A new intramolecular recyclization in water-base cleavage reaction of 2,2-dialkyl-4-hydroxymethylbenz[*f*]iso indolinium bromides and chlorides

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The water-base cleavage reaction of 2,2-dialkyl-4-hydroxymethylbenz[*f*]isoindolinium bromides and chlorides **(2b-g)** and **(4a-g)** was investigated. It was established that the above-mentioned salts in water-base cleavage reaction undergo intramolecular recyclization. As a result 1,3-dihydro-4-dialkylaminomethyl-naphto[1,2-*c*]furans **(5a-g)** are obtained in 62-72% yields. The same products in 65-70% yields may be obtained by step cyclization cleavage reaction of dialkyl-4-hydroxybutyn-2-yl-(3-phenylpropargyl) ammonium salts **(1b-g)** and **(3a-g)**, as well. The structure of the resulting amines **5a-g** are determined and approved by X-ray diffraction, nmr and ir spectroscopic methods.

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Introduction.

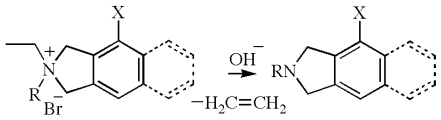
There are many publications and reviews in literature devoted to the issue of recyclization of carbo- and heterocyclic systems [1-6]. In this direction there are reactions of Yurev, Hafner, rearrangements of Dimrot, Boulton-Katritzky, Cornforth, Kost-Sagittulin, *etc*. In review of V. P. Litvinov [1] recyclization reactions of carbo- and heterocycles with malononitrile participation and recyclization of compounds containing a malononitrile fragment are discussed. In particular in this review the recyclization of three-, four-, five- and six-membered cycles are described. In all cases under the influence of various reagents (nucleophilic, electrophilic or dipolar) ring opening is the first step in the reaction. During recyclization, formation of a new ring is in most cases accompanied by implantation or replacement of a heteroatom, and enlargement or reduction of the ring. The recyclization reactions described in the literature relate to intermolecular recyclization. There is only one example of the purely intramolecular recyclization where the recyclization is caused by thermal treatment [7].

In this paper we describe a new intramolecular recyclization reaction of 2,2-dialkyl-4-hydroxymethylbenz[*f*]-isoindolinium salts **(2b-g)** and **(4a-g)** under water-base cleavage conditions.

Previously we reported, that 2,2-dialkylisoindolinium and -benz[*f*]isoindolinium salts in conditions of water-base cleavage reaction, with loss of an alkene, transform to 2-alkylisoindolines and –benz[*f*]isoindolines (Scheme 1). This reaction takes place if at least one of the alkyl groups connected with nitrogen atom can undergo β-elimination [8].

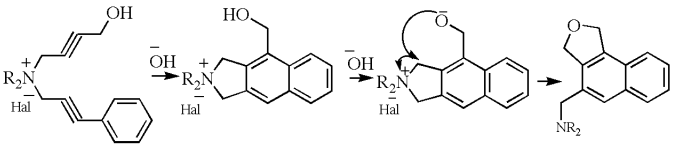
We were interested in studying the behavior of 2,2-dialkyl-4-hydroxymethylbenz[*f*]isoindolinium bromides and chlorides **(2b-g)** and **(4a-g)** under water-base cleavage reaction conditions. The salts were synthesized in 75-85%

Scheme 1



yields by intramolecular cyclization of dialkyl-4-hydroxybutyn-2-yl-(3-phenylpropargyl) ammonium bromides and chlorides **(1b-g)** and **(3a-g)** under base-catalyzed conditions (Scheme 2) [9].

