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SYNTHESIS OF 9,10-DIHYDRO-8bH-QUINO[1,2-f]PHENANTHRIDINE- AND 6-PHENYL-4,5,6,7-TETRAHYDROPYRIDO[3,2,1-j,k]-CARBAZOLE-DERIVATIVES

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Abstract—9,10 - dihydro - 8bH - quino[1,2-f]phenanthridine - derivatives **2** and 6 - phenyl - 4,5,6,7 - tetrahydropyrido[3,2,1 -j,k]carbazole - derivatives **17** were synthesized by photodehydrogenation of the 1,2 - diphenylquinoliniumperchlorates **7** and the 1,2 - diphenyl - 1,2,3,4 - tetrahydroquinolines **1** respectively.

The intermediate 1,2 - diphenylquinoliniumsalts **7** were obtained by Skraup-synthesis between diphenylamine and acrolein, followed by a Grignard-reaction and iodine/sodiumacetate oxidation. The intermediate tetrahydroquinoline derivatives **1** were prepared by two different routes, the key steps of which were respectively acid catalyzed cyclization of the corresponding 3 - (o - anilinophenyl) - 1 - phenyl - 1 - propanol - derivatives **16** and platinum(IV)oxide/palladium on activated carbon-reduction of the higher mentioned 1,2 - diphenylquinoliniumsalts **7**.

In the frame of a study of the spectroscopic and physiological properties of benzo- and indoloquinolizine derivatives,[1-10] we wish to report the synthesis of 9,10-dihydro - 8bH - quino[1,2 - f]phenanthridine **2** and some of the methoxy derivatives.

Successful use of the photodehydrogenation reaction as the key step in this synthetic route inspired us to consider this procedure also as a novel synthesis in the formation of the 6 - phenyl - 4,5,6,7 - tetrahydropyrido - [3,2,1 - j,k]carbazole - derivatives **17** starting from the intermediate 1,2 - diphenyl - 1,2,3 4 - tetrahydroquinoline derivatives **1**.

The synthetic pathways which have been developed are shown in Schemes 1a and b.

RESULTS AND DISCUSSION

1. *Synthesis of the* 1,2 - *diphenylquinoliniumsalts* 7

By a thorough adjustment of the conditions of the Skraup-reaction described by Stadniichuk,[11] we obtained the desired 1-phenyl - quinoliniumperchlorate **4a** in a 48% yield. The same reaction starting from 4,4' - dimethoxydiphenylamine **3b**, which was prepared according to Goldberg[12] and Chen *et al.*,[13] and acrolein yielded 40–45% of 6 - methoxy - 1 - (4' - methoxyphenyl)quinoliniumperchlorate **4b**.

Grignard reaction with phenylmagnesiumbromide **5a** or *p* - methoxyphenylmagnesiumbromide **5b** on the obtained derivatives **4a** and **4b**, immediately followed by iodine/sodium acetate oxidation yielded the desired quinoliniumperchlorate **7a–d**, of which the results are summarized in Table 1.

II. *Synthesis of the* 1,2 - *diphenyl* - 1,2,3,4 - *tetrahydroquinolines* 1

(a) *Procedure A—by catalytical reduction of the* 1,2 - *diphenyl* - *quinoliniumsalts* **8**. Previous reduction studies on quinoliniumsalts[2,14] led us to the catalytic reduction of compounds **7**. The results are summarized in Table 2.

(b) *Procedure B—by acid-catalyzed cyclization of the* 3-(o-anilinophenyl) - 1 - phenyl - 1 - propanol - derivatives **16**. Through condensation of 2 - (2 - oxocyclohexyl)propionic acid **9**, prepared according to Stork *et al.*[15] and Tourwé,[2] and aniline **10a** or *p*-anisidine **10b**, we obtained 90% of **11a** and 63% of **11b** respectively.

Dehydrogenation, carried out in previously mentioned conditions,[3] yielded 90% of **12a** and 70% of **12b**. Those were catalytically reduced with Raney-nickel W2 towards the desired 2 - phenyl - 3,4 - dihydrocarbostyril **13a** (70%) and 1 - (4' - methoxyphenyl) - 3,4 - dihydrocarbostyril **13b** (87%).

Phenyllithium reaction on **13a**, carried out in the conditions mentioned by Bell *et al.*,[20] yielded 95% of 3 - (*o* - anilinophenyl) - propiophenon **15a** which was further reduced by sodium borohydride into 3 - (*o* - anilinophenyl) - 1 - phenyl - 1 - propanol **16a** (77%). The same reaction carried out on **13b** yielded 70% of **15b** and 95% of **16b**.

