10b** and **10c**, respectively. The yields, however, were lower (56 and 57%, respectively) and only traces of the fragmentation product **11** could be detected by ^{1}H NMR spectroscopy.

From a mechanistic point of view the formation of the tetracyclic compounds **10** can be explained by a three-step sequence including a propargyl-allene isomerization, deprotonation with formation of the aza dipole [**9**] and subsequent 8π-electrocyclization. There is no obvious criterion for deciding the relative order of the first two steps. It should be mentioned that the product forming process [**9**] → **10** represents the first example of the 1,7-electrocyclization of an azomethine ylide onto an allene moiety.

A further point deserves consideration: The pyridoazepine derivatives **10** could serve as precursors for the tautomeric structure **12**, which is of interest because of its 12π-parameter representing a potentially antiaromatic system.[10,11] However, neither under the basic conditions of the transformation nor upon separate treatment of solutions of **10a** in methanol with an excess of sodium methoxide, sodium hydroxide or potassium carbonate at room temperature, any indications for the presence of **12a** were obtained. Therefore the conclusion can be drawn that the formation of **12** did not take place at all, or that rapid decomposition of the supposedly highly unstable heterocycle had occurred (Scheme 4).[12] Although some efforts have been made in the past for synthesizing such pyridoazepines, up to now only the existence of the thioether **14**, obtained by a three step sequence from the benzoazepinone **13**, has been proven by means of spectroscopic methods.[12]



Scheme 4

Conclusion

The base-induced transformation of the pyridinium bromides **8a−c** into the annulated methylene-pyridoazepines **10a−c** was successfully achieved, thus representing the first example of the participation of an allene moiety in a 1,7-electrocyclization involving a conjugated azomethine ylide. No evidence for the formation of the 12π-antiaromatic system **12** from **10** was found.

Experimental Section

General: Melting points are uncorrected. IR: Perkin−Elmer 257 Infracord. ^{1}H NMR: Bruker WM 250 (250 MHz), WM 400 (400 MHz), and DRX 500 (500 MHz). ^{13}C NMR: Bruker WM 400 (100 MHz) and DRX 500 (125 MHz); $CDCl_3$ as solvent and TMS as internal standard. MS: Finnigan MAT 44 S (70 eV) with Datasystem MAT SS 200. Elemental analyses: Perkin−Elmer Elemental Analyzer 240. Flash chromatography: silica gel (Silica 32−36, ICN).

(3′,4′-Dihydro-1′-prop-2′′-ynylnaphthalen-2′-yl)methanol (5): A solution of **4**[8] (1.69 g, 8.60 mmol) in dry methanol (60 mL) was treated with sodium borohydride (163 mg, 4.30 mmol) at 0 °C. The stirred solution was allowed to warm up to room temp. for 2 h, ca. 30 mL of the methanol were distilled off, the resulting solution was poured onto aqueous NH_4Cl (1:1) and the mixture was extracted with diethyl ether (3 × 25 mL). The combined organic phase was washed with brine, dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 10:1) yielded **5** (1.59 g, 94%) as colourless crystals. M.p. 104−105 °C ($CHCl_3$). IR (CCl_4): ṽ = 3615 (O−H), 3310 (≡C−H), 3060, 3015, 2940, 2880, 2830, 2115 (C≡C), 1490, 1450, 1375, 1045 cm^{-1}. ^{1}H NMR (250 MHz): δ = 1.73 (s, 1 H, OH), 2.04 (t, $^4J_{3'',1''}$ = 2.7 Hz, 1 H, 3′′-H), 2.42 (t, $^3J_{3',4'}$ = 7.8 Hz, 2 H, 3′-H), 2.72 (t, $^3J_{4',3'}$ = 7.8 Hz, 2 H, 4′-H), 3.44 (d, $^4J_{1'',3''}$ = 2.7 Hz, 2 H, 1′′-H), 4.39 (s, 2 H, 1-H), 7.10−7.28 (m, 3 H, Ar-H), 7.46 (m, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = 17.2 (C-1′′), 26.2 (C-3′/4′), 28.3 (C-3′/4′), 63.3 (C-1), 69.0 (C-3′′), 82.8 (C-2′′), 123.6 (Ar-C), 126.6 (Ar-C), 127.2 (Ar-C), 127.4 (Ar-C), 128.3 (C_q), 134.6 (C_q), 136.2 (C_q), 137.0 (C_q) ppm. MS (70 eV, EI): *m*/*z* (%) = 198 (94) [M$^+$], 179 (54), 165 (100), 159 (87), 141 (70), 128 (84). HRMS ($C_{14}H_{14}O$): calcd. 198.1045; found 198.1042.

