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Rearrangement of 1-Arylindoles to 5H-Dibenz[b,f]azepines

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Abstract: An unusual acid-catalyzed rearrangement of 1-arylindoles **1** to 5H-dibenz[b,f]azepines **2** has been discovered. It can be used for the preparation of **2**. The influence of the nature and the position of the substituents in the initial molecule **1** on the rearrangement is discussed. A possible mechanism of the reaction is suggested. A convenient method for preparation of 1-arylindoles **1c-k** by means of arylation of 1-unsubstituted indoles with aryl halides by the Ullmann reaction is described.

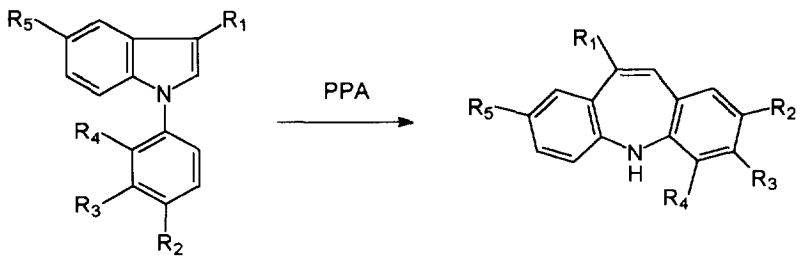
When treated with acids, some substituted indoles are known to undergo different rearrangements which lead either to migration of substituents or to recyclization of the pyrrole ring. In acidic medium 3-alkyl- and 3-arylindoles convert into corresponding 2-substituted isomers[1]. Under the same conditions acyl groups migrate from the 2-position to the 3-position of the indole ring[2,3]. Some 3-(arylthio)indoles have been shown recently[4] to undergo acid-catalyzed rearrangement in which arylthio group migrates to the 2-position or the indole ring is cleaved and then a benzothiophene nucleus is formed.

We have discovered a new rearrangement accompanied by recyclization of the indole ring. 1-Arylindoles **1a-i** have been found to convert into 5H-dibenz[b,f]azepines (DBA) **2a-h** by heating in polyphosphoric acid (PPA) (Scheme 1).

This unusual rearrangement of indoles to DBA's in some cases gives satisfactory yield of products (to 65%) and can be used for their preparation. This method is especially useful for the synthesis of unsymmetrically substituted DBA's preparation of which by known methods is rather complicated. For example, the synthesis of 2-methyl-DBA includes seven steps and its overall yield does not exceed 7%[5]. DBA derivatives are interesting because of their high physiological activity. Some of them are used as drugs. 5-Carbamoyl-DBA ("Carbamazepine") is the most known and is used as an anticonvulsant and an analgesic.

The initial 1-arylindoles **1c-k** were synthesized by arylation of indole or 5-methylindole **3** by means of the Ullmann reaction by analogy with arylation of 1,2,3,4-tetrahydrocarbazoles[6]. 3-Methyl- and 2,3-dimethyl-1-phenylindoles **1b** and **5** were prepared by the Fischer reaction of 1,1-diphenylhydrazine with propionic aldehyde or methyl ethyl ketone respectively.

The influence of substituents in the molecule of 1-arylindole on the rearrangement to DBA has been studied on a series of monomethyl derivatives of 1-phenylindole **1b-e,i** and **4**. When heated in PPA, 1-phenylindole **1a** and its methyl derivatives with the methyl groups at the benzene nuclei **1c-e,i** rearranged to the corresponding DBA derivatives **2a,c-e** with a yield of 25-65% (Table 1). For 1-(*m*-tolyl)indole **1d** the formation of two isomeric products (1- and 3-methyl-DBA) could



1a-k **2a-h**

1c PPA → **2c** ← PPA **1i**

	R_1	R_2	R_3	R_4	R_5
a	H	H	H	H	H
b	CH_3	H	H	H	H
c	H	CH_3	H	H	H
d	H	H	CH_3	H	H
e	H	H	H	CH_3	H

	R_1	R_2	R_3	R_4	R_5
f	H	Cl	H	H	H
g	H	OCH_3	H	H	H
h	H	H	$(CH=CH)_2$		H
i	H	H	H	H	CH_3
j	H	NO_2	H	H	H
k	H	H	CF_3	H	H

Scheme 1.

