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CONDENSATION OF 1-CARBAMOYLMETHYL-2,3,3-TRIMETHYL-3H-INDOLIUM CHLORIDE WITH AROMATIC ALDEHYDES

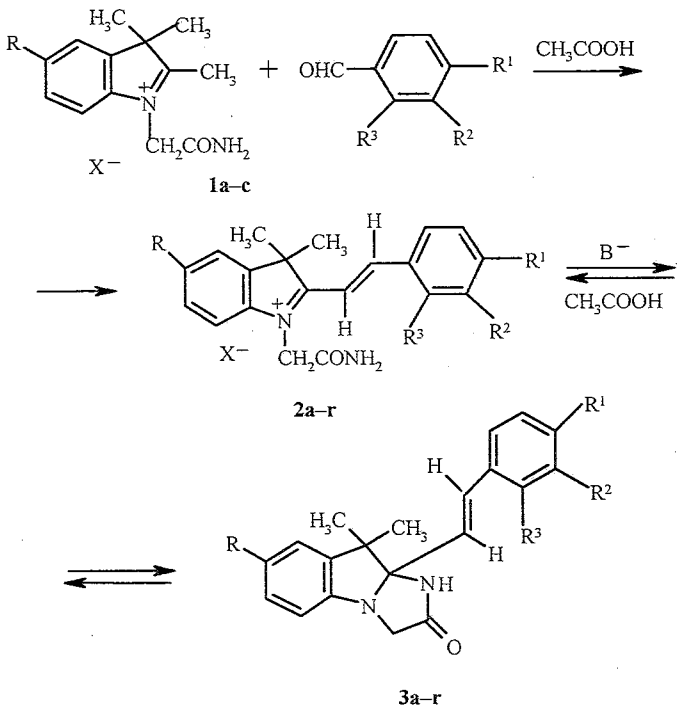
The reaction of 1-carbamoylmethyl-2,3,3-trimethyl-3H-indolium chloride with various aromatic aldehydes in acetic acid and the following workup of the intermediate styrylic derivatives with strong bases yielded 9a-(2-arylethenyl)-1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]indol-2-one derivatives. Condensation of the mentioned salt with salicylaldehyde in acidic or basic medium afforded the derivative of 1'-carbamoylmethylspiro[benzopyran-2,2'-indole]. Alkylation of the latter compound with benzyl chloride in the presence of potassium hydroxide gave 9a-[2-(2-benzyloxyphenyl)ethenyl]-1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]-indol-2-one.

Keywords: aromatic aldehydes, 1-carbamoyl-2,3,3-trimethyl-3H-indolium chloride, condensation, 1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]indol-2-ones.

It has been reported that the reaction of 2,3,3-trimethyl-3H-indole with ethylene oxide in acetic acid and subsequent treatment of the reaction mixture with sodium hydroxide afforded derivatives of 2,3,9,9a-tetrahydrooxazolo-[3,2-*a*]indole [1]. Alkylation of 2,3,3-trimethyl-3H-indole with 2-haloacetamide gave 1-carbamoylalkyl-2,3,3-trimethyl-3H-indolium salts, which under the action of a base underwent cyclization into derivatives of 1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]indole [2, 3]. The derivatives of 1,2,3,4,10,10a-hexahydropyrimido[1,2-*a*]indole were synthesized by the reaction of 2,3,3-trimethyl-3H-indolium salts with amides of 2,3-unsaturated acids [4,5]. These tricyclic compounds bear an active methyl group and are able to take part in the condensation reactions with aromatic and heterocyclic aldehydes [1, 4–8]. 1,2-Annelated derivatives of 2-(2-phenylethenyl)indole have an important application as organic dyes for synthetic fibers and in an information processing [8—15].

We have now examined the condensation of 1-carbamoylmethyl-2,3,3-trimethyl-3H-indolium salts with a series of aromatic aldehydes and synthesized new derivatives of 9a-(2-phenylethenyl)-1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]indol-2-one.