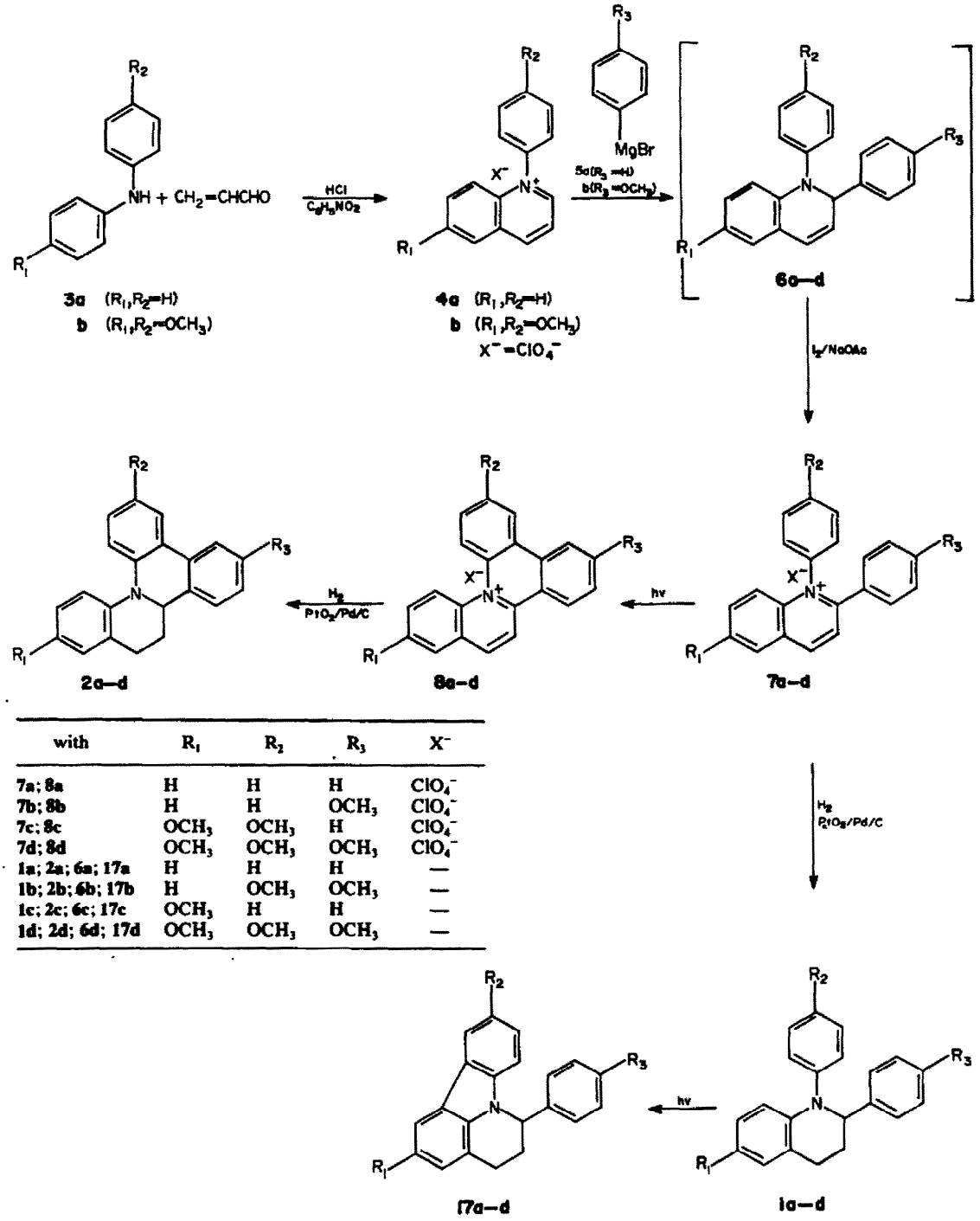
Acid-catalyzed cyclization of **16a** and **16b**, followed by column chromatography purification, delivered the desired structures **1a** and **1e**, of which the results figure in Table 2.

III. *Photodehydrogenation*

(a) *Synthesis of the quino*[1,2 - *f*]*phenanthridinium-perchlorates* **8**. The 1,2 - diphenylquinoliniumsalts **7** can be considered as N-analogues of stilbene. Since the latter can be cyclodehydrogenated photochemically,[8] we irradiated an acetonitrile solution of **7** in the presence of a trace of iodine.

By this procedure we only obtained **8a** in a 50% yield. All attempts to obtain the corresponding phenanthridiniumperchlorates **8b**, **8c** and **8d** by photodehydrogenation of **7b**, **7c** and **7d** failed, which is somewhat in agreement with the negative results of Salsmans[8] in his photocyclisation of very analogous structures.

(b) *Synthesis of the* 6 - *phenyl* - 4,5,6,7 - *tetrahydropyrido*[3,2,1 - *j,k*]*carbazoles* **17**. Based on the results of Parker and Barnes,[16] who mentioned the formation of carbazole during the irradiation of a diphenylamine solution, reaction which in the meantime

