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CYCLIZATION OF DIALKYL(3-PHENYLPROPEN-2-YL)-(3-PHENYLPROPYN-2-YL)AMMONIUM BROMIDES BY THE ACTION OF AN AQUEOUS ALKALI SOLUTION. AQUEOUS-ALKALINE CLEAVAGE OF THE CYCLIZATION PRODUCTS – *N,N*-DIALKYL-4(9)-PHENYL-3a,4-DIHYDRO-BENZO[*f*]ISOINDOLINIUM BROMIDES

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When heated in an alkaline aqueous medium, dialkyl(3-phenylpropen-2-yl)(3-phenylpropyn-2-yl)-ammonium bromides undergo intramolecular cyclization, forming N,N-dialkyl-4(9)-phenyl-3a,4-dihydrobenzo[f]isoindolinium bromides. The cyclization products undergo aqueous-alkaline cleavage at the C(1)–N(2) or N(2)–C(3) bond, which leads to a mixture of 2-(dialkylaminomethyl)-3-methyl- and 3-(dialkylaminomethyl)-2-methyl-1-phenylnaphthalenes. However, only the C(1)–N(2) bond cleavage product is formed in the case of 2,2-pentamethylene-9-phenyl-3a,4-dihydrobenzo-[f]isoindolinium bromide.

Keywords: (dialkylaminomethyl)naphthalenes, dialkyl(3-phenylpropen-2-yl)(3-phenylpropyn-2-yl)ammonium bromides, isoindolinium salts, aqueous-alkaline cleavage, intramolecular cyclization.

Earlier in papers by A. T. Babayan and co-workers it was established that under conditions of base catalysis at room temperature ammonium salts with the general formula $Alk_2(HC{\equiv}CCH_2)(ArC{\equiv}CCH_2)N^+X^-$ (X = Hal; Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4) undergo intramolecular cyclization with spontaneous heating [1-4]. The cyclization of similar salts with an allyl fragment in place of the propargyl fragment under conditions of base catalysis occurs on heating (2-3 h, 90-92°C) [2, 3, 5, 6].

After the publication of investigations into the cyclization of (allyl)(3-phenylpropargyl)-substituted ammonium salts [5], papers with similar content were also published by British scientists [7, 8]. Japanese researchers obtained 2-methylbenzo[*f*]isoindoline in 22% yield from dimethyl(propargyl)(3-phenylpropargyl)ammonium bromide with sodium ethoxide in absolute ethanol [9]. In the same investigation the expected 2-methyl-4-phenylbenzo[*f*]isoindoline was not obtained from dimethylbis(3-phenylpropargyl)-ammonium bromide either with sodium ethoxide in absolute ethanol or with NaOH in aqueous solution, and

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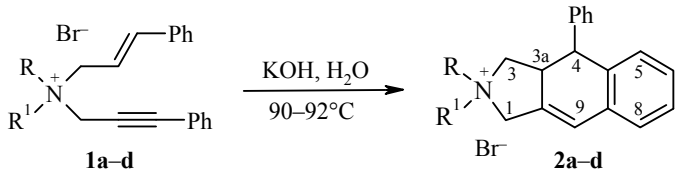
the authors explained this by steric effects. A. T. Babayan and co-workers established that the $Alk_2(PhC{\equiv}CCH_2)_2N^+X^-$ salts undergo cyclization when their aqueous solutions are heated even in the absence of bases, i.e., the cyclization is apparently facilitated by the second phenyl group [10].

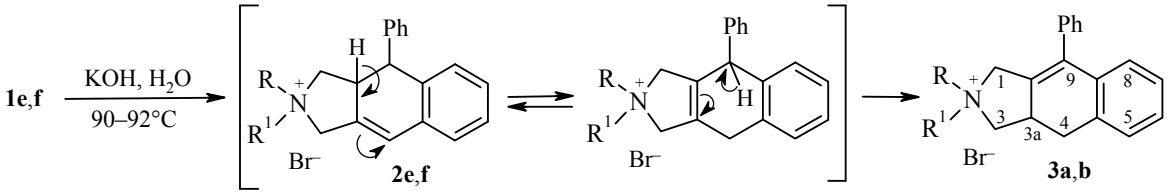
Based on those considerations we assumed that the second phenyl group, located at the γ-position of the allyl substituent (in place of one phenylpropargyl group), must also promote cyclization. To check this assumption in the present work, we studied the behavior of dialkyl(3-phenylpropen-2-yl)(3-phenylpropyn-2-yl)ammonium bromides **1a-f** under the conditions of base catalysis. Contrary to our expectations, the cyclization of the salts **1a-f** took place under fairly rigorous conditions (salt:alkali molar ratio 2:1, reaction time 5-6 h at 90-92°C). The salts **1a-f** are poorly soluble in water, and the reaction was therefore conducted in a water-alcohol solution. As a result of the cyclization of salts **1a-d**, the corresponding dialkyl-4-phenyl-3a,4-dihydrobenzo[*f*]isoindolinium bromides **2a-d** are formed in 62-72% yields.