The condensation of 1-carbamoylmethyl-3H-indolium chlorides **1a—c** with benzaldehyde and its derivatives substituted in the aromatic ring was performed in glacial acetic acid at 90—100°C. A colored solution (λ_{max} = 560 nm, acetic acid) of the 1-carbamoylmethyl-2-[2-(4-dimethylaminophenyl)ethenyl]-3H-indolium salt **2a** is formed during heating of a mixture of chloride **1a** with 4-dimethylaminobenzaldehyde. The ^{1}H NMR spectrum of compound **2a** is characterized by the presence of singlets at 1.78 (3,3-CH_3), 3.16 (N,N-CH_3), 5.33 ppm (CH_2) and two doublets of AB-system ($^3J_{AB}$ = 15.0 Hz) of the vinyl protons at 7.13 and 8.32 ppm.



1a–c

2a–r

3a–r

1a R = H, **b** R = CH_3, **c** R = Br; **2, 3 a** R = R^2 = R^3 = H, R^1 = $N(CH_3)_2$;
b R = R^2 = R^3 = H, R^1 = $N(C_2H_5)_2$; **c** R = R^2 = R^3 = H, R^1 = $N(C_2H_4)_2O$;
d R = CH_3, R^1 = $N(CH_3)_2$, R^2 = R^3 = H; **e** R = CH_3, R^1 = $N(C_2H_5)_2$, R^2 = R^3 = H;
f R = Br, R^1 = $N(CH_3)_2$, R^2 = R^3 = H; **g** R = R^1 = R^2 = R^3 = H; **h** R = CH_3, R^1 = R^2 = R^3 = H;
i R = R^2 = R^3 = H, R^1 = CH_3; **j** R = R^2 = R^3 = H, R^1 = F; **k** R = R^2 = R^3 = H, R^1 = Cl;
l R = R^1 = R^2 = H, R^3 = Cl; **m** R = R^2 = H, R^1 = R^3 = Cl; **n** R = R^2 = R^3 = H, R^1 = Br;
o R = CH_3, R^1 = Br, R^2 = R^3 = H; **p** R = R^2 = R^3 = H, R^1 = OCH_3; **q** R = R^3 = H, R^1 = R^2 = OCH_3;
r R = R^1 = H, R^2 + R^3 = CH=CH=CH=CH; X = Cl, CH_3COO

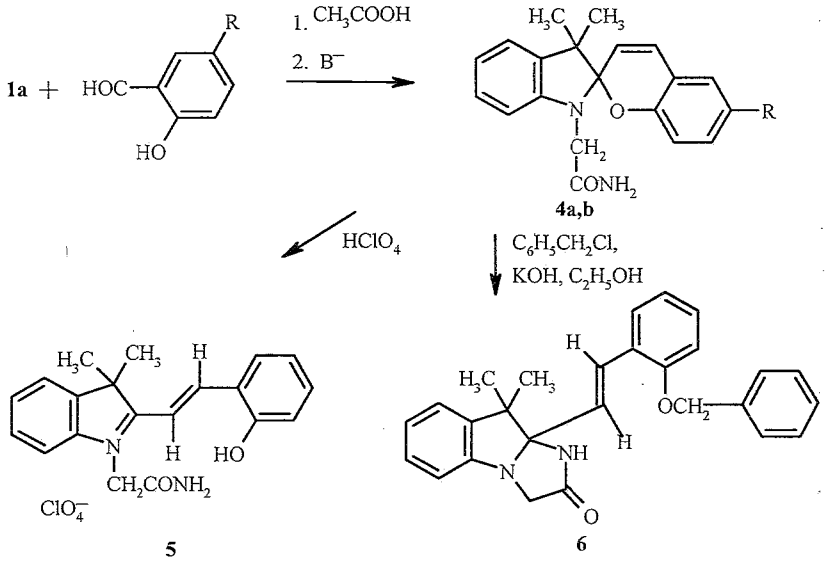
During the treatment of the aqueous solution of chloride **2a** with potassium hydroxide, the nucleophilic addition of nitrogen atom of amide group to α-carbon of indole moiety occurs and the derivative of 9a-[2-(4-dimethylaminophenyl)ethenyl]-1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]indol-2-one (**3a**) is formed. The structure of compound **3a** was confirmed by means of spectral investigations. An absorption band at 1705 cm^{-1}, which is due to a carbonyl group, and a band at 3200 cm^{-1}, which corresponds to the stretching vibrations of the N-H bond, are observed in the IR spectrum of **3a.** The signals of the diastereotopic geminal methyl groups are present at 1.03 and 1.30 ppm in the ^1H NMR spectrum. The methylene protons of the imidazolidine ring resonate in the form of an AB-quadruplet (δ_A 3.51, δ_B 3.65, $^2J_{AB}$ = 16.0 Hz). The vicinal spin-spin coupling constant of the vinyl protons is 16.0 Hz and attests to their *trans* orientation.