3′-Bromomethyl-1′,2′-dihydro-4′-prop-2′′-ynylnaphthalene (6): A solution of **5** (1.59 g, 8.04 mmol) in dry diethyl ether (50 mL) was treated with phosphorus tribromide (1.09 g, 4.02 mmol) and pyridine (4 drops). After stirring for 3.5 h at room temperature the white suspension was hydrolysed with water and extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with saturated $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 20:1) yielded **6** (1.97 g, 94%) as colourless crystals. M.p. 54−55 °C (diethyl ether). IR (CCl_4): ṽ = 3310 (≡C−H), 3065, 3020, 2935, 2890, 2835, 2115 (C≡C), 1490, 1450, 1235, 1200, 1040 cm^{-1}. ^{1}H NMR (250 MHz): δ = 2.05 (t, $^4J_{3'',1''}$ = 2.8 Hz, 1 H, 3′′-H), 2.45 (t, $^3J_{2,1}$ = 7.8 Hz, 2 H, 2-H), 2.81 (t, $^3J_{1,2}$ = 7.8 Hz, 2 H, 1-H), 3.45 (d, $^4J_{1'',3''}$ = 2.8 Hz, 2 H, 1′′-H), 4.25 (s, 2 H, 1′-H), 7.10−7.29 (m, 3 H, Ar-H), 7.49 (m_c, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = 18.0 (C-1′′), 27.3 (C-1/2), 28.3 (C-1/2), 33.8 (C-1′), 69.3 (C-3′′), 81.4 (C-2′′), 123.9 (Ar-C), 126.7 (Ar-C), 127.5 (Ar-C), 127.7 (Ar-C), 130.9 (C_q), 133.7 (C_q), 134.3 (C_q), 136.1 (C_q) ppm. MS (70 eV, EI): *m*/*z* (%) = 262 (11) [M$^+$, for ^{81}Br], 260 (22) [M$^+$, for ^{79}Br], 181 (84) [M − Br]$^+$, 179 (65), 165 (100), 152 (22). $C_{14}H_{13}Br$ (261.16): calcd. C 64.39, H 5.02; found C 64.17, H 4.96.