1a–d **2a–d**

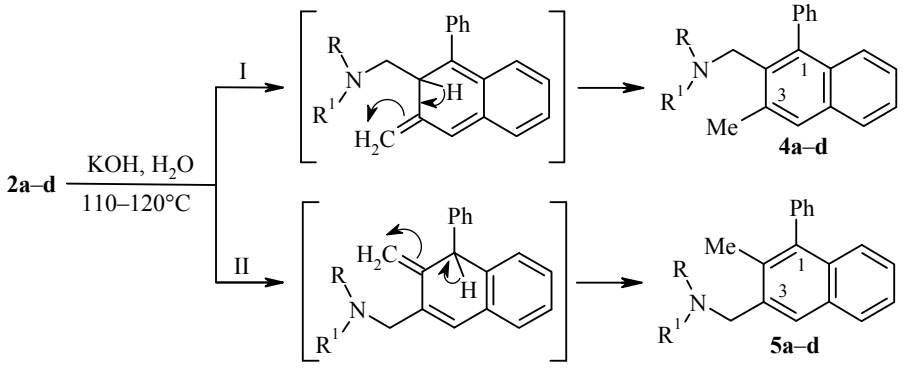
a R = R¹ = Me, **b** R = R¹ = Pr, **c** R+R¹ = –$(CH_2)_4$–, **d** R+R¹ = –$(CH_2)_2O(CH_2)_2$–

The bromides **1e**,**f** under the same conditions did not produce the 4-phenyl-substituted salts **2e**,**f**, but rather their 9-phenyl-substituted isomers **3a**,**b** with yields of 65-68%.



1e, **2e**, **3a** R = R¹ = Et, **1f**, **2f**, **3b** R+R¹ = –$(CH_2)_5$–

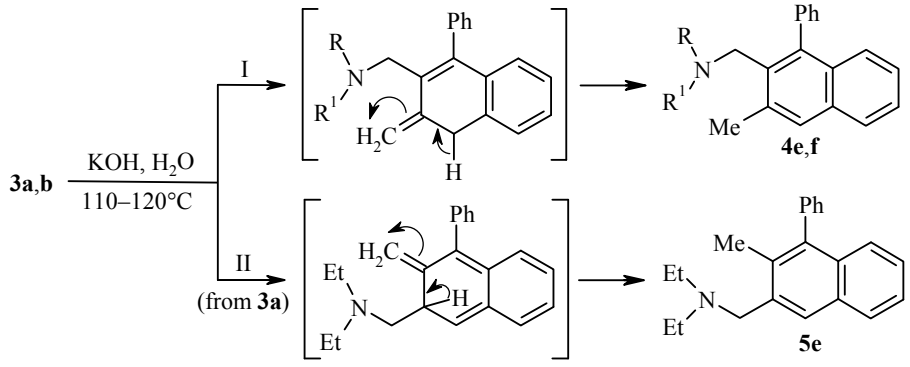
It should be noted that the product formed upon the cyclization of salt **1b** under the conditions of base catalysis could not be obtained in the crystalline state, and it was therefore used in further transformations without isolation of the cyclic salt **2b**.



4,**5** **a** R = R¹ = Me, **b** R = R¹ = Pr, **c** R+R¹ = –$(CH_2)_4$–, **d** R+R¹ = –$(CH_2)_2O(CH_2)_2$–

When refluxed in a 25% KOH solution, the salts **2a-d** are cleaved quite smoothly at the C(1)–N(2) bond (path I) or N(2)–C(3) bond (path II), forming a mixture of the isomeric 2-(dialkylaminomethyl)-3-methyl-1-phenylnaphthalenes **4a-d** and 3-(dialkylaminomethyl)-2-methyl-1-phenylnaphthalenes **5a-d** with overall yields of 65-68%.

Under the same conditions, a mixture of the amines **4e** and **5e** was formed from the salt **3a**, while only the isomer **4f** was obtained from compound **3b** with a yield of 75%.



4 e R = R^1 = Et, **f** R+R^1 = –$(CH_2)_5$–

The presented structures of the salts **1a-f**, **2a-d**, **3a**,**b** and the amines **4a-f**, **5a-e** agree well with their IR and ^{1}H NMR spectral data. The structure of the salts **2a**,**c**,**d** and **3a**,**b** was also confirmed by ^{13}C NMR spectroscopy. Double resonance and two-dimensional correlation spectroscopy (COSY, NOESY, DEPT, HMQC) were used to assign the signals in the ^{1}H and ^{13}C NMR spectra. Thus, in the spectra of the isomers **4a-f**, a nuclear Overhauser effect is observed for the signals of the protons of the 3-CH_3 group and H-4, and also for the protons of the CH_2 group and the *ortho*-proton of the phenyl substituent. On the other hand, the spectra of the isomers **5a-e** exhibit a nuclear Overhauser effect for the signals of the 2-CH_2 group and the *ortho*-proton of the phenyl substituent, and also for the signals of the CH_2 group and the H-4 proton. The signals of the 2-CH_2 and 3-CH_2 groups and also the 2-CH_3 and 3-CH_3 groups have different chemical shifts, allowing to determine fairly accurately the content of the isomers **4** and **5** from the signal intensity ratio in the reaction product spectra. It was shown that the content of the isomer **4** in the mixtures obtained from compounds **2a-d**, **3a** amounts to 68-80%.