The condensation of salts **1a—c** with benzaldehyde, 4-diethylamino-, 4-alkyl-, 4-methoxy-, 2- or 4-halobenzaldehydes and various disubstituted benzaldehydes was carried out by a similar method. It was found that 3H-indolium salts **Ia—c** undergo condensation with 4-dialkylaminobenzaldehydes in acetic acid easier than with benzaldehyde or its substituted derivatives bearing methoxy group or halogens. Treatment of the reaction mixtures with a

solution of a strong base afforded 9a-(2-phenylethenyl)-1,2,3,9a-tetrahydro-9H-imidazo[1,2-a]indol-2-one derivatives **3b—r**. ^{13}C NMR spectrum of 9a-[2-(4-methylphenyl)ethenyl]-imidazo[1,2-a]indol-2-one **3i** showed the signals of sp^3 hybridized carbon atoms at 20.78 (CH_3), 21.91 (CH_3), 27.90 (CH_3), 47.25 (C-9), 54.44 (NCH_2) and 92.90 ppm (C-10a). The signals of sp^2 hybridized carbon atoms of compound **3i** are situated in the area of 112.47—173.69 ppm.

Compounds **3a—r** have no absorption bands in the visible region of electronic spectra. However, protonic acids promote ring opening and the formation of colored cations of salts **2a—r**. The wavelength of band is mainly dependent on the substituent in the styryl fragment, e.g. solutions of 9a-[2-(4-diethylaminophenyl)ethenyl]- and 9a-[2-(4-methoxyphenyl)ethenyl]-imidazo[1,2-*a*]indol-2-ones **3b,p** in acetic acid have the intense peak at 570 and 439 nm respectively, while a solution of unsubstituted compound **3g** is characterized by a peak at 398 nm.

Heating of salt **1a** with salicyl aldehyde in acetic acid and subsequent treatment of the reaction mixture with a solution of sodium acetate yields 1'-carbamoylmethylspiro-[benzopyran-2,2'-indole] **4a**. The identical product was obtained when condensation was carried out in ethanol in the presence of piperidine. 6-Bromospirobenzopyrane **4b** was obtained by a similar procedure.



4a R = H, **b** R = Br

Absorption bands characteristic to the primary amides at 3464, 3192 (NH_2) and 1688 cm^{-1} (C=O) are observed in the IR spectrum of compound **4a.** The ^1H NMR spectrum of compound **4a** is characterized by the presence of two singlets of diastereotopic 3',3'-CH_3 groups at 1.20 and 1.33, AB-quadruplet of NCH_2 group in the region of 3.55—4.03 and a doublet of one of the protons of pyrane ring at 5.62 ppm. Vicinal coupling between protons 3-H and 4-H is 10.0 Hz and evidences their *cis*-location [16]. The presence of the pyrane ring is also confirmed by the fact that the signal of indole α-carbon atom of

Table 1

9,9-Dimethyl-9a-(2-phenylethenyl)-1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]indol-2-ones 3a—r, 6

Compound	Empirical formula	R	R^1	R^2	R^3	Found, % / Calculated, %			mp, °C	Yield, %
						C	H	N		
3a	$C_{22}H_{25}N_3O$	H	$N(CH_3)_2$	H	H	76.25 76.04	7.11 7.25	12.46 12.09	214–215*	82
3b	$C_{24}H_{29}N_3O$	H	$N(C_2H_5)_2$	H	H	76.92 76.76	7.49 7.78	11.20 11.19	186–187*	78
3c	$C_{24}H_{27}N_3O_2$	H	$N(C_2H_4)_2O$	H	H	74.25 74.01	6.71 6.98	10.71 10.79	199–200*[3]	21
3d	$C_{23}H_{27}N_3O$	CH_3	$N(CH_3)_2$	H	H	76.84 76.44	7.32 7.53	11.94 11.63	211–212*[3]	22
3e	$C_{25}H_{31}N_3O$	CH_3	$N(C_2H_5)_2$	H	H	77.36 77.08	7.72 8.02	10.75 10.79	196–197*[3]	26
3f	$C_{22}H_{24}BrN_3O$	Br	$N(CH_3)_2$	H	H	62.19 61.98	5.55 5.67	9.81 9.86	218–219*	73
3g	$C_{20}H_{20}N_2O$	H	H	H	H	79.08 78.92	6.83 6.62	9.41 9.20	205–206*[3]	50
3h	$C_{21}H_{22}N_2O$	CH_3	H	H	H	79.25 79.21	7.03 6.96	9.01 8.79	215–216*[3]	38
3i	$C_{21}H_{22}N_2O$	H	CH_3	H	H	78.75 79.21	6.56 6.96	8.71 8.79	189–190*[3]	36
3j	$C_{20}H_{19}FN_2O$	H	F	H	H	74.12 74.51	6.18 5.94	8.32 8.69	218–219*[3]	43