Scheme 2



1b-g, 3a-g **2b-g, 4a-g** **5a-g**

R= Me (3a, 4a, 5a); Et (1b, 2b, 3b, 4b, 5b); Pr (1c, 2c, 3c, 4c, 5c); Bu (1d, 2d, 3d, 4d, 5d); $(-CH_2-)_4$ (1e, 2e, 3e, 4e, 5e); $(-CH_2-)_5$ (1f, 2f, 3f, 4f, 5f); $(-CH_2-)_2O(-CH_2-)_2$ (1g, 2g, 3g, 4g, 5g)
Hal= Br (1b-g, 2b-g); Cl (3a-g, 4a-g)

At first we investigated the water-base cleavage reaction of 2,2-diethyl-4-hydroxymethylbenz[*f*]isoindolinium bromide **(2b)**. Surprisingly the nmr spectra of the resulting compound did not confirm the expected structure of 2-ethyl-4-hydroxymethylbenz[*f*]isoindoline. To determine the structure of resulting amine an X-ray diffraction experiment the bromomethylate of this amine was carried out (detailed experimental data is given in table 1). The structure was determined by direct methods using the crystallographic programs SHELXL-93. The positional parameters of hydrogen atoms were found from geometrical calculations. In the final refinement positional, anisotropic and thermal parameters for all

Table 1

X-ray Experimental Data

a	13.474 (3)
b	9.052 (2)
c	15.013 (3)
α	90.00
β	108.57(3)
γ	90.00
V	1735.6 (6)
Z	4
ρ_{exp}	1.406
radiation	MoKα λ=0.71073
monochromator	Graphite 002
N_{ref} measured	1810
ϑ_{max}	25.84
N_{ref} observed I>σ (I)	1725
N_{param}	203
$\Delta\rho_{max}$	0.691
$\Delta\rho_{min}$	-0.291
R	0.0502
S	1.027

Table 2

The Fractional Coordinates of Basic Atoms in the Crystal

Atom	X/a	Y/b	Z/c	U_{eq}
Br1	0.62084 (5)	0.83046 (8)	0.64915 (5)	0.0597 (3)
O1	0.6267 (10)	0.0752 (10)	0.4787 (6)	0.083 (2)
C1	0.8316 (5)	0.7834 (7)	0.4985 (5)	0.050 (2)
C2	0.8162 (5)	0.6865 (8)	0.4265 (5)	0.056 (2)
C3	0.9005 (6)	0.6297 (8)	0.4023 (5)	0.064 (2)
C4	1.0004 (6)	0.6730 (8)	0.4502 (5)	0.058 (2)
C5	1.0208 (5)	0.7743 (7)	0.5262 (4)	0.0392 (14)
C6	0.9347 (4)	0.8299 (6)	0.5497 (4)	0.0366 (13)
C7	0.9569 (4)	0.9334 (6)	0.6242 (4)	0.0360 (13)
C8	0.8812 (5)	1.0192 (8)	0.6576 (4)	0.051 (2)
O9	0.9425 (3)	1.1183 (5)	0.7261 (3)	0.0610 (13)
C10	1.0515 (5)	1.0877 (7)	0.7455 (4)	0.048 (2)
C11	1.0570 (4)	0.9748 (6)	0.6736 (4)	0.0348 (13)
C12	1.1433 (4)	0.9179 (6)	0.6514 (4)	0.0351 (14)
C13	1.1226 (4)	0.8220 (7)	0.5761 (4)	0.0409 (14)
C14	1.2551 (4)	0.9649 (7)	0.6997 (4)	0.0397 (14)
N15	1.3173 (4)	0.8651 (6)	0.7811 (3)	0.0467 (13)
C16	1.2707 (6)	0.8834 (11)	0.8646 (6)	0.094 (3)
C17	1.3110 (6)	0.7067 (8)	0.7558 (7)	0.073 (2)
C18	1.3654 (7)	0.6704 (10)	0.6939 (7)	0.090 (3)
C19	1.4277 (5)	0.9236 (8)	0.8131 (5)	0.054 (2)
C20	1.5030 (6)	0.8365 (10)	0.8941 (6)	0.093 (3)