Thus, in comparison with the other allyl analogs, the cyclization of (3-phenylpropen-2-yl)-(3-phenylpropyn-2-yl)ammonium bromides in an water-alcohol solution of alkali leads to high yields of dialkyl-4(9)-phenyl-3a,4-dihydrobenzo[*f*]isoindolinium bromides. It was found that these salts undergo aqueous-alkaline cleavage at the C(1)–N(2) and N(2)–C(3) bonds. 2,2-Pentamethylene-9-phenyl-3a,4-dihydrobenzo-[*f*]isoindolinium bromide is only cleaved at the C(1)–N(2) bond.

EXPERIMENTAL

The IR spectra of the salts **1a-f**, **2a**,**c**,**d**, **3a**,**b** (films from chloroform) and the amines **4a-f**, **5a-e** (thin layers) were recorded on a Specord IR-75 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 VX spectrometer (300 and 75 MHz, respectively) in 1:3 DMSO-d_6–CCl_4 with TMS as internal standard. Elemental analysis was performed on a Vario MICRO Cube compact element analyzer. The melting points of the salts were determined on a VEB Wägetechnik Rapido instrument. The purity of the obtained compounds was monitored by TLC on Silufol UV-254 plates in the 10:2:1:5 *n*-BuOH–EtOH–H_2O–AcOH system and visualization with iodine vapor.

Preparation of Salts 1a-f (General Method). 3-Bromo-1-phenylpropene [14] (4.2 g, 22.5 mmol) was added to a solution of the corresponding dialkyl(3-phenylpropyn-2-yl)amine [11-13] (15.0 mmol) in Et_2O (20 ml) and MeCN (5 ml). The reaction occurred with moderate spontaneous heating. The precipitated salts **1a-f** were washed with absolute Et_2O (2×30 ml). The product was recrystallized from absolute EtOH.

Dimethyl(3-phenylpropen-2-yl)(3-phenylpropyn-2-yl)ammonium Bromide (1a). Yield 5.2 g (97%). White crystals, mp 130–132°C. IR spectrum, ν, cm^{-1}: 1580, 1600, 3010, 3060 (Ar), 2240 (C≡C), 1630 (C=C), 1940, 730, 700, 680 (Ph). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.60-7.55 (6H, m, H Ph); 7.45-7.25 (4H, m, H Ph); 7.06 (1H, d, *J* = 15.6, =C<u>H</u>Ph); 6.55 (1H, dt, *J* = 15.6, *J* = 7.5, $CH_2C\underline{H}$=); 4.87 (2H, s, $NCH_2C{\equiv}C$); 4.52 (2H, d, *J* = 7.5, $NC\underline{H}_2CH$=); 3.37 (6H, s, $N(CH_3)_2$). Found, %: C 67.88; H 6.49; Br 22.77; N 4.18. $C_{20}H_{22}BrN$. Calculated, %: C 67.42; H 6.22; Br 22.43; N 3.93.

Dipropyl(3-phenylpropen-2-yl)(3-phenylpropyn-2-yl)ammonium Bromide (1b). Yield 6.0 g (97%). White crystals, mp 170-174°C. IR spectrum, ν, cm^{-1}: 1580, 1600, 3010, 3050 (Ph), 2240 (C≡C), 1640 (C=C), 1930, 720, 700, 680 (Ph). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.61-7.50 (6H, m, H Ph); 7.45-7.25 (4H, m, H Ph); 7.08 (1H, d, *J* = 15.6, =C<u>H</u>Ph); 6.54 (1H, dt, *J* = 15.6, *J* = 7.4, $CH_2C\underline{H}$=); 4.79 (2H, s, $NCH_2C{\equiv}C$); 4.41 (2H, d, *J* = 7.4, $NC\underline{H}_2CH$=); 3.52-3.46 (4H, m, $N(C\underline{H}_2CH_2CH_3)_2$); 1.98-1.84 (4H, m, $N(CH_2C\underline{H}_2CH_3)_2$); 1.06 (6H, t, *J* = 7.2, $2CH_3$). Found, %: C 69.43; H 6.96; Br 19.67; N 3.77. $C_{24}H_{30}BrN$. Calculated, %: C 69.90; H 7.33; Br 19.37; N 3.40.

***N*-(3-Phenylpropen-2-yl)-*N*-(3-phenylpropyn-2-yl)pyrrolidinium Bromide (1c)**. Yield 5.6 g (97%). White crystals, mp 92-95°C. IR spectrum, ν, cm^{-1}: 1590, 1610, 3020, 3060 (Ph), 2230 (C≡C), 1640 (C=C), 1930, 720, 700, 680 (Ph); ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.61-7.50 (6H, m, H Ph); 7.45-7.25 (4H, m, H Ph); 7.08 (1H, d, *J* = 15.6, =C<u>H</u>Ph); 6.59 (1H, dt, *J* = 15.6, *J* = 7.6, $CH_2C\underline{H}$=); 4.80 (2H, s, $NCH_2C{\equiv}C$); 4.50 (2H, d, *J* = 7.6, $NC\underline{H}_2CH$=); 3.95-3.80 (4H, m, 2,5-CH_2 pyrrolidine); 2.35-2.21 (4H, m, 3,4-CH_2 pyrrolidine). Found, %: C 69.57; H 6.59; Br 21.22; N 4.06. $C_{22}H_{24}BrN$. Calculated, %: C 69.11; H 6.33; Br 20.90; N 3.66.