3k	$C_{20}H_{19}ClN_2O$	H	Cl	H	H	70.60 70.89	5.61 5.65	8.51 8.27	219–220*	52
3l	$C_{20}H_{19}ClN_2O$	H	H	H	Cl	71.21 70.89	5.59 5.65	8.12 8.27	186–187*[3]	32
3m	$C_{20}H_{18}Cl_2N_2O$	H	Cl	H	Cl	64.40 64.35	4.64 4.86	7.33 7.50	229–230*[2]	54
3n	$C_{20}H_{19}BrN_2O$	H	Br	H	H	62.80 62.67	4.85 5.00	7.25 7.31	227–228*[2]	56
3o	$C_{21}H_{21}BrN_2O$	CH_3	Br	H	H	63.35 63.48	5.37 5.33	6.85 7.05	223–224*[3]	65
3p	$C_{21}H_{22}N_2O_2$	H	OCH_3	H	H	75.68 75.42	6.74 6.63	8.39 8.37	192–193*	30
3q	$C_{22}H_{24}N_2O_3$	H	OCH_3	OCH_3	H	72.70 72.50	6.52 6.64	7.92 7.68	199–200*	55
3r	$C_{24}H_{22}N_2O$	H	H	CH=CH–CH=CH		80.81 81.32	6.51 6.27	7.62 7.90	227–228*[3]	22
6	$C_{28}H_{28}N_2O_2$	H	H	H	$CH_2C_6H_5$	79.12 79.21	6.51 6.65	6.73 6.60	129–130*[3]	44

* From ethanol.
*[2] From DMF.
*[3] From acetone.

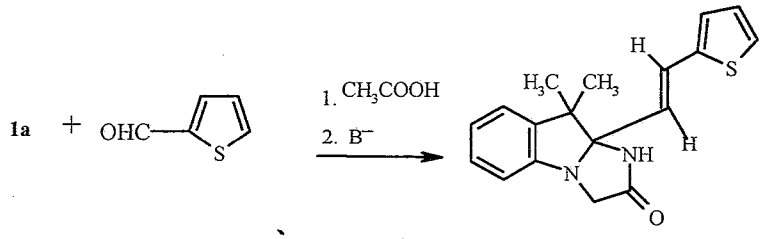
Table 2

^{1}H NMR Spectra of 9,9-dimethyl-9a-(2-phenylethenyl)-1,2,3,9a-tetrahydro-9H-imidazo [1,2-*a*]indol-2-ones 3a–r, 6