nonhydrogen atoms and the constrained positional and isotropic thermal parameters of hydrogen atoms were refined by the full-matrix least-squares procedure. The final values of positional and equivalent thermal parameters of nonhydrogen atoms are given in the table 2. The main interatomic distances and angles are given in Tables 3 and 4 respectively. The structure of molecule is represented in the Figure 1. The results of the structural investigation allow for the explanation of the nmr spectra and show that for salt **2b** a new intramolecular recyclization takes place, due to breaking of the isoindoline ring and formation of the dihydrofuranic ring (Scheme 2). In other words the water-cleavage reaction

Table 3

Main Interatomic Distances in the Molecule

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C1	C2	1.355 (9)	O9	C10	1.430 (7)
C1	C6	1.421 (8)	C10	C11	1.504 (8)
C2	C3	1.396 (10)	C11	C12	1.406 (7)
C3	C4	1.366 (10)	C12	C13	1.381 (8)
C4	C5	1.422 (9)	C12	C14	1.511 (7)
C5	C13	1.405 (8)	C14	N15	1.536 (7)
C5	C6	1.407 (8)	N15	C17	1.479 (9)
C6	C7	1.417 (8)	N15	C19	1.506 (7)
C7	C11	1.368 (7)	N15	C16	1.580 (9)
C7	C8	1.490 (8)	C17	C18	1.393 (11)
C8	O9	1.416 (7)	C19	C20	1.530 (9)

Table 4

Bonding Angles in Molecule

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C2	C1	C6	111.9 (6)	C7	C11	C12	121.2 (5)
C1	C2	C3	121.0 (6)	C7	C11	C10	108.1 (5)
C4	C3	C2	120.3 (7)	C12	C11	C10	130.7 (5)
C3	C4	C5	120.9 (7)	C13	C12	C11	117.2 (5)
C13	C5	C6	119.9 (5)	C13	C12	C14	118.7 (5)
C13	C5	C4	122.2 (6)	C11	C12	C14	123.9 (5)
C6	C5	C4	117.9 (5)	C12	C13	C5	122.5 (5)
C5	C6	C7	116.8 (5)	C12	C14	N15	115.1 (4)
C5	C6	C1	120.0 (6)	C17	N15	C19	113.1 (5)
C7	C6	C1	123.2 (5)	C17	N15	C14	113.2 (5)
C11	C7	C6	122.2 (5)	C19	N15	C14	106.3 (4)
C11	C7	C8	109.7 (5)	C17	N15	C16	107.5 (6)
C6	C7	C8	128.0 (5)	C19	N15	C16	108.2 (5)
O9	C8	C7	105.8 (5)	C14	N15	C16	108.4 (5)
C8	O9	C10	110.4 (5)	C18	C17	N15	113.6 (7)
O9	C10	C11	105.5 (5)	N15	C19	C20	114.2 (5)

results in 1,3-dihydro-4-diethylaminomethylnaphto[1,2-*c*]-furan **(5b)** instead of the expected 2-ethyl-4-hydroxymethyl-benz[*f*]isoindoline.

In order to state the general nature of the discovered recyclization we have studied the behaviour of **2c-g** and **4a-g** salts in water-base cleavage conditions. It turned out, that these salts smoothly undergo the intramolecular recyclization too, forming 1,3-dihydro-4-dialkylaminomethylnaphto[1,2-*c*]furans **(5a-g)** in 62-72% yields. The data obtained show that the discovered recyclization reaction is general. It should be noted, that the amines **5a-g** obtained in the cyclization reaction of salts **1b-g** and **3a-g** combined with that obtained in the subsequent cleavage reaction of cyclic salts **2b-g** and **4a-g**, give amines **5a-g** in 65-70% yields (Scheme 2).