***N*-(3-Phenylpropen-2-yl)-*N*-(3-phenylpropyn-2-yl)morpholinium Bromide (1d)**. Yield 5.9 g (98%). White crystals, mp. 178-181°C. IR spectrum, ν, cm^{-1}: 1590, 1600, 3020, 3060 (Ph), 2230 (C≡C), 1630 (C=C), 1940, 740, 700, 680 (Ph). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.61-7.56 (6H, m, H Ph); 7.45-7.25 (4H, m, H Ph); 7.13 (1H, d, *J* = 15.5, =C<u>H</u>Ph); 6.58 (1H, dt, *J* = 15.5, *J* = 7.6, $CH_2C\underline{H}$=); 5.01 (2H, s, $NCH_2C{\equiv}C$); 4.67 (2H, d, *J* = 7.6, $NC\underline{H}_2CH$=); 4.15 (2H, dt, *J* = 13.9, *J* = 4.8) and 4.07 (2H, dt, *J* = 13.9, *J* = 4.8, $(OCH_2)_2$); 3.80 (4H, t, *J* = 4.8, $(NCH_2)_2$). Found, %: C 66.81; H 6.36; Br 20.36; N 3.82. $C_{22}H_{24}BrNO$. Calculated, %: C 66.34; H 6.07; Br 20.06; N 3.52.

Diethyl(3-phenylpropen-2-yl)(3-phenylpropyn-2-yl)ammonium Bromide (1e). Yield 5.5 g (96%). White crystals, mp 143-145°C. IR spectrum, ν, cm^{-1}: 1590, 1600, 3020, 3060 (Ph), 2230 (C≡C), 1640 (C=C), 1940, 740, 710, 690 (Ph). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.61-7.53 (6H, m, H Ph); 7.45-7.26 (4H, m, H Ph); 7.08 (1H, d, *J* = 15.5, =C<u>H</u>Ph); 6.53 (1H, dt, *J* = 15.5, *J* = 7.5, $CH_2C\underline{H}$=); 4.73 (2H, s, $NCH_2C{\equiv}C$); 4.35 (2H, d, *J* = 7.5, $NC\underline{H}_2CH$=); 3.62 (4H, q, *J* = 7.2, $(N(C\underline{H}_2CH_3)_2$); 1.46 (6H, t, *J* = 7.2, $(N(CH_2\underline{CH}_3)_2$). Found, %: C 69.21; H 7.08; Br 21.09; N 3.90. $C_{22}H_{26}BrN$. Calculated, %: C 68.75; H 6.82; Br 20.79; N 3.64.

***N*-(3-Phenylpropen-2-yl)-*N*-(3-phenylpropyn-2-yl)piperidinium Bromide (1f)**. Yield 5.7 g (96%). White crystals, mp 94-96°C. IR spectrum, ν, cm^{-1}: 1590, 1610, 3020, 3060 (Ph), 2240 (C≡C), 1640 (C=C), 1940, 730, 720, 680 (Ph). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.60-7.54 (6H, m, H Ph); 7.45-7.25 (4H, m, H Ph); 7.08 (1H, d, *J* = 15.5, =C<u>H</u>Ph); 6.54 (1H, dt, *J* = 15.5, *J* = 7.6, $CH_2C\underline{H}$=); 4.83 (2H, s, $NCH_2C{\equiv}C$); 4.50 (2H, d, *J* = 7.6, $NC\underline{H}_2CH$=); 3.75 (4H, t, *J* = 5.7, 2,6-CH_2 piperidine); 2.09-1.92 (2H, m) and 1.83-1.71 (4H, m, 3,4,5-CH_2 piperidine). Found, %: C 70.16; H 6.26; Br 20.51; N 3.88. $C_{23}H_{26}BrN$. Calculated, %: C 69.70; H 6.61; Br 20.16; N 3.53.

Cyclization of Salts 1a-f (General Method). A 3 N KOH aqueous solution (2 ml) was gradually added to a solution of the salt **1a-f** (12 mmol) in water (5 ml) and EtOH (2.5 ml) (salt:KOH molar ratio 2:1). Spontaneous heating of the reaction mixture was not observed. The reaction mixture was maintained at 90-92°C for 5-6 h, cooled, and extracted with Et_2O (3×30 ml). Crystals of the products **2a**,**c**,**d** and **3a**,**b** separated from the aqueous layer at room temperature. They were filtered off and recrystallized from absolute

EtOH (compounds **2c**,**d**, **3a**,**b**) or water (compound **2a**). Crystals of the starting salt **1a-f** separated from the filtrate at -2-3°C (~10-15% on the amount used in the reaction). They did not give a melting point depression in a mixed melting test with an authentic sample of this salt. To isolate the product **2b**, the aqueous layer after extraction of the reaction mixture with ether and separation of the starting salt **1b** was treated with an HBr aqueous solution to an acidic reaction and evaporated to dryness. The salt **2b** was extracted from the residue with absolute ethanol and was precipitated from the alcohol extract with absolute ether in the form of a honeylike substance. Attempts to obtain the salt **2b** in crystalline form were unsuccessful. Therefore, the substance isolated after decantation of the liquid phase was used for aqueous-alkaline cleavage (see below) without further purification.