Compound	Solvent	Chemical shifts, ppm
3a	DMSO-d_6	1.03 (3H, s, 9-CH_3), 1.30 (3H, s, 9-CH_3), 2.88 (6H, s, N,N-CH_3), 3.40–3.75 (2H, AB-q, J = 16.0 Hz, CH_2), 6.05–7.43 (10H, CH=CH, ArH), 8.75 (1H, br. s, NH).
3b	DMSO-d_6	1.08 (3H, s, 9-CH_3), 1.08 (6H, t, J = 7.0 Hz, $CH_2\underline{CH_3}$), 1.32 (3H, s, 9-CH_3), 3.33 (4H, q, J = 7.0 Hz, $\underline{CH_2}CH_3$), 3.48–3.74 (2H, AB-q, J = 16.3 Hz, CH_2CO), 6.09–7.29 (10H, m, CH=CH, ArH), 8.84 (1H, br.s, NH).
3c	DMSO-d_6	1.05 (3H, s, 9-CH_3), 1.33 (3H, s, 9-CH_3), 3.08 - 3.13 (4H, m, 2 x CH_2), 3.50–3.73 (2H, AB-q, J = 16.3 Hz, CH_2), 3.70–3.75 (4H, m, 2 x CH_2), 6.25–6.71 (2H, AB-q, J = 16.0 Hz, CH=CH), 6.87–7.38 (8H, m, ArH), 8.82 (1H, br. s, NH).
3d	DMSO-d_6	1.15 (3H, s, 9-CH_3), 1.30 (3H, s, 9-CH_3), 2.19 (3H, s, 7-CH_3), 2.89 (6H, s, N,N-CH_3), 3.30-3.75 (2H, AB-q, J = 16.0 Hz, CH_2), 6.01–7.45 (9H, m, CH=CH, ArH), 8.80 (1H, br. s, NH)
3e	DMSO-d_6	1.07 (3H, s, 9-CH_3), 1.07 (6H, t, J = 7.0 Hz, $CH_2\underline{CH_3}$), 1.30 (3H, s, 9-CH_3), 2.23 (3H, s, 7-CH_3), 3.44–3.68 (2H, AB-q, J = 16.2 Hz, CH_2), 6.08–7.29 (9H, m, CH=CH, ArH), 8.80 (1H, br. s, NH)
3f	DMSO-d_6	1.08 (3H, s, 9-CH_3), 1.33 (3H, s, 9-CH_3), 2.93 (6H, s, N,N-CH_3), 3.20–3.88 (2H, AB-q, J = 16.2 Hz, CH_2), 6.11–7.48 (9H, m, CH=CH, ArH), 8.88 (1H, br. s, NH)
3g	DMSO-d_6	1.11 (3H, s, 9-CH_3), 1.36 (3H, s, 9-CH_3), 3.52–3.71 (2H, AB-q, J = 16.2 Hz, CH_2), 6.38–7.45 (11H, m, CH=CH, ArH), 8.77 (1H, br. s, NH)
3h	DMSO-d_6	1.06 (3H, s, 9-CH_3), 1.35 (3H, s, 9-CH_3), 2.25 (3H, s, 7-CH_3), 3.53–3.70 (2H, AB-q, J = 16.2 Hz, CH_2), 6.43–7.52 (10H, m, CH=CH, ArH), 8.81 (1H, br. s, NH).
3i	DMSO-d_6	1.05 (3H, s, 9-CH_3), 1.34 (3H, s, 9-CH_3), 2.29 (3H, s, p-CH_3), 3.52–3.76(2H, AB-q, J = 16.4 Hz, CH_2), 6.35–6.78 (2H, AB-q, J = 16.0 Hz, CH=CH), 6.88–7.41 (8H, m, ArH), 8.85 (1H, br. s, NH).
3j	DMSO-d_6	1.16 (3H, s, 9-CH_3), 1.37 (3H, s, 9-CH_3), 3.56–3.75 (2H, AB–q, J = 16.2 Hz, CH_2), 6.40–6.82 (2H, AB-q, J = 16.2 Hz, CH=CH), 6.89–7.59 (8H, m, ArH), 8.83 (1H, br. s, NH)
3k	$CDCl_3$	1.16 (3H, s, 9-CH_3), 1.43 (3H, s, 9-CH_3), 3.80 (2H, s, CH_2), 6.25–7.20 (10H, CH=CH, ArH), 7.99 (1H, br. s, NH)
3l	DMSO-d_6	1.09 (3H, s, 9-CH_3), 1.39 (3H, s, 9-CH_3), 3.57–3.78 (2H, AB-q, J = 16.2 Hz, CH_2), 6.47–7.77 (10H, CH=CH, ArH), 8.96 (1H, br. s, NH)
3m	DMSO-d_6	1.08 (3H, s, 9-CH_3), 1.37 (3H, s, 9-CH_3), 3.34–4.14 (2H, AB-q, J = 16.2 Hz, CH_2), 6.43–7.73 (9H, CH=CH, ArH), 8.63 (1H, br. .s, NH)
3n	pyridine-d_5	1.13 (3H, s, 9-CH_3), 1.50 (3H, s, 9-CH_3), 3.75–4.10 (2H, AB-q, J = 16.0 Hz, CH_2), 6.75–7.55 (9H, CH=CH, ArH), 8.63 (1H, br. .s, NH).
3o	DMSO-d_6	1.06 (3H, s, 9-CH_3), 1.36 (3H, s, 9-CH_3), 2.50 (3H, s, 7-CH_3), 3.54–3.72 (2H, AB-q, J = 16.2 Hz, CH_2), 6.45–7.64 (9H, m, CH=CH, ArH), 8.74 (1H, br. s, NH).
3p	DMSO-d_6	1.11 (3H, s, 9-CH_3), 1.36 (3H, s, 9-CH_3), 3.52–3.70 (2H, AB-q, J = 16.2 Hz, CH_2), 3.58 (3H, s, OCH_3), 6.22–7.39 (10H, m, CH=CH, ArH), 8.75 (1H, br. .s, NH).
3q	DMSO-d_6	1.08 (3H, s, 9-CH_3), 1.36 (3H, s, 9-CH_3), 3.55–3.75 (2H, AB-q, J = 16.5 Hz, CH_2), 3.76 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 6.32–6.75 (2H, AB-q, J = 15.0 Hz, CH=CH), 6.91–7.17 (7H, m, ArH), 8.79 (1H, br. s, NH)
3r	DMSO-d_6	1.15 (3H, s, 9-CH_3), 1.41 (3H, s, 9-CH_3), 3.78–3.82 (2H, AB-q, J = 16.2 Hz, CH_2), 6.50–8.21 (13H, m, CH=CH, ArH), 9.00 (1H, br. s, NH).
6	DMSO-d_6	1.00 (3H, s, 9-CH_3), 1.30 (3H, s, 9-CH_3), 3.54–3.75 (2H, AB-q, J = 16.2 Hz, NCH_2), 5.55 (2H, s, OCH_2), 6.50–7.81 (16H, m, CH=CH, ArH, NH)