be expected. However, in this case 3-isomer **2d** is formed as a sole rearrangement product. ^{1}H-NMR spectrum, TLC and GLC analyses showed the absence of 1-methyl-DBA in the reaction mixture. When rearranged, 1-(*p*-tolyl)indole **1c** and 5-methyl-1-phenylindole **1i** give the same 2-methyl-DBA **2c** (the mixed melting point depression was not observed). Thus, the use of the 1-arylindoles rearrangement enables one to choose the most convenient route for DBA synthesis by having the substituent either on the indole benzene ring or on the 1-phenyl substituent. Phenylindoles with methyl groups at the 2- or 3-positions behave differently under the rearrangement conditions. 2-Methyl-1-phenylindole **4** was very stable and did not change upon heating in PPA up to 250°C. 3-Methyl-1-phenylindole **1b** rearranged by two paths (Scheme 2): recyclization to 10-methyl-DBA **2b** (path a) and migration of the 3-methyl group to the 2-position with the formation of stable 2-methyl-1-phenylindole **4** (path b). The ratio of the rearrangement products **2b** and **4** as showed by GLC analysis was 37:63.

2,3-Dimethyl-1-phenylindole **5** did not undergo rearrangement in PPA. Under vigorous conditions (250°C) the elimination of methyl group from the 3-position took place with the formation of indole **4** (Scheme 2). Thus, the absence of the substituent at the 2-position of the indole ring is apparently a necessary condition for the rearrangement of 1-arylindoles to DBA derivatives.

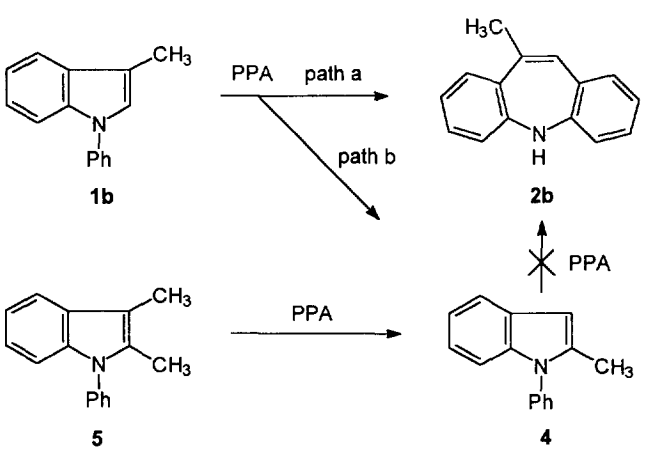
The electronic nature and the position of substituents on the 1-aryl group are also very important for the success of the rearrangement. For the arylindoles with electron-withdrawing groups (*p*-NO_2, *m*-CF_3) **1j** and **1k**, rearrangement was not observed. In contrast, electron-donating groups promote the rearrangement. The reaction is most rapid and gives a highest yield

Table 1. Transformation of Indoles **1, 4, 5** in PPA

Starting indole	PPA/indole, ml/100 mg	Temp., °C	Time, h	Products (% yield)[a,b]	Recovered indole, %[b]
1a	2.6	75-85	55	**2a**(43)	13
1b	1.5	85-115	150	**2b**(34), **4**(57)[c]	0
1c	1.3	110-120	25	**2c**(32)	24
1d	3.6	90-100	41	**2d**(65)	20
1e	3.6	90-100	130	**2e**(35)	34
1f	3.6	90-110	150	**2f**(25)	13
1g	2.0	85-100	100	**2g**(8)	17
1h	3.6	90	27	**2h**(47)	20
1i	1.3	85-115	100	**2c**(25)	8
1j	1.7	90	4	-	0[d]
1k	2.5	90	65	-	68
4	2.0	230-250	25	-	83
5	1.7	230-250	28	**4**(34)[e]	26[e]

[a]Non-optimized. [b]Isolated yield after column chromatography, except where otherwise stated. [c]Ratio **2b:4** is 37:63 (determined by GLC analysis of the crude mixture). [d]Total decomposition. [e]Based on GLC analysis and combined yield of the isolated mixture of **4** and recovered **5**.