2,2-Dimethyl-4-phenyl-3a,4-dihydrobenzo[*f*]isoindolinium Bromide (2a). Yield 2.65 g (65%). Shiny crystals, mp 180-182°C. IR spectrum, ν, cm^{-1}: 1580, 1600, 3000, 3020, 3060 (Ar), 670, 700, 740, 770, 1940 (Ph), 1630 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.45-7.39 (4H, m, H Ph); 7.37-7.30 (1H, m, H Ph); 7.21-7.12 (2H, m, H-7,8); 7.03 (1H, td, *J* = 7.3, *J* = 1.9, H-6); 6.72 (1H, q, *J* ≈ 1.5, H-9); 6.54 (1H, d, *J* = 7.6, H-5); 4.74 (1H, d, *J* = 16.4) and 4.70 (1H, d, *J* = 16.4, 1-CH_2); 4.22 (1H, d, *J* = 14.0, 4-CH); 3.89-3.82 (1H, m) and 3.65 (1H, dd, *J* = 9.5, *J* = 7.0, 3-CH_2); 3.81-3.70 (1H, m, 3a-CH); 3.44 (3H, s, CH_3); 3.26 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 139.8; 137.3; 135.5; 133.5; 128.5; 127.1; 126.9; 126.4; 126.3; 126.2; 121.3; 68.1 and 67.4 (CH_2); 52.1 (CH_3); 51.5 (CH_3); 48.6 (CH); 41.9 (CH). Found, %: C 66.96; H 5.87; Br 22.91; N 4.04. $C_{20}H_{22}BrN$. Calculated, %: C 67.42; H 6.22; Br 22.43; N 3.93.

2,2-Tetramethylene-4-phenyl-3a,4-dihydrobenzo[*f*]isoindolinium Bromide (2c). Yield 2.84 g (62%). Shiny crystals, mp 163-164°C. IR spectrum, ν, cm^{-1}: 1590, 1620, 3010, 3020, 3060 (Ar), 680, 710, 750, 770, 1930 (Ph), 1640 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.41-7.37 (4H, m, H Ph); 7.35-7.26 (1H, m, H Ph); 7.16-7.09 (2H, m, H-7,8); 7.00 (H, ddd, *J* = 7.7, *J* = 6.3, *J* = 2.5, H-6); 6.67 (1H, dt, *J* = 2.1, *J*= 2.1, H-9); 6.52 (H, d, *J* = 7.6, H-5); 4.81 (1H, d, *J* = 15.8) and 4.79 (1H, d, *J* = 15.8, 1-CH_2); 4.19 (1H, d, *J* = 14.5, 4-CH); 4.07-3.90 (2H, m) and 3.85-3.55 (5H, m, 2,5-CH_2 pyrrolidine, 3-CH_2, 3a-CH); 2.32-2.07 (4H, m, 3,4-CH_2 pyrrolidine). ^{13}C NMR spectrum, δ, ppm: 139.7; 137.1; 134.9; 133.4; 128.5 (2C); 128.4; 127.0; 126.8; 126.4 (3C); 126.1; 121.3 (=CH); 65.5 and 64.8 (C-1); 62.9; 62.5; 48.6; 42.2; 21.5; 21.3. Found, %: C 68.64; H 5.97; Br 21.41; N 3.79. $C_{22}H_{24}BrN$. Calculated, %: C 69.11; H 6.33; Br 20.90; N 3.66.

Spiro[morpholine-4′,2-(4-phenyl-3a,4-dihydrobenzo[*f*]isoindolinium)] Bromide (2d). Yield 3.44 g (72%). Shiny crystals, mp 265-267°C. IR spectrum, ν, cm^{-1}: 1590, 1620, 3010, 3020, 3060 (Ar), 680, 720, 760, 770, 1940 (Ph), 1630 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.46-7.39 (4H, m, H Ph); 7.38-7.31 (1H, m, H Ph); 7.22-7.12 (2H, m, H-7,8); 7.03 (1H, td, *J* = 7.4, *J* = 1.8, H-6); 6.73 (1H, dt, *J* = 2.0, *J* ≈ 2.0, H-9); 6.52 (1H, d, *J* = 7.7, H-5); 5.04 (1H, dt, *J* = 16.0, *J*= 1.5) and 4.86 (1H, dt, *J* = 16.0, *J*= 1.5, 1-CH_2); 4.25 (1H, d, *J* = 14.4, 4-CH); 4.07-3.71 (9H, m) and 3.65-3.59 (2H, m, $N(CH_2CH_2)_2O$, 3-CH_2, 3a-CH). Found, %: C 65.86; H 5.72; Br 20.34; N 3.98. $C_{22}H_{24}BrNO$. Calculated, %: C 66.34; H 6.07; Br 20.06; N 3.52.