1-[(3′′,4′′-Dihydro 1′′-prop-2′′′-ynylnaphthalen-2′′-yl)methyl]pyridinium Bromide (8a): A mixture of **6** (1.25 g, 4.79 mmol) and pyridine (454 mg, 5.74 mmol) in dry acetonitrile (5 mL) was stirred for 3 days at room temperature. After addition of dry diethyl ether a brownish viscous oil separated which was dissolved in a minimum amount of dry acetonitrile. On repeated addition of dry diethyl ether **8a** (1.61 g, 99%) was obtained as beige crystals. M.p. 178−180 °C (acetonitrile). IR (PTFE): ṽ = 3420 (≡C−H), 3195, 3025, 2935, 2830, 2190 (C≡C), 1630 (C=C), 1485, 1450, 1295, 1210, 1150 cm^{-1}. ^{1}H NMR (250 MHz): δ = 2.19 (t, $^4J_{3''',1'''}$ = 2.5 Hz, 1 H, 3′′′-H), 2.27 (t, $^3J_{3'',4''}$ = 7.8 Hz, 2 H, 3′′-H), 2.77 (t, $^3J_{4'',3''}$ = 7.8 Hz, 2 H, 4′′-H), 3.73 (d, $^4J_{1''',3'''}$ = 2.5 Hz, 2 H, 1′′′-H), 6.10 (s, 2 H, 1′-H), 7.13 (m, 1 H, Ar-H), 7.19−7.32 (m, 2 H, Ar-H), 7.54 (m_c, 1 H, Ar-H), 8.14 (m_c, 2 H, Ar-H), 8.58 (m, 1 H, Ar-H), 9.60 (m, 2 H, 2-H, 6-H) ppm. ^{13}C NMR (100 MHz): δ = 18.9 (C-1′′′), 26.1 (C-3′′/4′′), 27.6 (C-3′′/4′′), 63.2 (C-1′), 71.0 (C-3′′′), 81.5 (C-2′′′), 124.4 (Ar-C), 126.9 (Ar-C), 127.7 (Ar-C), 128.3 (C_q), 128.4 (Ar-C), 128.6 (Ar-C), 133.1 (C_q), 134.9 (C_q), 135.9 (C_q), 145.1 (C-2/6), 145.9 (C-2/6) ppm. $C_{19}H_{18}BrN$ (340.26): calcd. C 67.07, H 5.33, N 4.12; found C 66.74, H 5.22, N 3.89.

1-[(3′′,4′′-dihydro-1′′-prop-2′′′-ynylnaphthalen-2′′-yl)methyl]-3,5-dimethylpyridinium Bromide (8b): A mixture of **6** (500 mg, 1.91 mmol) and 3,5-dimethyl pyridine (246 mg, 2.30 mmol) in dry acetonitrile (2 mL) was stirred for 3 days at room temperature. After addition of a few mL of dry diethyl ether a pale yellow viscous oil precipitated. The oil was dissolved in a minimum amount of dry acetonitrile and treated with dry diethyl ether until separation occurred. After two repetitions **8b** (671 mg, 95%) was obtained as a pale yellow oil. IR (PTFE): ṽ = 3010, 2930, 2825, 1625 (C=C), 1495, 1450, 1295, 1205, 1155, 1045 cm^{-1}. ^{1}H NMR (250 MHz): δ = 2.16 (t, $^4J_{3''',1'''}$ = 2.7 Hz, 1 H, 3′′′-H), 2.24−2.35 (m, 4 H, 3′′-H, 4′′-H), 2.57 (s, 3 H, Ar-CH3), 2.59 (s, 3 H, Ar-CH3), 3.69 (d, $^4J_{1''',3'''}$ = 2.7 Hz, 2 H, 1′′′-H), 5.80 (s, 2 H, 1′-H), 6.84 (s, 1 H, 4-H), 7.02−7.29 (m, 3 H, Ar-H), 7.56 (m, 1 H, Ar-H), 9.24 (m, 2 H, 2-H, 6-H).