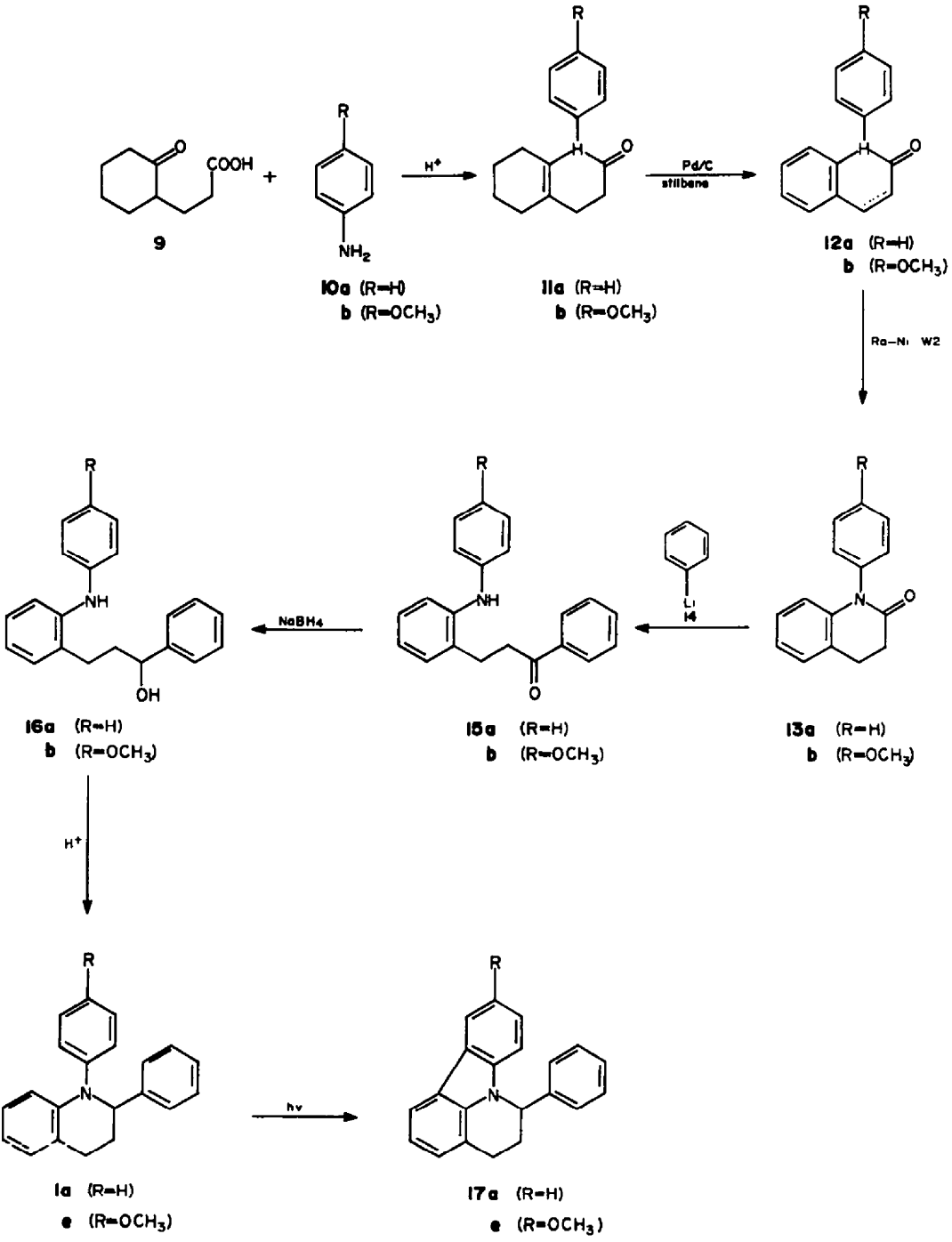


with	R_1	R_2	R_3	X^-
7a; 8a	H	H	H	ClO_4^-
7b; 8b	H	H	OCH_3	ClO_4^-
7c; 8c	OCH_3	OCH_3	H	ClO_4^-
7d; 8d	OCH_3	OCH_3	OCH_3	ClO_4^-
1a; 2a; 6a; 17a	H	H	H	—
1b; 2b; 6b; 17b	H	OCH_3	OCH_3	—
1c; 2c; 6c; 17c	OCH_3	H	H	—
1d; 2d; 6d; 17d	OCH_3	OCH_3	OCH_3	—

Scheme 1a.

Table 1.

Product	R_1	R_2	R_3	% Yield (Grignard + Oxidation)
7a	H	H	H	47 - 55
7b	H	H	OCH_3	32
7c	OCH_3	OCH_3	H	30 - 35
7d	OCH_3	OCH_3	OCH_3	25 - 30



Scheme 1b.

has been extended by Grellman[17] to N-substituted derivatives, we considered this procedure as a novel synthesis of the pyrido-carbazole derivatives 17 starting from our 1,2 - diphenyl - 1,2,3,4 - tetrahydroquinoline derivatives 1a, 1b and 1e.

By irradiation of an ethanolic solution of 1a, 1b and 1e we obtained the desired compounds 17a, 17b and 17e of which the results are summarized in Table 3.

IV. *Synthesis of the* 9,10 - *dihydro* - 8*bH* -*quino*[1,2-*f*]*phenanthridines* 2

As all attempts failed to synthesize derivatives 8b, 8c and 8d (dr4. III,a) we only succeeded in obtaining 9,10 - dihydro - 8bH - quino - [1,2 - f]phenanthridine 2a by catalytical reduction of 8a both with platinum(IV)oxide/palladium on activated carbon in acetonitrile and with platinum(IV)oxide in ethanol. After

Table 2.

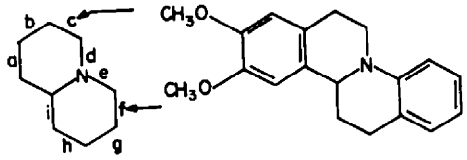
Product	R_1	R_2	R_3	Procedure	Catalyst	% Yield
1a	H	H	H	A	PtO_2/Pd/C	90
				A	PtO_2	85 - 90
				B	H^+	62
1b	H	H	OCH_3	A	PtO_2	70
1c	OCH_3	OCH_3	H	not performed		
1d	OCH_3	OCH_3	OCH_3	not performed		
1e	H	OCH_3	H	B	H^+	56

Table 3.

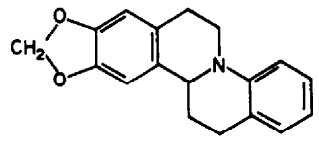
Product	R_1	R_2	R_3	% Yield
17a	H	H	H	70
17b	H	H	OCH_3	84
17e	H	OCH_3	H	32 - 36

purification by column chromatography we obtained a pale yellow to colourless oil, which quickly coloured to dark brown. The yield was 90% for the PtO_2/Pd/C/CH_3CN-procedure and 50% for the PtO_2/C_2H_5OH-procedure.

This apparent instability corresponds with the statement made by Sugasawa[18] that a fusion of a benzene nucleus in *c* or *f* position of quinolizidine **18** greatly reduces his stability in contrast with the other positions. A similar instability was noted by Tourwé[19] in the 9,10 - dimethoxy - 6,7,12,13 - tetrahydro - 11bH - dibenzo-[a,f]quinolizidines **19** and by Brown[14b] in the analoguous 9,10 - methylenedioxy - derivative **20**.



18 **19**



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EXPERIMENTAL

The IR spectra were determined on a Perkin–Elmer 257 spectrometer. NMR spectra were obtained with a Varian T60 or a Bruker HX270 apparatus. Sample concentration was about 10% (w/v) with TMS as internal reference. The reported chemical shifts refer to the center of the multiplets. The mass spectra were obtained with an AEI-MS 902S mass spectrometer, operating at 70 eV and 12 eV. Samples were introduced via the direct insertion lock. The intensity of the fragments is expressed as the percentage of the base peak. The elemental composition of the fragments was determined by the peak matching technique. M.ps were recorded on a Mettler FP 5.

1-Phenylquinoliniumperchlorate **4a** ($C_{15}H_{12}N^+ClO_4^-$)

In a 3-necked 500 ml flask, equipped with a mechanical stirrer and reflux condenser, we introduced 34 g (0.2 mole) of diphenylamine, 70 ml dry toluene, 50 ml freshly distilled nitrobenzene and 24 ml conc. HCl (p.a.). In this way we obtained a thick and yellow salt suspension.

A second 100 ml flask, containing 13 g (0.22 mole) freshly distilled acroleine, was heated on a water bath ($t° \leq 25°$) and connected with the first reaction vessel. By blowing a stream of dry N_2 through the 100 ml flask we slowly introduced the acroleine.

During the reaction the salt suspension coloured to red. After complete addition (2–3 hr) stirring was continued during 1 hr.

The mixture was then steam distilled to eliminate the toluene and nitrobenzene. The resulting water phase was boiled after adding of two spoonfuls of charcoal. Hot filtration and addition of perchloric acid started the precipitation of **4a**.

Filtration and crystallization from water yielded 30 g (48%) of **4a**. m.p. 157°; IR (KBr) ν(cm^{-1}): 3090, 3070, 1625, 1590, 1520, 1485, 1455, 1400, 1375, 1325, 1250, 1230, 1140–1030 (broad), 810, 775, 710, 690; NMR (60 MHz/$CDCl_3$) δ (ppm): 9.5–9.1 (m), 8.6–7.6 (massive); MS (70 eV-source temp. 200°): 237(8), 222(15), 221(100), 220(78), 207(6), 206(8), 196(9), 195(9), 194(5), 193(29), 191(10), 180(10), 167(10), 165(11), 129(3), 128(6), 110.5(7), 95.5(13), 90(9) 89(11), 83.5(12), 77(25). Found: C, 58.90; H, 3.92; N, 4.57. $C_{15}H_{12}N^+ClO_4^-$ requires: C, 58.93; H, 3.96; N, 4.58%.