Comparing the results of the reactions given in Scheme 1 with those in Scheme 2, shows that the hydroxymethyl group of **2b-g** and **4a-g** plays the role of base in this recyclization reaction. In water-base medium the hydroxymethyl group is deprotonated to give the alkoxy anion shown in Scheme 2. The positive charge on the nitrogen atom induces a partial positive charge on the neighboring

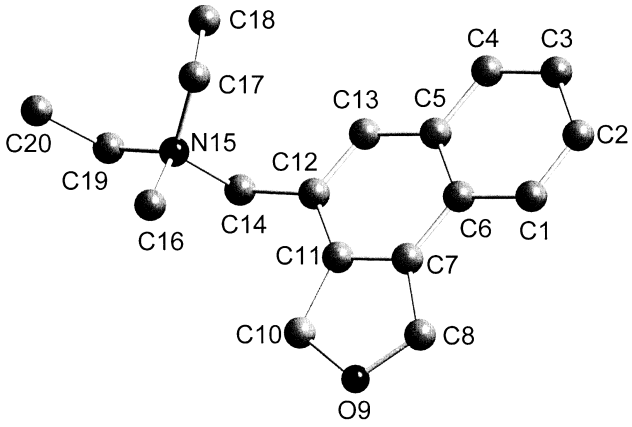


Figure 1. The molecular structure of brommethylate of amine **5b**.

carbon making it susceptible to intramolecular nucleophile attack of alkoxy anion. This leads to breaking of the isoindolinium N-C bond, as well as to formation of a new O-C bond, resulting in dihydrofurane ring formation (Scheme 2).

Unlike the recyclization reactions described in the literature, in the intramolecular recyclization reaction discovered by us the initial ring opening takes place due to nucleophile attack of the alkoxy anion in the molecule. Hence, the ring does not change size rather a five-membered isoindoline ring is replaced by dihydrofurane.

In the ir spectra of amines **5a-g** characteristic zones of absorption are presented respectively: for di- and pentasubstituted benzene rings - 750 and 870 cm^{-1}, for aromatic ring - 1500, 1600, 3060 and for cyclic ethereal group - 1050, 1100 cm^{-1}.

Structures of amines **5a-e** and amines **5f**, **5g** hydrochloride were established by ^1H nmr spectroscopy and the structures of amines **5a**, **5c**, **5d**, and amine **5g** hydrochloride were supported by ^{13}C nmr, DEPT, HETCOR. Composition of amines **5a-g** was consistent with the results of elemental analysis.

EXPERIMENTAL

The initial salts **1b-g** and **3a-g** were prepared in laboratory conditions. The ir spectra were recorded on an IR-20 spectrometer. Samples were prepared as potassium bromide tablets or in Vaseline oil. The nmr spectra were carried out on a "Varian Mercury 300" spectrometer at 300.08 MHz for ^1H and 75.46 MHz for ^{13}C at temperature of 303 K using TMS as an internal standard. The X-ray diffraction measurements were performed on a CAD-4 "Enraf-Nonius" diffractometer.

General Procedure for the Water-base Cleavage Reaction of 2,2-Dialkyl-4-hydroxymethylbenz[*f*]isoindolinium Bromides and Chlorides (**2b-g**) and (**4a-g**).

To a solution of 11-20 mmole of initial salts **2b-g** and **4a-g** in 5-7 mL of water a two-fold molar quantity of potassium hydroxide dissolved in 3-4 mL of water is added. The reaction mixture is refluxed during 2-3 hours at 90-92°, then extracted by ether (2x40 mL). The ethereal extract is washed with water and dried over magnesium sulfate. After removing ether the remaining amines **5a-g** are distilled.

General Procedure of Step Cyclization-cleavage Reaction of Dialkyl-4-hydroxybutyn-2-yl-(3-phenylpropargyl) Ammonium Bromides and Chlorides (**1b-g)** and (**3a-g**).