compound **4b** is situated in the area below 106.0 ppm in the ^{13}C NMR spectrum, which is the characteristic feature of spiro[benzopyran-2,2'-indole] derivatives [17].

When compound **4a** was treated with perchloric acid, the ring cleavage of pyrane ring occurred, and 1-carbamoylmethyl-[2-(2-hydroxyphenyl)ethenyl]-3H-indolium perchlorate **5** was isolated. A doublet of a vinylic proton at 6.30 with ^3J = 16.0 Hz in the ^1H NMR spectrum corresponds to the *trans* structure of the perchlorate **5**. The O-alkylation of compound **4a** with benzyl chloride proceeds efficiently in the presence of potassium hydroxide in ethanol and gives 9a-[2-(2-benzyloxyphenyl)ethenyl]imidazo[1,2-*a*]indol-2-one **6**.The absorption bands at 3256 (N—H) and 1704 cm^{-1} (C=O) in the IR spectrum of compound **6** indicate the presence of a five-member lactam ring. The singlet of methylene protons at 5.55 ppm in the ^1H NMR spectrum confirms the presence of a benzyl group at the oxygen atom.



7

9a-[2-(2-Thienyl)ethenyl]-1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]indol-2-one derivative **7** was synthesized by the reaction of 1-carbamoylmethyl-3H-indolium chloride with thiophene-2-carbaldehyde in acetic acid with the following treatment of the reaction mixture with a base.

EXPERIMENTAL

^1H NMR spectra were determined on a Tesla BS-487C (80 MHz), a Bruker DPX (200 MHz) and a Bruker ASW-300 (300 MHz) instruments, internal reference TMS. ^{13}C NMR spectra were obtained on a Bruker ASW-300 (75 MHz) spectrometer. IR spectra were recorded on a IR-75 spectrometer (KBr pellets). UV-vis spectra were obtained on a Specord UV-Vis spectrometer. The course of the reactions was observed using TLC on Silufol plates, eluent acetone — hexane, 1 : 2.

1-Carbamoylmethyl-3,3-dimethyl-2-[2-(4-dimethylaminophenyl)ethenyl]-3H-indolium chloride (2a). A solution of 3.79 g (15 mmol) of 1-carbamoylmethyl-2,3,3-trimethyl-3H-indolium chloride (**1a**) and 2.24 g (15 mmol) 4-dimethylaminobenzaldehyde in 20 ml of acetic acid was heated at 100°C for 2 h. The precipitated substance was filtered off and recrystallized from ethanol to give 4.20 g (73 %) of salt **2a** with mp 214—215°C. Electronic spectrum (ethanol): λ_{max} = 557 nm, lgε = 4.18. ^1H NMR spectrum (CD_3OD): 1.78 (6H, s, 3,3-CH_3), 3.16 (6H, s, N,N-CH_3), 5.33 (2H, s, CH_2), 6.80—8.40 ppm (10H, CH=CH, ArH). Found, %: Cl, 9.41. $C_{22}H_{26}ClN_3O$ Calculated, %: Cl, 9.23.