6 - Methoxy - 1 - (4' - methoxyphenyl) - quinoliniumperchlorate **4b** ($C_{17}H_{10}O_2N^+ClO_4^-$)

This was similarly prepared from 13.7 g (0.06 mole) of 4,4' - dimethoxydiphenylamine,[13] 21 ml dry toluene, 15 ml freshly distilled nitrobenzene, 72 ml conc HCl (p.a.) and 4 g (0.07 mole) freshly distilled acroleine.

Crystallization from water yielded 45% of **4b**. M.p. 139°; IR (KBr) ν (cm^{-1}): 3100, 3060, 2960, 1630, 1590, 1500, 1400, 1300, 1260, 1200, 1180, 1100–1080, 1020, 870, 840, 810, 750; NMR (270 MHz/CD_3CN) δ (ppm): 9.10 (d, 1H), 8.91 (dd, 1H), 8.08 (dd, 1H), 7.78 (d, 1H), 7.66–7.64 (m, 2H), 7.25 (m, 2H), 4.03 (s, 3H), 3.93 (s, 3H); MS (70 eV-source temp. 190°): 297(18), 281(93), 280(54), 266(100), 251(13), 250(18), 239(14), 223(16), 77(10), 44(61). Found: C, 56.71: H, 2.78; N, 3.87. $C_{17}H_{10}N^+ClO_4^-$ requires: C, 56.76; H, 2.80; N, 3.89%).

1,2 - Diphenylquinoliniumperchlorate **7a** ($C_{21}H_{16}N^+ClO_4^-$)

To a freshly prepared soln of 0.1 mole **5a**, 10 g (0.03 mole) of **4a** was added in powder form. The resulting homogeneous soln of **6a** was cooled and with stirring an alcoholic soln of I_2 (0.03 mole) and NaOAc (0.03 mole) was added.

After evaporation of the ether and EtOH, we dissolved the resulting mixture in boiling water out of which, after warm filtration, 7 g (55%) of **7a** crystallized. M.p. 226°; IR (KBr) ν (cm^{-1}): 3060, 1620, 1600, 1570, 1520, 1490, 1450, 1360, 1330 1120–1060 (broad), 840, 770, 700; MS (70 eV-source temp.

200°); 298 (17, $C_{21}H_{16}NO$ and $C_{20}{}^{13}CH_{15}NO$), 297 (100, $C_{21}H_{15}NO$), 296(21), 282 (16, $C_{21}H_{16}N$), 280(11), 269(29), 206(7), 193(6), 180(10), 179(13), 178(9), 165(10), 133(9), 105(37), 77(33). Found: C, 66.03; H, 4.20; N, 3.66. $C_{21}H_{16}N^+ClO_4^-$ requires: C, 66.06; H, 4.22; N, 3.67%).

1 - *Phenyl* - 2 - (4' - *methoxyphenyl*) - *quinoliniumperchlorate* **7b** ($C_{22}H_{18}ON^+ClO_4^-$)

This was similarly prepared from 0.1 mole of **5b** and 10 g (0.03 mole) of **4a**.

Crystallization from water yielded 10–11 g (74–80%) of **7b**. M.p. 198–201°; IR(KBr) $\nu(cm^{-1})$: 3050, 3010, 2920, 2830, 1620 (shoulder), 1600, 1565, 1505, 1450, 1435, 1355, 1335, 1300, 1260, 1180, 1120–1050, 1020, 830, 785, 765, 700; NMR (270 MHz/CD_3CN) δ(ppm): 9.23–7.48 (m's, 11H), 7.39(2H), 6.90(2H), 3.76 (S, 3H); MS (70 eV-source temp. 215°C): 328(20), 327 (100, $C_{22}H_{17}NO_2$), 326(28), 313(8), 312(20, $C_{22}H_{18}NO$), 299 (35, $C_{21}H_{17}NO$), 297(14), 284(16), 194(13), 192(7), 179(17), 152(8), 135(7), 127(7), 105(6), 92(8), 91(6), 89(5), 77(30). (Found: C, 64.10; H, 4.40; N, 3.38. $C_{22}H_{18}ON^+ClO_4^-$ requires: C, 64.16; H, 4.41; N, 3.40%).

6 - *Methoxy* - 1 - (4' - *methoxyphenyl*) - 2 - *phenylquinolinium* - *perchlorate* **7c** ($C_{23}H_{20}ON^+ClO_4^-$)

This was similarly prepared from 0.02 mole of **5a** and 2.4 g (6.5×10^{-3} mole) of **4b**. Crystallization from water yielded 1 g (35%) of **7d** as yellow needles. M.p. 196°; IR (KBr) $\nu(cm^{-1})$: 3060, 3020, 2960, 1620, 1590, 1500, 1390, 1310, 1250, 1180, 1100–1080, 1020, 870, 830, 770, 700; NMR (270 MHz/CD_3CN) δ (ppm): 9.11 (d, 1H), 8.06 (d, 1H), 7.81 (d, 1H), 7.64 (dd, 1H), 7.46 (d, 1H), 7.43–7.39 (m, 5H), 7.37 (m, 2H), 7.02 (m, 2H), 4.03 (s, 3H), 3.80 (s, 3H); MS (70 eV-source temp. 190°): 357(100), 356(66), 342(28), 327(16), 266(5), 212(7), 178(6), 142(13), 127(14); 105(6), 77(5), 50(27), 44(50). (Found: C, 64.86; H, 4.70; N, 3.28. $C_{23}H_{20}ON^+ClO_4^-$ requires: C, 64.87; H, 4.73; N, 3.29%).