4-Phenyl-1-[(3′′,4′′-dihydro-1′′-prop-2′′′-ynylnaphthalen-2′′-yl)-methyl]pyridinium Bromide (8c): A mixture of **6** (500 mg, 1.91 mmol) and 4-phenylpyridine (357 mg, 2.30 mmol) in dry acetonitrile (2 mL) was stirred for 3 days at room temperature. After addition of some drops of dry diethyl ether, a pale yellow viscous oil precipitated. The oil was dissolved in a minimum amount of dry acetonitrile and then treated with dry diethyl ether until precipitation of **8c** (649 mg, 81%) occurred as a colourless solid. M.p. 179−180 °C (acetonitrile, decomp.). IR (PTFE): ṽ = 3025, 2935, 2830, 1635, 1555, 1490, 1470, 1435, 1215, 1155 cm^{-1}. ^{1}H NMR (250 MHz): δ = 2.19 (d, $^4J_{3''',1'''}$ = 2.8 Hz, 2 H, 3′′′-H), 2.31 (t, $^3J_{3'',4''}$ = 7.8 Hz, 2 H, 3′′/4′′-H), 2.77 (t, $^3J_{3'',4''}$ = 7.8 Hz, 2 H, 3′′/4′′-H), 3.74 (d, $^4J_{3''',1'''}$ = 2.8 Hz, 1 H, 1′′′-H), 6.06 (s, 2 H, 1′-H), 7.11 (m_c, 1 H, Ar-H), 7.24 (m_c, 2 H, Ar-H), 7.50−7.61 (m, 4 H, Ar-H), 7.77−7.84 (m, 2 H, Ar-H), 8.24 (d, $^3J_{o\text{-}Ar\text{-}H}$ = 7.1 Hz, 2 H, 3-H, 5-H), 9.62 (d, $^3J_{o\text{-}Ar\text{-}H}$ = 7.1 Hz, 2 H, 2-H, 6-H) ppm. ^{13}C NMR (100 MHz): δ = 18.9 (C-1′′′), 26.2 (C-3′′/4′′), 27.7 (C-3′′/4′′), 62.4 (C-1′), 70.9 (C-3′′′), 81.7 (C-2′′′), 124.4 (Ar-C), 124.9 (Ar-C), 126.9 (Ar-C), 127.7 (Ar-C), 127.9 (Ar-C), 128.5 (Ar-C), 128.7 (C_q), 130.0 (Ar-C), 133.3 (C_q), 133.6 (C_q), 134.6 (C_q), 136.0 (C_q), 145.2 (C-2, C-4), 156.7 (C_q) ppm. $C_{25}H_{22}BrN$ (416.35): calcd. C 72.12, H 5.33, N 3.36; found C 71.94, H 5.28, N 3.18.

13-Methylene-5,6,12a,13-tetrahydronaphtho[1,2-*e*]pyrido[1,2-*a*]-azepine (10a): Upon treatment of a colourless solution of **8a**