To a solution of 11-20 mmole of salts **1b-g** and **3a-g** in 5-6 mL water 1.1-2.0 mL 2 *N* potassium hydroxide (mole-ratio salt/base=5/1) is added. After cyclization the reaction mixture is extracted by ether (2x20 mL). Ethereal extract is acidified by hydrochloric acid. The hydrochloride layer is separated from the ethereal layer. By alkalization of the hydrochloride layer and extracting by ether (2x25 mL) a first crop of amines **5a-g** are separated with 8-10% yields (mixed melting points of their picrates show these compounds to be identical with those obtained from salts **2b-g** and **4a-g**). After that a two-fold molar quantity of potassium hydroxide is added to the reaction mixture (promoting the water-base cleavage reaction of cyclic salts **2b-g** and **4a-g**). The reaction mixture is again extracted with ether, the ether layer acidified with hydrochloric acid then separated. The resulting hydrochloride layer is then made alkaline and extracted with ether (as described above) to give amines **5a-g**. After purification by vacuum distillation amines **5a** and **5e** crystallized by staying at room temperature.

1,3-Dihydro-4-dimethylaminomethylnaphto[1,2-*c*]furan (**5a)**.

Amine **5a** was obtained in 68% yield (2.31 g, 10 mmole) by water-base cleavage reaction of the salt **4a** (3.95 g, 15 mmole) with bp 180°/3 mm Hg, mp 40°; n_d^{20} = 1.5989; ir: 750 (*o*-substituted benzene ring), 860 (pentasubstituted benzene ring), 1050, 1100 (C–O in cycle), 1510, 1600 and 3060 (aromatic ring) cm^{-1}; ^1H nmr (DMSO-d_6/CCl_4 – 1/3): δ 7.83 (m, 1H, 6- or 9-H), 7.60 (s, 1H, 5-H), 7.56 (m, 1H, 9- or 6-H), 7.44 (m, 2H, 7-, 8-H), 5.39 (t, 2H, OCH_2, J=3.0 Hz), 5.23 (t, 2H, OCH_2, J=3.0 Hz), 3.49 (s, 2H, NCH_2), 2.23 (s, 6H, CH_3); ^{13}C nmr (DMSO-d_6/CCl_4 – 1/3): δ 135.9, 134.3, 132.5, 127.6, 126.5(2C), 126.3, 125.5, 124.9, 123.1, 73.4, 72.3, 62.2, 44.8(2C); mp 155° of **5a** picrate (ethyl alcohol); mp 201° of **5a** hydrochloride (absolute ethyl alcohol).

Anal. Calcd. for $C_{15}H_{17}NO$: C, 79.30; H, 7.49; N, 6.17. Found: C, 79.61; H, 7.69; N, 6.42.

1,3-Dihydro-4-diethylaminomethylnaphto[1,2-*c*]furan (**5b**).

Amine **5b** was obtained in 70% yield (2.6 g, 10.43 mmole) by water-base cleavage reaction of the salt **2b** (5.04 g, 15 mmole) or **4b** (4.38 g, 15 mmole) with bp 165°/3 mm Hg; n_d^{20} = 1.5850; ir: 730 (*o*-substituted benzene ring), 870 (pentasubstituted benzene ring), 1050, 1110 (C–O in cycle), 1500, 1580 and 3050 (aromatic ring) cm^{-1}; ^1H nmr (DMSO-d_6 /CCl_4 – 1/3): δ 7.92 (m, 1H, 6- or 9-H), 7.73 (s, 1H, 5-H), 7.67 (m, 1H, 9- or 6-H), 7.50 (m, 2H, 7-, 8-H), 5.41 (t, 2H, OCH_2, J=3.0 Hz), 5.32 (t, 2H, OCH_2, J=3.0 Hz), 3.67 (s, 2H, NCH_2), 2.52 (q, 4H, CH_2, J=7.0 Hz); 1.04 (t, 6H, CH_3, J=7.0 Hz); mp 168-170° of **5b** picrate (ethyl alcohol); mp 184-185° of **5b** hydrochloride (absolute ethyl alcohol).