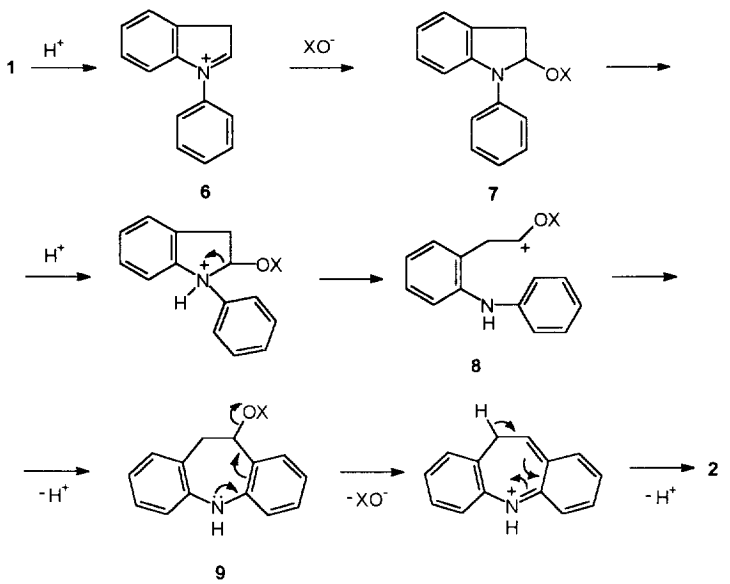
of DBA, if the aryl group is activated for an electrophilic attack at the ortho-position to the nitrogen atom of the indole. 1-(*m*-Tolyl)indole **1d** and 1-(1-naphthyl)indole **1h** gave maximum yields of DBA, 65 and 47% respectively. These facts suggest that the step of the azepine ring



Scheme 2.

closure proceeds *via* an electrophilic attack at the *ortho*-position of the aryl radical. Assuming that, a following mechanism of the rearrangement may be proposed (Scheme 3).

1-Arylindole **1**, as all indoles, is protonated in an acidic medium to the 3-position to give the 3H-indolium ion **6**, which forms indoline **7** by addition of the anion of PPA at the 2-position. Protonation of the indoline **7** at the nitrogen atom followed by rupture of the N-C_2 bond, gives carbocation **8**. The latter than undergoes intramolecular electrophilic substitution at the *ortho*-position of the aryl radical, forming dihydro-DBA **9**, which produces DBA **2** by elimination of PPA.



XO^- = anion of PPA

Scheme 3

The passivity of 2-methyl substituted indoles **4** and **5** under the rearrangement conditions may be explained by several factors. 2-Methyl group prevents the nucleophilic attack of the PPA anion at the 2-position in the ion **6** due to the increasing stability of the ion **6** and also probably due to steric reasons.

We do not exclude from consideration other possible mechanisms of this rearrangement, for example, direct attachment by the *ortho*-position of the 1-aryl group at the 2-position of the protonated indole ring. But we think this mechanism is less probable because it involves the unfavouravle four-membered σ-complex as an intermediate. More detailed study of the rearrangement mechanism we plan to carry out in our following works.

In order to find the most optimal conditions for the DBA synthesis, besides PPA we have also tested sulfuric, trifluoroacetic, trichloroacetic, and orthophosphoric acids as rearrangement catalysts. However, the DBA formation was observed only in the orthophosphoric acid in trace amount. In other acids the rearrangement was not observed.

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EXPERIMENTAL

UV spectra were recorded on a Specord M-40 spectrophotometer in propanol-2. ^{1}H-NMR spectra were recorded in $CDCl_3$ using either a Varian XL-400 or Bruker WM-250 spectrometer and in CCl_4 using Tesla BS-497 (100 MHz) spectrometer. Chemical shifts are expressed in ppm (δ) downfield from internal TMS. Mass spectra were obtained on a Kratos-MS-25-RFA spectrometer at 70 eV. GLC analyses were done on a Chrom-4 instrument using a 3 m x 4 mm glass column packed with 5% OV-101 on silanized Chromosorb G. Thin layer chromatography was performed on Kavalier silica gel aluminium sheets (Silufol UV_{254}). Column chromatography was performed using Chemapol silica gel L 0.10-0.25 mm. Melting points are uncorrected. Indole and aryl halides were used as commercial reagents without additional purification. 1-Phenylindole **1a** was prepared by the thermal decarboxylation of 1-phenylindole-2-carboxylic acid[7]. 2-Methyl-1-phenylindole **4** was prepared by the reaction of 1,1-diphenylhydrazine with acetone according to the earlier reported procedure[8].