(100 mg, 0.29 mmol) in dry methanol (1 mL) with sodium methoxide (25 mg, 0.46 mmol) the colour of the reaction mixture immediately changed to bright yellow, followed by slow precipitation of a solid. After stirring this mixture for 9 h at room temperature the mixture was filtered, yielding **10a** (53 mg, 71%) as a beige amorphous solid. The filtrate was treated with water and extracted with diethyl ether. The combined organic phase was washed with saturated NH_4Cl and brine, dried ($MgSO_4$) and concentrated in vacuo, leading to 1,2,3,4-tetrahydro-2-methylene-1-[(*E*)-prop-2′-ynylidene] naphthalene (**11**) (9 mg, 17%) as a dark yellow oil. **10a:** IR (PTFE): $\tilde{\nu}$ = 3055, 3020, 2930, 2835, 1615, 1590, 1560, 1525, 1435, 1380, 1250, 1150 cm^{-1}. ^1H NMR (250 MHz): δ = 2.47−2.54 (m, 2 H, 6-H), 2.77 (m_c, 2 H, 5-H), 3.96 (d, $^3J_{12a,12}$ = 5.2 Hz, 1 H, 12a-H), 4.45 (dd, ^2J = 1.5, J = 1.5 Hz, 1 H, 1′-Ha), 5.10 (ddd, $^3J_{10,9}$ = 7.0, $^3J_{10,11}$ = 5.8, $^4J_{10,12}$ = 1.2 Hz, 1 H, 10-H), 5.40 (dddd, $^3J_{12,11}$ = 9.5, $^3J_{12,12a}$ = 5.2, $^4J_{12,10}$ = 1.2, J = 1.2 Hz, 1 H, 12-H), 6.02 (dd, ^2J = 1.5, J = 1.5 Hz, 1 H, 1′-Hb), 6.23 (dddd, $^3J_{11,12}$ = 9.5, $^3J_{11,10}$ = 5.8, $^4J_{11,9}$ = 0.9, ^4J = 0.9 Hz, 1 H, 11-H), 6.28 (dd, $^3J_{9,10}$ = 7.0, $^4J_{9,11}$ = 0.9 Hz, 1 H, 9-H), 6.65 (s, 1 H, 7-H), 7.09−7.23 (m, 3 H, Ar-H), 7.31 (s, 1 H, 14-H), 7.52−7.58 (m, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 32.4 (C-5/6), 32.8 (C-5/6), 57.2 (C-12a), 98.9 (C-10), 115.2 (C_q), 115.5 (C-14), 120.9 (C-1′), 122.3 (C-11/12), 126.1 (C-11/12), 126.6 (Ar-C), 126.9 (Ar-C), 127.4 (Ar-C), 129.7 (Ar-C), 131.6 (C-7/9), 133.5 (C-7/9), 133.6 (C_q), 138.3 (C_q), 138.9 (C_q), 141.8 (C_q) ppm. MS (70 eV, EI): *m*/*z* (%) = 259 (23), 258 (7) [M^+], 180 (100) [$M - C_5H_4N]^+$, 178 (55), 165 (70), 152 (19). HRMS ($C_{19}H_{17}N$): calcd. 259.1361; found 259.1360.
11: IR (CCl_4): $\tilde{\nu}$ = 3155 (≡C−H), 2985, 2900, 2255 (C≡C), 1470, 1385, 1095, 900 cm^{-1}. ^1H NMR (250 MHz): δ = 2.57 (t, $^3J_{3,4}$ = 6.6 Hz, 2 H, 3-H), 2.88 (t, $^3J_{4,3}$ = 6.6 Hz, 2 H, 4-H), 3.35 (d, $^4J_{3',1'}$ = 2.7 Hz, 1 H, 3′-H), 5.38 (m_c, 1 H, 1′′-H_a), 6.04 (d,^2J = 1.5 Hz, 1 H, 1′′-H_b), 6.11 (d, $^4J_{1',3'}$ = 2.7 Hz, 1 H, 1′-H), 7.09−7.30 (m, 3 H, Ar-H), 7.55 (m_c, 1 H, Ar-H) ppm. MS (70 eV, EI): *m*/*z* (%) = 180 (58) [M^+], 179 (100), 165 (52), 152 (15), 105 (11), 44 (37). In a control experiment it was shown that the reaction of **8a** in methanol with an excess of potassium carbonate at room temperature likewise forms **10a**, albeit in lower yield (ca. 50%).