Anal. Calcd. for $C_{17}H_{21}NO$: C, 80.00; H, 8.23; N, 5.49. Found: C, 80.30; H, 8.43; N, 5.78.

1,3-Dihydro-4-dipropylaminomethylnaphto[1,2-*c*]furan (**5c**).

Amine **5c** was obtained in 62% yield (3.4 g, 12 mmole) by water-base cleavage reaction of the salt **2c** (7.28 g, 20 mmole) or

4c (6.39 g, 20 mmole) with bp 185°/3 mm Hg; n_d^{20} = 1.5710; ir: 760 (*o*-substituted benzene ring), 840 (pentasubstituted benzene ring), 1060, 1110 (C–O in cycle), 1510, 1600 and 3060 (aromatic ring) cm^{-1}; ^1H nmr (DMSO-d_6 /CCl_4 – 1/3): δ 7.82 (m, 1H, 6- or 9-H), 7.60 (s, 1H, 5-H), 7.56 (m, 1H, 9- or 6-H), 7.43 (m, 2H, 7-, 8-H), 5.38 (t, 2H, OCH_2, J=3.0 Hz), 5.24 (t, 2H, OCH_2, J=3.0 Hz), 3.61 (s, 2H, NCH_2), 2.37 (t, 4H, CH_2N, J=7.5 Hz), 1.49 (tq, 4H, CH_2, J=7.5, 7.2 Hz), 0.86 (t, 6H, CH_3, J=7.2 Hz); ^{13}C nmr (DMSO-d_6/CCl_4 – 1/3): δ 135.8, 134.3, 132.6, 131.9, 127.5, 126.4, 126.2, 125.3, 124.8, 123.1, 73.5, 72.3, 57.6, 55.4(2C), 19.5(2C), 11,5(2C); mp 159° of **5c** picrate (ethyl alcohol); mp 155-156° of **5c** hydrochloride (absolute ethyl alcohol).

Anal. Calcd. for $C_{19}H_{25}NO$: C, 80.56; H, 8.83; N, 4.95. Found: C, 80.93; H, 9.04; N, 5.23.

1,3-Dihydro-4-dibutylaminomethylnaphto[1,2-*c*]furan (**5d)**.

Amine **5d** was obtained in 66% yield (4.1 g, 13.2 mmole) by water-base cleavage reaction of the salt **2d** (7.84 g, 20 mmole) or **4d** (6.95 g, 20 mmole) bp 200-202°/3 mm Hg; n_d^{20} = 1.5603; ir: 760 (*o*-substituted benzene ring), 850 (pentasubstituted benzene ring), 1050, 1100 (C–O in cycle), 1520, 1600 and 3080 (aromatic ring) cm^{-1}; ^1H nmr (DMSO-d_6 /CCl_4 – 1/3): δ 7.82 (m, 1H, 6- or 9-H), 7.59 (s, 1H, 5-H), 7.56 (m, 1H, 9- or 6-H), 7.43 (m, 2H, 7-, 8-H), 5.38 (t, 2H, OCH_2, J=3.0 Hz), 5.23 (t, 2H, OCH_2, J=3.0 Hz), 3.60 (s, 2H, NCH_2), 2.39 (t, 4H, CH_2N, J=7.2 Hz), 1.44 (m, 4H, CH_2), 1.28 (m, 4H, CH_2), 0.87 (t, 6H, CH_3, J=7.2 Hz); ^{13}C nmr (DMSO-d_6/CCl_4 – 1/3): δ 135.8, 134.3, 132.5, 131.9, 127.5, 126.4, 126.2, 125.3, 124.8, 123.1, 73.4, 72.3, 57.6, 52.9(2C), 28.5(2C), 19.9(2C), 13,5(2C); mp 100° of **5d** picrate (ethyl alcohol); mp 120° of **5d** hydrochloride (absolute ethyl alcohol).