2,2-Diethyl-9-phenyl-3a,4-dihydrobenzo[*f*]isoindolinium Bromide (3a). Yield 2.90 g (65%). Shiny crystals, mp 178-180°C. IR spectrum, ν, cm^{-1}: 1570, 1610, 3000, 3020, 3060 (Ar), 680, 710, 740, 770, 1940 (Ph), 1640 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.49-7.43 (2H, m, H Ph); 7.41-7.35 (1H, m, H Ph); 7.34-7.30 (2H, m, H Ph); 7.24 (H, d, *J* =7.5, H Ar); 7.16 (1H, td, *J* = 7.8, *J* = 1.3, H Ar); 7.08 (1H, td, *J* = 7.5, *J* = 1.3, H Ar); 6.80 (1H, dd, *J* = 7.6, *J* = 1.2, H Ar); 4.65 (1H, dd, *J* = 16.0, *J* = 2.0) and 4.15 (1H, dd, *J* = 16.0, *J* = 2.5, 1-CH_2); 4.29 (1H, dd, *J* = 11.7, *J* = 8.5) and 3.73 (1H, dd, *J* = 11.7, *J* = 9.4, 3-CH_2); 3.65–3.43 (5H, m, $(CH_3C\underline{H}_2)_2N$, 3a-CH); 3.04 (1H, dd, *J* = 14.7, *J* = 6.7) and 2.98 (1H, d, *J* = 14.7, 4-CH_2); 1.35 (3H, t, *J* = 7.1) and 1.26 (3H, t, *J* = 7.1, $(C\underline{H}_3CH_2)_2N$). ^{13}C NMR spectrum, δ, ppm: 136.5; 134.8; 134.1; 133.7; 131.7, 128.8, 128.2; 127.4, 127.1, 126.3, 125.4; 64.7, 63.5 (1,3-CH_2); 54.8, 53.7 ($(CH_3\underline{C}H_2)_2N$); 35.7, 31.8 ($\underline{C}H\underline{C}H_2$); 8.4, 8.2 ($(\underline{C}H_3CH_2)_2N$). Found, %: C 68.28; H 6.45; Br 21.06; N 4.23. $C_{22}H_{26}BrN$. Calculated, %: C 68.75; H 6.82; Br 20.79; N 3.64.

2,2-Pentamethylene-9-phenyl-3a,4-dihydrobenzo[*f*]isoindolinium Bromide (3b). Yield 3.20 g (68%). Shiny crystals, mp 284-286°C (abs. EtOH). IR spectrum, ν, cm^{-1}: 1580, 1610, 3010, 3030, 3060 (Ar), 690, 720, 760, 780, 1940 (Ph), 1630 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.48-7.29 (5H, m, H Ph); 7.24 (1H,

d, J = 7.4, H Ar); 7.15 (1H, td, J = 7.4, J = 1.2, H Ar); 7.08 (1H, td, J = 7.4, J = 1.2, H Ar); 6.80 (1H, dd, J = 7.4, J = 1.2, H Ar); 4.69 (1H, dd, J = 15.9, J = 1.5) and 4.18 (1H, dd, J = 15.9, J = 2.7, 1-CH_2); 4.38 (1H, dd, J = 11.6, J = 8.2) and 3.75 (1H, dd, J = 11.6, J = 9.3, 3-CH_2); 3.74-3.45 (5H, m, 3a-CH, 2,6-CH_2 piperidine); 3.06 (1H, dd, J = 14.8, J = 6.5) and 2.93 (1H, d, J = 14.8, 4-CH_2); 2.01-1.81 (2H, m) and 1.77-1.52 (4H, m, 3,4,5-CH_2 piperidine). ^{13}C NMR spectrum, δ, ppm: 136.6; 134.8; 134.2; 133.8; 131.5; 128.8 (2C, Ph); 128.3 (2C, Ph); 127.5 (CH, Ph); 127.4 (CH, Ar); 127.1 (CH, Ar); 126.3 (CH, Ar); 125.3 (CH, Ar); 65.1 and 64.1 (C-1,3); 60.4 and 59.2 (2,6-CH_2 piperidine); 35.3 (C-3a); 31.9 (C-4); 20.8, 20.6. Found, %: C 69.22; H 6.24; Br 20.45; N 4.08. $C_{23}H_{26}BrN$. Calculated, %: C 69.70; H 6.61; Br 20.16; N 3.53.

Aqueous-Alkaline Cleavage of Salts 2a,c,d and 3a,b (General Method). A 25% KOH solution (2 g of KOH in 6 ml of H_2O) (~8 ml) was added to the salt **2a**,**c**,**d** or **3a**,**b** (6 mmol) in H_2O (4 ml). The mixture was maintained at 110-120°C for 1.5 h, and the water was then distilled from it with the periodic addition of new portions (10-15 ml) of water. The temperature of the reaction mixture was raised to 140-145°C for a few minutes (to complete the process). The reaction mixture and its distilled part were then extracted with Et_2O (3×50 ml). The combined extract was shaken with a 15% HCl solution, and the hydrochloric acid layer was separated, made alkaline, and extracted with Et_2O. The extract was washed with water and dried over $MgSO_4$. A mixture of the isomeric amines **4**, **5a**,**c-e** and the amine **4f**, produced during cleavage of the salt **3b**, were isolated from the residue by vacuum distillation after removal of the ether.

After cyclization of the salt **1b** under conditions of base catalysis aqueous-alkaline cleavage of the salt **2b** was performed directly without its isolation. The aqueous-alkaline cleavage and also the isolation of the isomeric amines **4b** and **5b** from the reaction mixture were carried out according to the method described above.