10,12-Dimethyl-13-methylene-5,6,12a,13-tetrahydronaphtho[1,2-*e*]-pyrido[1,2-*a*]azepine (10b): Upon treatment of a colourless solution of **8b** (320 mg, 0.87 mmol) in dry methanol (ca. 1 mL) with sodium methoxide (98 mg, 1.82 mmol) at room temperature the reaction mixture immediately heated up, the colour turned to a bright yellow, and a precipitate occurred. After this had been stirred for 24 h at room temperature the mixture was filtered, yielding **10b** (140 mg, 56%) as a bright orange amorphous solid. IR (CCl_4): $\tilde{\nu}$ = 3065, 3020, 2930, 2835, 1620, 1590, 1525, 1375, 1290, 1255, 1205 cm^{-1}. ^1H NMR (400 MHz): δ = 1.78 (d, 3J = 1.2 Hz, 3 H, CH_3), 1.81 (s, 3 H, CH_3), 2.44−2.53 (m, 2 H, 5/6-H), 2.71−2.79 (m, 2 H, 5/6-H), 3.78 (s, 1 H, 12a-H), 4.39 (t, ^2J = ^4J = 1.5 Hz, 1′-H_a), 5.67 (t, ^2J = ^4J = 1.5 Hz, 1′-H_b), 5.93 (s, 1 H, 9/11-H), 5.97 (s, 1 H, 9/11-H), 6.56 (s, 1 H, 7-H), 7.11 (m_c, 1 H, 4-H), 7.14−7.23 (m, 2 H, 2-H, 3-H), 7.26 (s, 1 H, 14-H), 7.58 (m, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz): δ = 17.9 (C-5/6), 21.6 (C-5/6), 31.6 (CH_3), 32.3 (CH_3), 61.7 (C-12a), 109.1 (C_q), 113.9 (C_q), 115.5 (C-1′), 122.9 (C-11), 123.4 (C-14), 125.9 (C_q), 126.1 (Ar-C), 126.6 (Ar-C), 126.8 (Ar-C), 127.4 (Ar-C), 131.6 (C-7/9), 133.1 (C-7/9), 134.2 (C_q), 138.2 (C_q), 138.7 (C_q), 139.0 (C_q) ppm. MS (70 eV, EI): *m*/*z* (%) = 287 (34) [M^+], 272 (8) [$M - CH_3]^+$, 180 (100), 165 (41), 152 (6), 108 (6). HRMS ($C_{21}H_{21}N$): calcd. 287.1674; found 287.1673.

13-Methylene-11-phenyl-5,6,12a,13-tetrahydronaphtho[1,2-*e*]-pyrido[1,2-*a*]azepine (10c): Upon treatment of a colourless solution of **8c** (100 mg, 0.24 mmol) in dry methanol (ca. 1 mL) with sodium methoxide (26 mg, 0.48 mmol) at room temperature the colour of the reaction mixture turned to dark green and then to bright yellow. After this had been stirred for 14 h at room temperature the mixture was filtered, yielding **10c** (46 mg, 57%) as a beige amorphous solid. IR (CCl_4): $\tilde{\nu}$ = 3060, 3025, 2935, 2840, 1620, 1565, 1530, 1450, 1275, 1240 cm^{-1}. ^1H NMR (250 MHz): δ = 2.42−2.62 (m, 2 H, 5/6-H), 2.72−2.89 (m, 2 H, 5/6-H), 4.08 (d, $^3J_{12a,12}$ = 5.5 Hz, 1 H, 12a-H), 4.50 (t, ^2J = ^4J = 1.4 Hz, 1 H, 1′-Ha), 5.47 (dd, $^3J_{10,9}$ = 7.3, $^4J_{10,12}$ = 1.8 Hz, 1 H, 10-H), 5.63 (m, $^3J_{12,12a}$ = 5.5 Hz, 1 H, 12-H), 6.02 (t, ^2J = ^4J = 1.4 Hz, 1 H, 1′-H_b), 6.47 (md, $^3J_{9,10}$ = 7.3 Hz, 1 H, 9-H), 6.71 (s, 1 H, 7-H), 7.10−7.23 (m, 4 H, Ar-H), 7.28−7.44 (m, 5 H, Ar-H), 7.54−7.60 (m, 3 H, Ar-H/14-H) ppm. ^{13}C NMR (100 MHz): δ = 31.4 (C-5/6), 32.5 (C-5/6), 57.6 (C-12a), 99.7 (C-10), 111.7 (C-1′), 116.0 (C_q), 121.0 (C-14), 125.8 (Ar-C), 126.7 (Ar-C), 127.0 (Ar-C), 127.5 (Ar-C), 131.2 (C-7/9), 133.6 (C-7/9), 133.7 (C_q), 134.6 (C_q), 138.4 (C_q), 139.0 (C_q), 139.6 (C_q), 142.3 (C_q) ppm. MS (70 eV. EI): *m*/*z* (%) = 335 (12) [M^+], 180 (100), 179 (46), 166 (69), 155 (12), 115 (8). HRMS ($C_{25}H_{21}N$): calcd. 335.1674; found 335.1675.

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