Anal. Calcd. for $C_{21}H_{29}NO$: C, 81.03; H, 9.32; N, 4.50. Found: C, 81.38; H, 9.57; N, 4.78.

1-(1,3-Dihydro-naphtho[1,2-*c*]furan-4-ylmethyl)-pyrrolidine **(5e)**.

Amine **5e** was obtained in 70% yield (2.48 g, 9.8 mmole) by water-base cleavage reaction of the salt **2e** (4.67 g, 14 mmole) or **4e** (4.1 g, 14 mmole) bp 198°/1 mm Hg, mp 43°; ir: 760 (*o*-substituted benzene ring), 870 (pentasubstituted benzene ring), 1050, 1110 (C–O in cycle), 1500, 1580 and 3050 (aromatic ring) cm^{-1}; ^1H nmr (DMSO-d_6 /CCl_4 – 1/3): δ 7.95 (m, 1H, 6- or 9-H), 7.73 (s, 1H, 5-H), 7.65 (m, 1H, 9- or 6-H), 7.50 (m, 2H, 7-, 8-H), 5.40 (t, 2H, OCH_2, J=3.2 Hz), 5.24 (t, 2H, OCH_2, J=3.2 Hz), 3.68 (s 2H, NCH_2), 2.45 (m, 4H, CH_2N); 1.70 (m, 4H, CH_2); mp 150° of **5e** picrate (ethyl alcohol); mp 165-168° of **5d** hydrochloride (absolute ethyl alcohol).

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.63; H, 7.51; N, 5.53. Found: C, 81.03; H, 7.72; N, 5.83.

1-(1,3-Dihydro-naphtho[1,2-*c*]furan-4-ylmethyl)-piperidine **(5f)**.

Amine **5f** was obtained in 72% yield (2.48 g, 9.3 mmole) by water-base cleavage reaction of the salt **2f** (4.52 g, 13 mmole) or **4f** (4.0 g, 1.3 mmole) mp 55° (hexane); ir: 740, 760 (*o*-substituted benzene ring), 870 (pentasubstituted benzene ring), 1050, 1110 (C–O in cycle), 1500, 1600 and 3050 (aromatic ring) cm^{-1}; ^1H nmr hydrochloride of amine **5f** (DMSO-d_6/CCl_4 – 1/3): δ 12.14 (br, 1H, hydrochloride proton), 8.54 (s, 1H, 5-H), 8.01 (d, 1H, 6- or 9-H, J=8.0 Hz), 7.52-7.60 (m, 3H, 7-, 8-, 9- or 6-H), 5.45 (t, 2H, OCH_2, J=3.0 Hz), 5.39 (t, 2H, OCH_2, J=3.0 Hz), 4.27 (d, 2H, NCH_2, J=5.4 Hz), 3.38 (d, 2H, CH_2N, J=11.0 Hz), 2.95 (m, 2H, CH_2N), 2.19 (m, 2H, CH_2), 1.80 (m, 3H, CH_2), 1.46 (m, 1H, CH_2); mp 163° of **5f** picrate (ethyl alcohol); mp 204-205° of **5f** hydrochloride (absolute ethyl alcohol).

Anal. Calcd. for $C_{18}H_{21}NO$: C, 80.90; H, 7.86; N, 5.24. Found: C, 81.32; H, 8.05; N, 5.56.

4-(1,3-Dihydro-naphtho[1,2-*c*]furan-4-ylmethyl)-morpholine **(5g)**.