2-(Dimethylaminomethyl)-3-methyl-1-phenylnaphthalene (4a) and 3-(Dimethylaminomethyl)-2-methyl-1-phenylnaphthalene (5a). Total yield 1.1 g (65%), bp 177-179°C (1.0-1.5 mm Hg). IR spectrum, ν, cm^{-1}: 680, 700, 730, 1940, 880, 1600, 3030, 3060 (Ar). Ratio of isomers **4a**:**5a**, 4:1. ^{1}H NMR spectrum of mixture of compounds **4a** and **5a**, δ, ppm (J, Hz): 7.75 (0.2H, br. d, J = 8.1, H Ar (**5a**)); 7.70 (0.8H, br. d, J = 8.1, H Ar (**4a**)); 7.68 (0.2H, s, H-4 (**5a**)); 7.61 (0.8H, s, H-4 (**4a**)); 7.48-7.38 (3H, m), 7.36-7.31 (1H, m), and 7.23-7.16 (4H, m, H Ar (**4a**+**5a**)); 3.53 (0.4H, s, $Me_2NC\underline{H}_2$ (**5a**)); 3.31 (1.6H, s, $Me_2NC\underline{H}_2$ (**4a**)); 2.64 (2.4H, s, 3-CH_3 (**4a**)); 2.28 (1.2H, s, $N(CH_3)_2$ (**5a**)); 2.20 (0.6H, s, 2-CH_3 (**5a**)); 2.01 (4.8H, s, $N(CH_3)_2$ (**4a**)). Found, %: C 87.62; H 7.89; N 5.24. $C_{20}H_{21}N$. Calculated, %: C 87.23; H 7.69; N 5.09.

2-(Dipropylaminomethyl)-3-methyl-1-phenylnaphthalene (4b) and 3-(Dipropylaminomethyl)-2-methyl-1-phenylnaphthalene (5b). Total yield 1.3 g (67%), bp 185-187°C (1 mm Hg). IR spectrum, ν, cm^{-1}: 680, 710, 740, 1930, 890, 1610, 3040, 3060 (Ar). Ratio of isomers **4b**:**5b,** 7:3. ^{1}H NMR spectrum of mixture of compounds **5b** and **4b**, δ, ppm (J, Hz): 7.76 (0.3H, s, H-4 (**5b**)); 7.59 (0.7H, s, H-4 (**4b**)); 7.74 (0.3H, d, J = 8.2, H Ar (**5b**)); 7.70 (0.7H, d, J = 8.2, H Ar (**4b**)); 7.50-7.29 (4H, m, H Ar (**4b**+**5b**)); 7.22-7.13 (4H, m, H Ar (**4b**+**5b**)); 3.69 (0.6H, s, $Pr_2NC\underline{H}_2$ (**5b**)); 3.49 (1.4H, s, $Pr_2NC\underline{H}_2$ (**4b**)); 2.67 (2.1H, s, 3-CH_3 (**4b**)); 2.21 (0.9H, s, 2-CH_3 (**5b**)); 2.48-2.42 (1.2H, m, $(CH_3CH_2C\underline{H}_2)_2N$ (**5b**)); 2.19-2.13 (2.8H, m, $(CH_3CH_2C\underline{H}_2)_2N$ (**4b**)); 1.56-1.44 (1.2H, m, $(CH_3C\underline{H}_2CH_2)_2N$ (**5b**)); 1.33-1.21 (2.8H, m, $(CH_3C\underline{H}_2CH_2)_2N$ (**4b**)); 0.87 (1.8H, t, J = 7.3, $(C\underline{H}_3CH_2CH_2)_2N$ (**5b**)); 0.75 (4.2H, t, J = 7.3, $(C\underline{H}_3CH_2CH_2)_2N$ (**4b**)). Found, %: C 87.36; H 9.03; N 4.43. $C_{24}H_{29}N$. Calculated, %: C 86.96; H 8.82; N 4.23.

3-Methyl-2-pyrrolidinomethyl-1-phenylnaphthalene (4c) and 2-Methyl-3-pyrrolidinomethyl-1-phenylnapthalene (5c). Total yield 1.2 g (67%), bp 195–197°C (1-2 mm Hg). IR spectrum, ν, cm^{-1}: 670, 700, 730, 1940, 880, 1600, 3030, 3050 (Ar). Ratio of isomers **4c**:**5c**, 68:32. ^{1}H NMR spectrum of mixture of compounds **5c** and **4c**, δ, ppm (J, Hz): 7.74 (0.32H, br. d, J = 8.1, H Ar (**5c**)); 7.69 (0.68H, br. d, J = 8.1, H Ar (**4c**)); 7.71 (0.32H, s, H-4 (**5c**)); 7.59 (0.68H, s, H-4 (**4c**)); 7.50-7.38 (3H, m), 7.36-7.29 (1H, m), and 7.23-7.14 (4H, m, H Ar (**4c**+**5c**)); 3.74 (0.64H, s, $NC\underline{H}_2Ar$ (**5c**)); 3.51 (1.36H, s, NCH_2Ar (**4c**)); 2.60-2.54 (1.28H, m, 2,5-CH_2 pyrrolidine (**5c**)); 2.30-2.23 (2.72H, m, 2,5-CH_2 pyrrolidine (**4c**)); 2.65 (2.04H, s, 3-CH_3 (**4c**)); 2.21 (0.96H, s, 2-CH_3 (**5c**)); 1.82-1.76 (1.28H, m, 3,4-CH_2 pyrrolidine (**5c**)); 1.66-1.54 (2.72H, m, 3,4-CH_2 pyrrolidine (**5c**)). Found, %: C 88.05; H 7.92; N 4.85. $C_{22}H_{23}N$. Calculated, %: C 87.66; H 7.69; N 4.65.