6 - *Methoxy* - 1 - (4' - *methoxyphenyl*) - 2 - (4'' - *methoxyphenyl*) - *quinoliniumperchlorate* **7d** ($C_{24}H_{22}ON^+ClO_4^-$)

This was similarly prepared from 8×10^{-3} mole of **5b** and 1.1 g (3×10^{-3} mole) of **4b**. Crystallization from water yielded 425 mg (30% of **7d**. M.p. 176.5°; IR (KBr) $\nu(cm^{-1})$: 3080, 2940, 2840, 1610, 1510, 1390, 1340, 1300, 1250, 1180, 1100–1080, 1020, 830; NMR (270 MHz/CD_3CN) δ(ppm): 9.04 (d, 1H), 8.05 (d, 1H), 7.78 (d, 1H), 7.61 (dd, 1H), 7.44 (d, 1H), 7.38 (m, 2H), 7.33 (m, 2H), 7.06 (m, 2H), 6.91 (m, 2H), 4.03 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H); MS (70 eV-source temp. 190°): 387(44), 386(22), 372(14), 359(10), 344(3), 316(2), 266(8), 212(3), 142.(100), 141(10), 135(7), 127(28), 77(2), 50(27), 44(7). (Found: C, 65.50; H, 5.03; N, 3.19. $C_{24}H_{22}ON^+ClO_4^-$ requires: C, 65.53; H, 5.04; N, 3.19%).

1 - *Phenyl* - 3,4,5,6,7,8 - *hexahydrocarbostyril* **11a** ($C_{15}H_{17}NO$)

Aniline (10.3 g; 0.11 mole), **9**[2] (17 g; 0.1 mole) and a trace of *p*-toluenesulphonic acid were refluxed in 150 ml dry toluene during 16 hr. The water was separated with a Dean & Stark apparatus.

After filtration of the hot mixture, cooling and washing, successively with a 20 M NaOH, a 20% HCl and water, the mixture was dried on $MgSO_4$.

After evaporation we obtained a reddish brown oil, which crystallized in ether (13.5 g – 60%). The mother liquor was then eluted with ether on a charcoal column and yielded after 7 g of pure material. Total yield 20.5 g (90%) M.p. 115°; IR(KBr) $\nu(cm^{-1})$: 3060, 3000, 2910, 2880, 2830, 1665, 1590, 1485, 1440, 1375, 1350, 1310, 1250, 1220, 1200, 765, 700; NMR (60 MHz/$CDCl_3$) δ (ppm): 7.5–7.0 (5H, aromatic's), 2.8–1.3 (12H); MS (70 eV-source temp. 200°): 228(17), 227(100), 226(22), 199(33), 198(36), 184(22), 172(11), 171(20), 170(22), 156(11), 143(6), 129(9), 122(8), 118(13), 117(9), 104(11), 93(7), 91(8), 77(36). (Found: C, 79.25; H, 7.51; N, 6.14. $C_{15}H_{17}NO$ requires: C, 79.26; H, 7.54; N, 6.16%).

1 - (4' - *Methoxyphenyl*) - 3,4,5,6,7,8 - *hexahydrocarbostyril* **11b** ($C_{16}H_{19}NO_2$)

This was similarly prepared from 12.3 g (0.1 mole) of *p*-anisidine, 17 g (0.1 mole of **9**[2] and a trace of *p*-toluenesulphonic acid. Total yield after crystallization in ether was 16.1 g (63%) of **11b**. M.p. 101°; IR(KBr) $\nu(cm^{-1})$: 3060, 3020, 2930, 2905, 2880, 2860, 2820, 1670, 1605, 1505, 1440, 1370, 1350, 1240, 1210, 1170, 1020, 840; NMR (60 MHz/$CDCl_3$) δ (ppm): 6.97 (m, 4H), 3.3 (s, 3H), 2.8–1.4 (12H); MS (70 eV-source temp. 2000°C): 258(18), 257(100), 256(15), 242(2), 229(21), 228(19), 214 (18), 210(14), 200(29), 198(10), 186(11), 173(5), 160(5), 147(5), 134(9), 133(5), 132(4), 123(5), 122(6), 121(5), 92(6), 91(5), 77(13). (Found: C, 74.65; H, 7.42; N, 5.41. $C_{16}H_{19}NO_2$ requires: C, 74.68; H, 7.44; N, 5.44%).

1 - *Phenyl* - 3,4 - *dihydrocarbostyril* **13** ($C_{15}H_{13}NO$)

In a one necked flask (500 ml) equipped with a magnetic stirrer and an air condenser, 0.05 mole (11.5 g) of **11a**, 0.1 mole (18 g) stilbene and 0.5 g 10% Pd/C were refluxed in 350 ml decalin for 100 hr. After filtration of the hot mixture, **12a** crystallized on cooling. Purification by crystallization in EtOH yielded 10 g of **12a**, consisting of 10% 1 - phenyl - 3,4 - dihydrocarbostyril and 90% 1-phenylcarbostyril, as proved by gaschromatography.

0.05 mole (11.1 g) of this mixture **12a**, dissolved in 150 ml abs. EtOH was hydrogenated during 3–4 hr in a steel autoclave under 50–60 atm. H_2 and 100° over a Ra–Ni W_2-catalyst (freshly prepared according to Mozingo[21]).

Filtration and evaporation of the solvent yielded 9 g of a light yellow solid, which crystallized from isopropanol, m.p. 123°; IR(KBr) $\nu(cm^{-1})$: 3060, 3030, 2995, 2940, 2895, 2850, 1670, 1600, 1490, 1450, 1360, 1335, 1295, 1270, 1220, 1200, 1180, 1155, 770, 730, 700; NMR (60 MHz/$CDCl_3$) δ (ppm): 7.7–6.2 (m's, 9H), 3.2–2.6 (m, 4H); MS (70 eV-source temp. 190°C): 224(17), 223(100), 222(5), 221(13), 220(13), 220(20), 195(33), 194(57), 181(7), 180(47), 167(6), 165(41), 152(5), 118(60), 91(11), 90(6), 89(5), 83.5(7), 77(15). (Found: C, 80.68; H, 5.86; N, 6.25. $C_{15}H_{13}NO$ requires: C, 80.69; H, 5.87; N, 6.27%).