3-Methyl-1-phenylindole (1b). A solution of 1,1-diphenylhydrazine (1.85 g, 10 mmol), propionic aldehyde (1 ml, 0.8 g, 13.9 mmol) and acetic acid (0.2 ml) in benzene (50 ml) was heated under reflux with a Dean-Stark apparatus for 2 h and the solvent was then removed under reduced pressure. The residue (crude diphenylhydrazone of propionic aldehyde) was dissolved in ethanol (20 ml), conc. H_2SO_4 (0.6 ml) was added and the resulting solution was heated under reflux for 2 h. After cooling the solution was neutralized with aqueous ammonia and evaporated under reduced pressure. The residue was shaken with benzene (50 ml) and water (50 ml). The organic layer was separated, washed with aq. HCl (1:2) and water, dried over $MgSO_4$ and concentrated under reduced pressure. The residual oil was purified by column chromatography on silica gel. Elution with petroleum ether (b.p. 40-70°C) gave indole **1b** (1.54 g, 74.5% yield) as a light yellow oil. R_f: 0.52 (hexane:benzene-9:1). ^{1}H-NMR (100 MHz): 2.33 (3H, s, 3-CH_3), 6.96-7.59 (10H, m, aromatic H). Anal. Calcd for $C_{15}H_{13}N$: C 86.92, H 6.32%. Found: C 86.79, H 6.44%.

5-Methylindole (3). A mixture of 5-methylindole-2-carboxylic acid[9] (3.15 g) and basic cupric carbonate (0.1 g) was heated under argon at 230°C for 3 h. The cooled reaction mixture was dissolved in benzene, filtered and the solvent was removed under reduced pressure. The residue was extracted with cold petroleum ether (b.p. 40-70°C) and filtered. Evaporation of the filtrate gave a pale yellow crystalline solid (1.45 g, 61.5%), which was used in the next step without further purification. M.p.: 58-60°C (lit.[9] m.p. 60°C).

General Procedure for the Preparation of the 1-Arylindoles (1c-k). A triturated mixture of indole or 5-methylindole (15 mmol), the corresponding aryl halide (17 mmol), K_2CO_3 (dried before use, 60 mmol), cooper powder (20 mmol) and cuprous iodide (1 mmol) was heated under nitrogen at 190-210°C for 6-8 h. The cooled reaction mixture was extracted with benzene, filtered

and the filtrate was evaporated under reduced pressure. The crude products were purified by crystallization (**1g** and **1j**) or column chromatography on silica gel using light petroleum ether for compounds **1c-f, 1i, 1k** and a mixture of light petroleum ether - benzene (9:1) for **1h** as eluents. Characteristics of preparated 1-arylindoles are indicated in Table 2.

Table 2. 1-Arylindoles **1c-k.**

Comp.	M.p., °C	R_f[a]	Sarting ArHal	Yield,[b] %	Found, % C	H	Formula	Calc., % C	H
1c	oil	0.49	4-$CH_3C_6H_4I$	84	86.64	6.15	$C_{15}H_{13}N$	86.92	6.32
1d	oil	0.51	3-$CH_3C_6H_4I$	84	86.79	6.32	$C_{15}H_{13}N$	86.92	6.32
1e	oil	0.50	2-$CH_3C_6H_4Br$	87	86.77	6.22	$C_{15}H_{13}N$	86.92	6.32
1f	64-6[c]	0.48	4-ClC_6H_4I	82	73.57	4.50	$C_{14}H_{10}ClN$	73.85	4.43
1g	57-8[de]	0.27[f]	4-$CH_3OC_6H_4I$	79[g]	80.96	5.99	$C_{15}H_{13}NO$	80.69	5.87
1h	76-8[d]	0.53[f]	α-NfBr	60	88.61	5.45	$C_{18}H_{13}N$	88.86	5.39
1i	oil	0.49	PhI	90	86.63	6.22	$C_{15}H_{13}N$	86.92	6.32
1j	131-2[h]	0.12[f]	4-$NO_2C_6H_4Br$	60[g]	70.82	4.41	$C_{14}H_{10}N_2O_2$	70.58	4.23
1k	oil	0.64[f]	3-$CF_3C_6H_4Br$	35	69.27	4.11	$C_{15}H_{10}F_3N$	68.96	3.86