***N*-[(3-Methyl-1-phenyl-2-naphthyl)methyl]morpholine (4d) and *N*-[(2-Methyl-1-phenyl-3-naphthyl)-methyl]morpholine (5d)**. Total yield 1.3 g (68%), bp 145–146°C (1 mm Hg), mp 65–67°C. IR spectrum (thin film), ν, cm^{-1}: 680, 700, 730 (Ph), 700, 730, 1940, 890, 1590, 3020, 3060 (Ar). Ratio of isomers **4d**:**5d,** 7:3. ^{1}H NMR spectrum of mixture of compounds **4d** and **5d**, δ, ppm (*J*, Hz): 7.75 (0.3H, br. d, *J* = 8.1, H Ar (**5d**)); 7.71 (0.7H, br. d, *J* = 8.1, H Ar (**4d**)); 7.68 (0.3H, s, H-4 (**5d**)); 7.62 (0.7H, s, H-4 (**4d**)); 7.50-7.39 (3H, m), 7.37-7.32 (1H, m), and 7.24-7.14 (4H, m, H Ar (**4d**+**5d**)); 3.62-3.59 (1.2H, m, $O(CH_2)_2$ (**5d**)); 3.47-3.44 (2.8H, m, $O(CH_2)_2$ (**4d**)); 3.62 (0.6H, s, $NC\underline{H}_2Ar$ (**5d**)); 3.40 (1.4H, s, NCH_2Ar (**4d**)); 2.66 (2.1H, s, 3-CH_3 (**4d**); 2.50-2.47 (1.2H, m, $(C\underline{H}_2)_2NCH_2Ar$ (**5d**)); 2.22 (0.9H, s, 2-CH_3 (**5d**)); 2.20-2.17 (2.8H, m, $(C\underline{H}_2)_2NCH_2Ar$ (**4d**)). Found, %: C 83.65; H 7.53; N 4.66. $C_{22}H_{23}NO$. Calculated, %: C 83.24; H 7.30; N 4.41.

2-(Diethylaminomethyl)-3-methyl-1-phenylnaphthalene (4e) and 3-(Diethylaminomethyl)-2-methyl-1-phenylnaphthalene (5e). Total yield 1.2 g (66%), bp 175-177°C (1-2 mm Hg). IR spectrum, ν, cm^{-1}: 690, 710, 740, 1930, 870, 1590, 3020, 3050 (Ar). Ratio of isomers **4e**:**5e**, 69:31. ^{1}H NMR spectrum of mixture of compounds **4e** and **5e**, δ, ppm (*J*, Hz): 7.75 (0.31H, s, H-4 (**5e**)); 7.59 (0.69H, s, H-4 (**4e**)); 7.75 (0.31H, d, *J* = 8.2, H Ar (**5e**)); 7.69 (0.69H, d, *J* = 8.2, H Ar (**4e**)); 7.50-7.29 (4H, m) and 7.23-7.13 (4H, m, H Ar (**4e**+**5e**)); 3.69 (0.62H, s, $Et_2NC\underline{H}_2$ (**5e**)); 3.47 (1.38H, s, $Et_2NC\underline{H}_2$ (**4e**)); 2.59 (1.24H, q, *J* = 7.1, $(CH_3C\underline{H}_2)_2N$ (**5e**)); 2.30 (2.76H, q, *J* = 7.1, $(CH_3C\underline{H}_2)_2N$ (**4e**)); 2.67 (2.07H, s, 3-CH_3 (**4e**)); 2.21 (0.93H, s, 2-CH_3 (**5e**)); 1.07 (1.86H, t, *J* = 7.1, $(C\underline{H}_3CH_2)_2N$ (**5e**)); 0.82 (4.14H, t, *J* = 7.1, $(C\underline{H}_3CH_2)_2N$ (**4e**)). Found, %: C 87.49; H 8.53; N 4.87. $C_{22}H_{25}N$. Calculated, %: C 87.08; H 8.30; N 4.62.

3-Methyl-1-phenyl-2-piperidinomethylnapthalene (4f). Yield 1.4 g (75%), bp 155-157°C (1-2 mm Hg), mp 85-87°C. IR spectrum, ν, cm^{-1}: 680, 700, 730, 1940, 880, 1600, 3010, 3060 (Ar). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.60 (1H, s, H-4); 7.69 (1H, d, *J* = 8.2, H Ar); 7.47-7.30 (4H, m, H Ar); 7.21-7.12 (4H, m, H Ar); 3.33 (2H, s, $NC\underline{H}_2Ar$); 2.65 (3H, s, 3-CH_3); 2.19-2.13 (4H, m, 2,6-CH_2 piperidine); 1.45-1.36 (4H, m, 3,5-CH_2 piperidine); 1.35-1.28 (2H, m, 4-CH_2 piperidine). Found, %: C 87.96; H 8.22; N 4.59. $C_{23}H_{25}N$. Calculated, %: C 87.57; H 7.99; N 4.44.

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