1 - (4' - *Methoxyphenyl*) - 3,4 - *dihydrocarbostyril* **13b** ($C_{16}H_{13}NO_2$)

This was similarly prepared from 0.03 mole (7.8 g) of **11b**, 0.06 mole (10.8 g) stilbene and 1 g 10% Pd/C, which yielded after purification by crystallization from ethanol 5.3 g of **12b**, consisting of 20% 1 - (4' - methoxyphenyl) - 3,4 - dihydrocarbostyril and 80% 1 - (4' - methoxyphenyl) - carbostyril as proved by gaschromatography. 0.012 mole (3 g) of this mixture was then similarly hydrogenated to yield, after crystallization from isopropanol, 2.9 g of a white solid. M.p. 162–163°; IR(KBr) $\nu(cm^{-1})$: 3020, 2950, 2840, 1675, 1600, 1510, 1490, 1450, 1360, 1250, 1025, 830, 760; NMR (60 MHz/$CDCl_3$) δ (ppm): 7.3–6.2 (m's, 8H), 3.8 (s, 3H), 2.9 (m, 4H); MS (70 eV-source temp. 185°C): 254(18), 253(100), 236(6), 225(15), 224(33), 211(5), 210(30), 196(21), 194(8), 182(5), 181(5), 180(12), 168(18), 167(27), 118(30), 117(11), 91(7), 90(6), 89(5), 83.5(2), 78(6), 77(15). (Found: C, 76.47; H, 5.20; N, 5.57. $C_{16}H_{13}NO_2$ requires: C, 76.48; H, 5.22, N 5.57%).

1,2 - *Diphenyl* - 1,2,3,4 - *tetrahydroquinoline* **1a** ($C_{21}H_{19}N$)

(a) PtO_2/Pd/C-*procedure*. 200 mg of **7a** in 100 ml acetonitrile were hydrogenated in a Parr-apparatus over 30 mg 10% Pd/C and 10 mg PtO_2 under 4 atm. H_2 during 4 hr. Filtration, evaporation of the solvent and crystallization from EtOH yielded 90% of **1a**.

(b) PtO_2-*procedure*. 500 mg **7a** in 400 ml EtOH were hydrogenated in a Parr-apparatus over 10 mg Pto_2 under 4 atm. H_2 during 4 hr. Filtration, evaporation of the solvent and crystallization from EtOH yielded 85–90% of **1a**.

(c) *Acid catalyzed cyclization procedure*. A warm soln of 10.5 g (0.047 mole) of **13a** in 70 ml dry benzene was added to a well dosed phenyllithium soln (150 ml of a 8.3×10^{-4} mole/ml soln), prepared according to Vogel[22] and standardized according to Gilman.[23] The mixture was stirred at reflux for 90 min under N_2. Benzene and ice-water were added at ice temp. and the organic phase was separated, washed with water and dried on $MgSO_4$. Evaporation of the solvent and further purification by column chromatography (Al_2O_3(II–III)/ether) yielded 13.8 g (97%) of **15a**. IR(film) $\nu(cm^{-1})$: 3340, 3060, 3030, 2960, 2900, 2850, 1670, 1590, 1495, 1460,1360, 750, 690; MS(70 eV): 301 (M^+-peak).

To a soln of 1.38 g (0.046 mole) of **15a** in 150 ml MeOH we

added by portions an excess of $NaBH_4$. A reflux of 2.5 hr was maintained, whereafter, under ice-cooling, water was added to the mixture. After evaporation of the MeOH we extracted the remaining water phase with ether. Drying and evaporation yielded 11.2 g of a red oil, which could be purified by column chromatography (Al_2O_3 (II–III)/$CHCl_3$). So we obtained 10.6 g 76%) of **16a** as a light yellow oil. IR(film) $\nu(cm^{-1})$: 3600–3200 (broad, centered at 3550 and 3350), 3060, 3015, 2980, 2930, 2870, 1600, 1580, 1500, 1455, 1300, 1110, 750, 700; MS (70 eV): 303 (M^+-peak).

A mixture of 9.8 g (0.032 mole) of **16a**, 1 g *p*-toluenesulphonic acid and 400 ml xylene was stirred at reflux for 5 hr under N_2. After cooling and addition of ether, we washed the mixture with a sat $NaHCO_3$ aq. The dried filtrate was concentrated to give 8.7 g of a brown oil, which could be purified by column chromatography (Al_2O_3(II–III)/hexane) and crystallization from EtOH. Total yield 5.6 g of **1a** (61%) m.p. 77°; IR(KBr) $\nu(cm^{-1})$: 3060, 3020, 2950, 2930, 2895, 2840, 1590, 1570, 1495, 1460, 1445, 1380, 1270, 1215, 755, 695; NMR (60 MHz/$CDCl_3$) δ(ppm): 7.3–6.6 (m's, 14H), 4.95 (t, 1H), 2.75–2.4 (massive, 2H), 2.4–2.0 (massive, 2H); MS (70 eV-source temp. 210°): 286 (23, $C_{20}{}^{13}CH_{19}N$), 285 (100, M^+, $C_{21}H_{19}N$), 209(8), 208 (59, $C_{15}H_{14}N$), 206(6), 194(36), 193(8), 181(10), 180(64), 167(3), 165(4), 152(5), 115(6), 104(6), 103(5), 91(13), 89(3), 78(10), 77(18). (Found: C, 88.37; H, 6.68; N, 4.92. $C_{21}H_{19}N$ requires: C, 88.38; H, 6.71; N, 4.91%).

1 - Phenyl - 2 - (4' - methoxyphenyl) - 1,2,3,4 - tetrahydroquinoline **1b** ($C_{22}H_{21}NO$)

Compound **7b** (822 mg; 0.002 mole) in 400 ml EtOH were hydrogenated in a Parr apparatus over 20 mg PtO_2 under 4 atm H_2 during 4 hr. Filtration, evaporation of the solvent and further purification by column chromatography (Al_2O_3(II–III/$CHCl_3$) and crystallization from MeOH yielded 450 mg (70%) of **1b** as colourless crystals; m.p. 114°; IR(KBr) $\nu(cm^{-1})$: 3060, 3030, 3000, 2950, 2830, 1610, 1585, 1575, 1490, 1455, 1445, 1380, 1250, 1175, 1035, 840, 750, 715, 700; (NMR MHz/$CDCl_3$) δ (ppm): 7.38–6.70 (m's, 13 H), 4.89 (m, 1H), 3.75 (s, 3H), 2.79–2.49 (m, 2H), 2.31 (m, 1H), 2.10 (m, 1H); MS (70 eV-source temp. 175°C): 316 (21, $C_{21}{}^{13}CH_{21}NO$), 315 (100, M^+, $C_{22}H_{21}NO$), 208 (14, $C_{15}H_{14}N$), 206(8), 197(9), 195(11), 194(71), 193(12), 181(16), 180(93, $C_{13}H_{10}N$), 168(14), 167(9), 121(17), 91(14), 78(11), 77(24). (Found: C, 83.76; H, 6.70; N, 4.41. $C_{22}H_{21}NO$ requires: C, 83.78; H, 6.71; N, 4.44%).