[a]Hexane-benzene (9:1), except where otherwise stated. [b]Isolated yield after column chromatography, except where otherwise stated. [c]From methanol. [d]From ethanol. [e]Lit.[10] m.p. 52-54°C. [f]Hexane-benzene (4:1). [g]Isolated yield after crystallization. [h]From a mixture of heptane-benzene; lit.[11] 133-134°C.

General Procedure for the Rearrangement of 1-Arylindoles 1 to 5H-Dibenz[b,f]azepines 2. A stirred mixture of 1-arylindole **1** (200 mg) and PPA (2.5-7.0 ml) was kept under the conditions indicated in each case (Table 1). After cooling the reaction mixture was treated with cold water (50-70 ml) and extracted with $CHCl_3$ (3 x 15 ml). The combined extracts were dried over K_2CO_3, filtered and concentrated under reduced pressure. The residue was chromatographed on silica gel column using a mixture of light petroleum ether-benzene (2:1) as an element.

5H-Dibenz[b,f]azepine (2a). Yellow plates from ethanol. M.p.: 195-196°C (lit.[12] m.p. 196.5-198°C). R_f: 0.63 (benzene). UV, λ_{max} nm (lg ε): 209 (4.32), 226 (4.18), 260 (4.62), 295 sh (3.36), in agreement with the earlier reported data[13]. ^{1}H-NMR (250 MHz): 4.95 (1H, br. s, 5-H), 6.31 (2H, s, 10,11-H), 6.48 (2H, d, J = 7.8 Hz, 4,6-H), 6.82 (2H, t, J = 7.5 Hz, 2,8-H), 6.86 (2H, dd, J = 7.3, 2.4 Hz, 1,9-H), 7.02 (2H, ddd, J = 7.8, 6.6, 2.4 Hz, 3,7-H), in agreement with the earlier reported data[14]. MS, m/z: 194 (16), 193 (M^+, 100), 192 (23), 191 (15), 165 (19). Anal. Calcd for $C_{14}H_{11}N$ (193.25): C 87.01, H 5.74%. Found: C 86.73, H 5.80%.

10-Methyl-5H-dibenz[b,f]azepine (2b). Light yellow crystals from hexane. M.p.: 129-131°C (lit.[15] m.p. 133-134°C). R_f: 0.60 (benzene). UV, λ_{max} nm (lg ε): 209 (4.41), 226 (4.20), 254 (4.51), 285 sh (3.64), 350 sh (2.94). ^{1}H-NMR (400 MHz): 2.26 (3H, s, 10-CH_3), 5.10 (1H, br. s, 5-H), 6.57 (1H, s, 11-H), 6.64, 6.67 (1H each, two d, J = 8.9 Hz, 4,6-H), 6.89, 6.96 (1H each, two t, J = 7.8 Hz,

2,8-H), 6.95, 7.20 (1H each, two dd, J = 7.8, 1.0 Hz, 1,9-H), 7.05, 7.11 (1H each, two td, J = 7.2, 1.1 Hz, 3,7-H). MS, m/z: 208 (17), 207 (M^+, 100), 206 (22), 204 (16), 192 (13), 180 (28). Anal. Calcd for $C_{15}H_{13}N$ (207.28): C 86.92, H 6.32%. Found: C 86.67, H 6.09%.