Amine **5g** was obtained in 71% yield (2.1 g, 7.8 mmole) by water-base cleavage reaction of the salt **2g** (3.85 g, 11 mmole) or **4g** (3.36 g, 11 mmole) bp 189°/3 mm Hg; ir: 750 (*o*-substituted benzene ring), 870 (pentasubstituted benzene ring), 1060, 1110 (C–O in cycle), 1510, 1600 and 3050 (aromatic ring) cm^{-1}; ^1H nmr of amine **5g** hydrochloride (DMSO-d_6/CCl_4 – 1/3): δ 12.40 (br, 1H, hydrochloride proton), 8.43 (br, 1H, 5-H), 7.98 (dd, 1H, 6- or 9-H, J=7.2, 1.8 Hz), 7.50-7.64 (m, 3H, 7-, 8-, 9- or 6-H), 5.43 (s, 4H, OCH_2), 4.37 (br, 2H, NCH_2), 4.07 (br, 2H, CH_2), 3.88 (br, 2H, CH_2), 3.21 (br, 4H, CH_2); ^{13}C nmr of amine **5g** hydrochloride (DMSO-d_6 /CCl_4 – 1/3): δ 136.8, 134.9, 132.3, 131.9, 128.5, 127.1, 126.9, 125.6, 123.4, 120.8, 73.6, 72.9, 62.7(2C), 56.3, 50.5(2C); mp 155-156° of **5g** picrate (ethyl alcohol); mp 194-195° of **5g** hydrochloride (absolute ethyl alcohol).

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.84; H, 7.06; N, 5.20. Found: C, 76.18; H, 7.25; N, 5.48.

1-(4-Hydroxy-but-2-ynyl)-1-(3-phenyl-prop-2-ynyl)-pyrrolidinium Chloride **(3e).**

This compound was obtained in 95% yield, mp 92°; ir: 700, 750 (monosubstituted benzene ring), 1020, (C–O in C–OH), 1500, 1560, 1600 and 3060 (aromatic ring), 3200-3350 (O–H) cm^{-1}, ^1H nmr (DMSO-d_6 /CCl_4 – 1/3): δ 7.58 (m, 2H, *ortho*-phenyl protons), 7.40 (m, 3H, *meta*- and *para*-phenyl protons), 5.26 (br, 1H, OH), 4.91 (s, 2H, NCH_2), 4.72 (t, 2H, NCH_2, J=2.0 Hz), 4.19 (br, 2H, OCH_2), 3.88 (t, 4H, CH_2N, J=7.2, Hz), 2.28 (m, 4H, CH_2).

Anal. Calcd. for $C_{17}H_{20}ClNO$: C, 70.46; H, 6.96; N, 4.83. Found: C, 70.85; H, 7.15; N, 5.13.

2,2-Tetramethylen-4-hydroxymethylbenz[*f*]isoindolinium Chloride (**4e**).

This compound was obtained in 75% yield, mp 231-232°; ir: 730, 760 (*o*-substituted benzene ring), 860 (pentasubstituted benzene ring), 1050 (C–O in C–OH), 1500, 1550, 1600 and 3030 (aromatic ring), 3300-3400 (O–H) cm^{-1}, ^1H nmr (DMSO-d_6 /CCl_4 – 1/3): δ 8.14 (d, 1H, 8-H, J=8.1, Hz), 7.90 (dd, 1H, 5-H, J=7.2, 2.2 Hz), 7.81 (s, 1H, 9-H), 7.53 (m, 2H, 6-, 7-H), 5.82 (br, 1H, OH), 5.35 (s, 2H, 3-H), 5.09 (s, 2H, 1-H), 4.97 (s, 2H, 4-H), 3.81 (m, 4H, CH_2N), 2.28 (m, 4H, $2CH_2$); ^{13}C nmr (DMSO-d_6/CCl_4 – 1/3): δ 133.2, 133.0, 131.6, 130.8, 129.9, 128.2, 126.1, 125.8, 123.9, 121.2, 66.1, 65.4, 62.5(2C), 58.2, 21.4(2C).

Anal. Calcd. for $C_{17}H_{20}ClNO$: C, 70.46; H, 6.96; N, 4.83. Found: C, 70.86; H, 7.14; N, 5.13.

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