1 - (4' - Methoxyphenyl) - 2 - phenyl - 1,2,3,4 - tetrahydroquinoline **1e** ($C_{22}H_{21}NO$)

A warm soln of 3.15 g (1.2×10^{-2} mole) of **13b** in 30 ml dry benzene was added to a well dosed phenyllithium soln (60 ml of an 8.3×10^{-4} mole/ml-soln) prepared according to Vogel[22] and standardized according to Gilman.[23]

The mixture was stirred at reflux for 75 min under N_2. Benzene and ice-water were added at ice temp. and the organic phase was separated, washed with water and dried on $MgSO_4$. Evaporation of the solvent and further purification by crystallization from isopropanol yielded 2.75 g (69%) of **15b**, m.p. 110–111°; IR(KBr) $\nu(cm^{-1})$: 3370, 3060, 3040, 3000, 2950, 2930, 2910, 2840, 1675, 1600, 1580, 1510, 1450, 1400, 1295, 1235, 1200, 1035, 970, 845, 745, 690; NMR(60 MHz/$CDCl_3$) δ(ppm): 8.1–6.7 (m's, 13H), 6.2 (broad, 1H), 3.8 (s, 3H), 3.2 (m, 4H); MS (70 eV-source temp. 200°C): 332(25), 331(100), 313(7), 312(10), 226(5), 212(8), 210(11), 196(22), 181(8), 180(28), 168(10), 167(11), 106(8) 105(36), 91(34), 78(4), 77(25).

To a soln of 4 g (1.2×10^{-2} mole) of **15b** in 80 ml MeOH we added in portions an excess of $NaBH_4$. A reflux of 2 hr was maintained, whereafter, under ice cooling, water was added to the mixture. After evaporation of the MeOH we extracted the remaining water phase with ether. Drying and evaporation yielded 3.8 g (95%) of **16b** as a reddish brown oil, which solidified on cooling; IR(film) $\nu(cm^{-1})$: 3520, 3320, 3030, 2960, 2870, 1600, 1580, 1580, 1510, 1450, 1295, 1230, 1030, 930, 820, 760, 750, 700; NMR (60 MHz/$CDCl_3$) δ(ppm): 7.5–6.7 (m's, 15H), 4.7 (t, 1H), 3.8 (s, 3H), 2.9–2.6 (m, 2H), 2.3–1.8 (m, 2H); MS (70 eV-source temp. 200°C): 334(24), 333(100), 315(19), 238(22), 224(22), 213(14), 212(11), 210(27), 198(14), 196(46), 181(11), 180(38), 168(22), 167(19), 91(19), 79(19), 77(24).

A mixture of 3.8 g (1.15×10^{-2} mole) of crude **16b**, 0.4 g *p*-toluenesulphonic acid and 180 ml xylene was stirred at reflux for 2 hr under N_2. After cooling and addition of ether, we washed the mixture with a sat. $NaHCO_3$ aq. The dried filtrate was concentrated to give a brown oil, which crystallized from EtOH and yielded 2 g (56%) of **1e**, m.p. 90°; IR(KBr) $\nu(cm^{-1})$: 3060, 3030, 3010, 2940, 2910, 2840, 1605, 1595, 1570, 1490, 1450, 1300, 1240, 1030, 830, 750, 735, 700; NMR (60 MHz/$CDCl_3$)δ(ppm): 7.3–6.3 (m's, 13H), 4.8 (m, 1H), 3.7 (s, 3H), 2.6 (m, 2H), 2.1 (m, 2H); MS(70 eV-source temp. 200°C): 316 (22, $C_{21}{}^{13}C_{21}NO$), 315 (100, M^+, $C_{22}H_{21}NO$), 239(4), 238(22), 224(9), 210(9), 196(19), 180(7), 168(9), 167(10), 130(3), 115(4), 104(2), 103(2), 91(10), 78(4), 77(6), (Found: C, 83.76; H, 6.67; N, 4.41. $C_{22}H_{21}NO$ requires: C, 83.78; H, 6.71; N, 4.44%).

Quino[1,2 - f]phenanthridiniumperchlorate **8a** ($C_{21}H_{14}N^+ClO_4^-$)

Compound **7a** (1.91 g; 0.005 mole) was irradiated during 6–8 hr in 350 ml acetonitrile soln with a trace of I_2, using a high pressure 450 W mercury vapour HANOVIA-lamp. After evaporation of the solvent, we dissolved the crude mixture in boiling water to which, after warm filtration, was added a 70 M $HClO_4$-soln. The ppt was filtered off and crystallized from EtOH in a 50% yield, m.p. 232–233°; IR(KBr) $\nu(cm^{-1})$: 3080, 3040, 1610, 1595, 1540, 1520, 1450, 1355, 1160, 1130–1030, 840, 765; MS(70 eV-source temp. 200°): 298(7) 297(5), 296(16), 295 (79, $C_{21}H_{13}NO$), 294(7), 281(24), 280 (43, $C_{12}H_{14}N$), 270(9), 268(22), 267 (100, $C_{20}H_{13}N$), 266(16), 265(18), 264(9), 254(3), 252(4), 241(4), 240(4), 239(9), 133.5(17), 132.5(22), 120.5(8), 119.5(7). (Found: C, 66.38; H, 3.70; N, 3.71. $C_{21}H_{14}N^+ClO_4^-$ requires: C, 66.41; H, 3.72; N, 3.69%).

6 - Phenyl - 4,5,6,7 - tetrahydropyrido[3,2,1 - j,k]carbazole **17a** ($C_{21}H_{17}N$)

A soln of 0.5 g (1.75×10^{-3} mole) of **1a** in 160 ml EtOH was irradiated during 2 hr using a high pressure 450 W HANNOVIA mercury vapour lamp. After evaporation of the solvent, the crude product was purified by column chromatography (Al_2O_3(II–III)/*n*-hexane) and yielded, after crystallization in EtOH, 70% of pure **17a**, m.p. 140°; IR(KBr) $\nu(cm^{-1})$: 3050, 3020, 2950, 2920, 2880, 2830, 1625, 1605, 1509, 1485, 1460, 1440, 1340, 1240, 1130, 1015, 755, 745, 695; NMR (60 MHz/$CDCl_3$) δ(ppm): 8.2–6.6 (massive, 12H), 5.6 (m, 1H), 2.8 (m, 2H), 2.4 (m, 2H); MS (70 eV-source temp. 210°): 284 (23, $C_{20}{}^{13}CH_{17}N$), 283 (100, M^+, $C_{21}H_{17}N$), 282(10), 207(7), 206(53, $C_{15}H_{12}N$), 205(5), 204(14), 192(6), 191(4), 180(9), 179(18), 178(7), 167(3), 152(5), 151(3), 141(5), 115(3), 91(5), 78(2), 77(3); MS(12 eV-source temp. 210°C): 284(25), 283 (100, M^+), 206(5). (Found: C, 88.98; H, 6.02; N, 4.89. $C_{21}H_{17}N$ requires: C, 89.01; H, 6.05; N, 4.94%).