2-Methyl-5H-dibenz[b,f]azepine (2c). Yellow plates from ethanol. M.p.: 164-166°C (lit.[5] m.p. 159-162°C). R_f: 0.63 (benzene). UV, λ_{max} nm (lg ε): 210 (4.33), 228 (4.19), 261 (4.56), 294 sh (3.49), 372 sh (2.69). ^{1}H-NMR (400 MHz): 2.17 (3H, s, 2-CH_3), 4.89 (1H, br. s, 5-H), 6.28, 6.32 (1H each, two d, J = 11.7 Hz, 10,11-H), 6.40 (1H, d, J = 8.0 Hz, 4-H), 6.48 (1H, dd, J = 7.8, 1.7 Hz, 6-H), 6.67 (1H , d, J = 1.7 Hz, 1-H), 6.78-6.87 (3H, m, 3,8,9-H), 7.01 (1H, ddd, J = 7.8, 7.2, 1.9 Hz, 7-H). MS, m/z: 208 (20), 207 (M^+, 100), 206 (32), 204 (14), 191 (11). Anal. Calcd for $C_{15}H_{13}N$ (207.28): C 86.92, H 6.32%. Found: C 86.74, H 6.13%.

3-Methyl-5H-dibenz[b,f]azepine (2d). Yellow plates from benzene. M.p.: 213-215°C. R_f: 0.66 (benzene). UV, λ_{max} nm (lg ε): 227 (4.15), 234 (4.15), 261 (4.53), 294 (3.38). ^{1}H-NMR (400 MHz): 2.19 (3H, s, 3-CH_3), 4.86 (1H, br. s, 5-H), 6.21, 6.25 (1H each, two d, J = 11.5 Hz, 10,11-H), 6.29 (1H, s, 4-H), 6.44 (1H, d, J = 7.9 Hz, 6-H), 6.61 (1H , d, J = 7.7 Hz, 2-H), 6.72 (1H, d, J = 7.7 Hz, 1-H), 6.78 (1H, td, J = 6.6, 1.0 Hz, 8-H), 6.82 (1H, dd, J = 6.6, 2.6 Hz, 9-H), 6.98 (1-H, ddd, J = 7.9, 6.6, 2.6 Hz, 7-H). Anal. Calcd for $C_{15}H_{13}N$: C 86.92, H 6.32%. Found: C 86.68, H 6.26%.

4-Methyl-5H-dibenz[b,f]azepine (2e). Orange crystals from hexane. M.p.: 85-87°C. R_f: 0.72 (benzene). UV, λ_{max} nm (lg ε): 210 (4.38), 225 (4.22), 260 (4.63), 286 (3.60), 351 sh (2.95). ^{1}H-NMR (400 MHz): 2.29 (3H, s, 4-CH_3), 5.10 (1H, br. s, 5-H), 6.40, 6.43 (2H together, two d, J = 11.7 Hz, 10,11-H), 6.60 (1H, dd, J = 7.5, 1.0 Hz, 6-H), 6.76 and 6.79 (2H together, t, J = 7.2 Hz, 2-H and dd, J = 7.2, 2.4 Hz, 1-H respectively), 6.86 (1H , td, J = 7.4, 1.0 Hz, 8-H), 6.91 (1H, dd, J = 7.4, 1.8 Hz, 9-H), 6.98 (1H, dd, J = 7.2, 2.4 Hz, 3-H), 7.06 (1H, td, J = 7.5, 1.8 Hz, 7-H). Anal. Calcd for $C_{15}H_{13}N$: C 86.92, H 6.32%. Found: C 87.18, H 6.47%.

2-Chloro-5H-dibenz[b,f]azepine (2f). Yellow plates from ethanol. M.p.: 166-167°C (lit.[16] m.p. 168-170°C). R_f: 0.74 (benzene). UV, λ_{max} nm (lg ε): 204 (4.43), 253 (4.66), 282 sh (3.54), 395 sh (2.71). ^{1}H-NMR (400 MHz): 4.91 (1H, br. s, 5-H), 6.20 (1H, d, J = 11.6 Hz, 11-H), 6.34 (1H, d, J = 11.6 Hz, 10-H), 6.41(1H, d, J = 8.5 Hz, 4-H), 6.48 (1H , d, J = 6.6 Hz, 6-H), 6.82 (1H, d, J = 2.5 Hz, 1-H), 6.83-6.88 (2H, m, 8,9-H), 6.96 (1H, dd, J = 8.5, 2.5 Hz, 3-H), 7.04 (1H, ddd, J = 8.2, 6.6, 2.8 Hz, 7-H). Anal. Calcd for $C_{14}H_{10}ClN$: C 73.85, H 4.43%. Found: C 73.61, H 4.67%.