6 - Phenyl - 10 - methoxy - 4,5,6,7 - tetrahydropyrido[3,2,1 - j,k]carbazole **17e** ($C_{22}H_{19}NO$)

A soln of 0.5 g (1.6×10^{-3} mole) of **1e** in 160 ml EtOH was irradiated during 3–4 hr using a high pressure 450-W HANNOVIA mercury vapour lamp. After evaporation of the solvent, the crude product was purified by column chromatography (Al_2O_3 (II–III)/*n*-hexane/benzene(1/1)) and yielded, after crystallization in ethanol, 32–36% of pure **17e**, m.p. 164°; IR(KBr) $\nu(cm^{-1})$: 3060, 3020, 2990, 2960, 2930, 2850, 2830, 1625 (shoulder), 1605, 1575, 1470, 1450, 1440, 1380, 1350, 1285, 1220, 1210, 1170, 1080, 1070, 1035, 810, 785, 760, 740, 700; NMR(60 MHz/$CDCl_3$) δ(ppm): 8.0–6.8 (massive, 11H) 5.7 (m, 1H), 3.9 (s, 3H), 2.8 (m, 2H), 2.45 (m, 2H); MS (70 eV-source temp. 210°C): 314 (24, $C_{21}{}^{13}CH_{19}NO$), 313 (100, M^+, $C_{22}H_{19}NO$), 298 (24, $C_{21}H_{16}NO$), 236 (20), 209(14), 194(36, $C_{13}H_8NO$) 166(9), 156.5(5), 140(3), 139(5), 91(11), 78(2), 77(2); MS(12 eV-source temp. 210°): 314(25), 313(100, M^+), 298 (0.7), 236 (0.6), 209(0.2). (Found: C, 84.29; H, 6.13; N, 4.47. $C_{22}H_{19}NO$ requires: C, 84.32; H, 6.11; N, 4.47%).

6 - (4' - Methoxyphenyl) - 4,5,6,7 - tetrahydropyrido[3,2,1-j,k]carbazole **17b** ($C_{22}H_{19}NO$)

A soln of 0.5 g (1.6×10^{-3} mole) of **1b** in 160 ml EtOH was irradiated during 4 hr using a high pressure 450 W HANNOVIA mercury vapour lamp. After evaporation of the solvent, the crude product was purified by column chromatography (Al_2O_3(II–III)/*n*-hexane/benzene(1/1)) and yielded, after crystallization in methanol, 84% of pure **17b**, m.p. 137–137.5°; IR(KBr)

ν(cm^{-1}): 3050, 3000, 2950, 2920, 2850, 2830, 1610, 1585, 1510, 1480, 1450, 1440, 1330, 1295, 1275, 1245, 1170, 1030, 830, 745, 735; NMR(60 MHz/$CDCl_3$) δ(ppm): 8.3–6.6 (massive, 11H), 5.6 (m, 1H), 3.7 (s, 3H), 2.8 (m, 2H), 2.3 (m, 2H); MS(70 eV-source temp. 210°): 314 (27, $C_{21}{}^{13}CH_{19}NO$), 313 (100, M^+, $C_{22}H_{19}NO$), 312(11), 298(3), 282(3), 207(3), 206(17, $C_{15}H_{12}N$), 205(6), 204(14), 192(6), 191(2), 180(8), 179(17), 178(5), 156.5(3), 134(10), 121(6), 91(3), 78(6), 77(3); MS(12eV-source temp. 210°C): 314(26), 313(100, M^+), 298 (0.4), 282(0.4), 206(2.6), 204(0.9), 192(0.5), 179(1.1). (Found: C, 84.30; H, 6.08; N, 4.46. $C_{22}H_{19}NO$ requires: C, 84.32; H, 6.11; N, 4.47%).

9,10 - *Dihydro - 8bH - quino*[1,2 - *f*]*phenanthridine* **2a** ($C_{21}H_{17}N$)

PtO_2/Pd/C-*procedure.* 200 mg of **8a** in 100 ml acetonitrile were hydrogenated in a Parr apparatus over 30 mg 10% Pd/C and 10 mg PtO_2 under 4 atm H_2 during 3–4 hr.

Filtration and evaporation yielded an oil, which could be purified by column chromatography (Al_2O_3(II–III)/$CHCl_3$/hexane) and yielded 135 mg (90%) of **2a** as a colourless oil, which however quickly coloured to brown.

PtO_2-*procedure.* 1 g of **8a** in 400 ml EtOH were hydrogenated in a Parr apparatus over 20 mg PtO_2 under 4 atm H_2 during 4–5 hr.

Filtration, evaporation of the solvent and purification as mentioned above by column chromatography yielded 60% of **2a**. IR(film) ν(cm^{-1}): 3065, 3030, 2950, 2930, 2850, 1600, 1580, 1490, 1440, 1380, 1320, 1220, 750; NMR(60 MHz/$CDCl_3$) δ(ppm): 7.8–7.5 (m, 2H), 7.4–6.6 (m, 10H), 4.4 (dd, 1H), 3.0–2.7 (m, 2H), 2.4–2.1 (m, 2H); MS (70 eV-source temp. 210°) 284 (18, $C_{20}{}^{13}CH_{17}N$), 283 (88, M^+, $C_{21}H_{17}N$ and $C_{20}{}^{13}CH_{16}N$), 282 (100, $C_{21}H_{16}N$ and $C_{20}{}^{13}CH_{15}N$), 281 (6, $C_{21}H_{15}N$ and $C_{20}{}^{13}CH_{14}N$), 280(7), 267(24), 254 (36, $C_{19}H_{12}N$), 180(1), 179(2), 178(3), 177(2), 165(2), 152(2), 151(2), 133.5(18), 127(5), 77(4); MS (12 eV-source temp. 210°): 284(23), 283 (100, M^+), 282(13), 281(4).

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