2-Methoxy-5H-dibenz[b,f]azepine (2g). Yellow plates from ethanol. M.p.: 157.5-159.5°C. R_f: 0.36 (benzene). UV, λ_{max} nm (lg ε): 259 (4.42), 296 (3.45), 368 sh (2.37). ^{1}H-NMR (400 MHz): at room temperature 3.72 (3H, s, OCH_3), 6.48, 6.20-6.65 (6H, br. s and br. m), 6.61 (1H, dd, J = 8.0, 2.3 Hz, 3-H), 6.90 (1H, br. d, 9-H), 7.05 (1H, t, J = 7.6 Hz, 7-H), 5-H not observed; at -60°C 3.73 (3H, s, OCH_3), 4.90 (1H , br. s, 5-H), 6.36, 6.43 (2H, two d AB, J = 11.5 Hz, 10,11-H), 6.49, 6.50, 6.55 (3H together, d, J = 2.7 Hz; br. s; br. d, 1-H, 4-H, and 6-H respectively), 6.63 (1H, dd, J = 8.5, 2.7 Hz, 3-H), 6.86, 6.92 (2H together, br. s and d, J = 7.2 Hz, 8-H and 9-H respectively), 7.06 (1H, t, J = 7.2 Hz, 7-H). MS, m/z: 224 (21), 223 (M^+, 95), 208 (M-CH_3, 68), 181 (25), 180 [(M-CH_3)-CO, 100], 179 (36), 178 (40), 152 (40), 69 (50). Anal. Calcd for $C_{15}H_{13}NO$ (223.28) : C 80.69, H 5.87%. Found: C 81.01, H 5.79%.

13H-Benzo[b]naphth[2,1-f]azepine (2h). Reddish-brown crystals from benzene. M.p.: 160-162°C. R_f: 0.71 (benzene). UV, λ_{max} nm (lg ε): 229 (4.59), 240 sh (4.30), 262 (4.44), 282 sh (4.20), 344 (3.08). ^{1}H-NMR (400 MHz): 5.79 (1H, br. s, 13-H), 6.60, 6.63 (2H together, two d, J = 11.6 Hz, 7,8-H), 6.77 (1H, d, J = 7.7 Hz, 12-H), 6.91 (1H , t, J = 7.5 Hz, 10-H), 6.96 (1H, d, J = 7.5 Hz, 9-H), 7.08 (1H, d, 6-H), 7.12 (1H, t, 11-H) 7.39 (1H, d, 5-H), 7.40, 7.47 (1H each, two t, 2,3-H), 7.73, 7.93 (1H each, two d, J = 7.9, 8.4 Hz respectively, 1,4-H). Anal. Calcd for $C_{18}H_{13}N$: C 88.86, H 5.39%. Found: C 88.61, H 5.45%.

2,3-Dimethyl-1-phenylindole (5). A solution of 1,1-diphenylhydrazine hydrochloride (2.2 g, 10 mmol) and methyl ethyl ketone (0.9 ml, 0.72 g, 10 mmol) in acetic acid (35 ml) and conc. HCl (2 ml) was heated under reflux for 2 h. The solvent was then removed under reduced pressure and the residue was shaken with benzene (50 ml) and water (50 ml). The organic layer was separated, washed with aq. HCl (1:2) and water, dried over $MgSO_4$ and concentrated under reduced pressure. The residual oil was purified by column chromatography on silica gel. Elution with light petroleum ether gave indole **5** (1.92 g, 87% yield) as a light yellow oil. R_f: 0.41 (hexane:benzene-9:1). ^{1}H-NMR (100 MHz): 2.17 (3H, s, 2-CH_3), 2.28 (3H, s, 3-CH_3), 6.95-7.52 (9H, m, aromatic H). Anal. Calcd for $C_{16}H_{15}N$: C: 86.84, H 6.83%. Found: C 86.55, H 6.71%.

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