9,9-Dimethyl-9a-[2-(4-dimethylaminophenyl)ethenyl]-1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]-indol-2-one (3a). A. A solution of 3.83 g (10 mmol) of chloride **2a** in 30 ml of ethanol was poured into 150 ml of 5 % potassium hydroxide. The substance separated out was filtered off, dissolved in 10 ml of boiling acetone and poured again into 200 ml of water. The precipitated substance was filtered off, dried and recrystallized from ethanol to afford 2.90 g (83.5 %) of compound **3a.** UV spectrum (in ethanol): λ_{max} at 209, 230 and 285 nm (lgε 4.24, 3.97, 4.38); mp and elemental analysis data of compound **3a** are presented in Table 1, ^1H NMR spectrum data see in Table 2.

B. A solution of 5.06 g (20 mmol) of chloride **1a** and 2.98 g (20 mmol) 4-dimethylaminobenzaldehyde in 30 ml of acetic acid was heated at 100°C for 2 h. The reaction mixture was poured into 200 ml of water, treated with 10% potassium hydroxide until alkaline, the substance separated out was filtered off, dissolved in 30 ml of boiling acetone, and poured into 300 ml of water. The precipitated substance was filtered off, dried and recrystallized from ethanol. Yield of compound **3a** are given in Table 1.

A similar procedure was used to obtain compounds **3b**—**f** (Tables 1 and 2).

9a-[2-(4-Bromophenyl)ethenyl]-9,9-dimethyl-1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]indol-2-one (3n). A solution of 2.53 g (10 mmol) of chloride **1a** and 1.85g (10 mmol) of 4-bromobenzaldehyde in 10 ml of acetic acid was heated at 100°C for 4 h, after which the mixture was poured into 100 ml of water, treated with 10 % potassium hydroxide until alkaline, and extracted with 20 ml of ether. The mixture was kept at 5°C for 18 h, the precipitated substance was filtered off, dried and recrystallized from dimethylformamide. Yield, mp and elemental analysis data of compound **3n** are presented in Table 1, ^{1}H NMR spectrum data are given Table 2.

A similar procedure was used to obtain 9a-(2-phenylethenyl)imidazo[1,2-*a*]indol-2-one derivatives **3g**—**m, 3o**—**r** (Tables 1 and 2).

1'-Carbamoylmethyl-3',3"-dimethyl-1'3'-dihydrospiro[2H-1-benzopyran-2,2'-[2H]indole] (4a). A. A solution of 2.53 g (10 mmol) chloride **1a** and 1.68 g (13.5 mmol) of salicyl aldehyde in 10 ml of acetic acid was heated at 100°C for 6 h. The reaction mixture was poured into 75 ml of 5% sodium acetate and extracted with ether (2 x 15 ml). The extract was washed with 20 ml of 5% sodium carbonate, 20 ml of water, dried with calcium chloride, organic solvent evaporated and the residue crystallized from ethanol to yield 2.14 g (58 %) of compound **4a** mp 195—196°C. ^{1}H NMR spectrum ($CDCl_3$): 1.20 (3H, s, 3'-CH_3), 1.33 (3H, s, 3'-CH_3), 3.55 - 4.03 (2H, AB-q, J = 16.0 Hz, NCH_2), 5.62 (1H, d, J = 10 Hz, C**H**=CH), 5.94–7.21 ppm (11H, m, ArH, $CONH_2$, CH=C**H**). Found, %: C, 75.22; H, 6.57; N, 9.00.$C_{20}H_{20}N_2O_2$. Calculated, %: C, 74.97; H 6.29; N, 8.74.

B. To a solution of 5.06g (20 mmol) of 1-carbamoylmethyl-2,3,3-trimethyl-3H-indolium chloride **1a** and 3.36 g (27 mmol) of salicyl aldehyde in 15 ml of ethanol [3 Drops of piperidine were added] and the mixture was refluxed for 6 h. The reaction mixture was kept at –5°C for 12 h, crystalline compound filtered off and recrystallized from ethanol to yield 3.84 g (52 %) of compound **4a**, which is identical to the sample obtained in experiment **A**.

6-Bromo-1'-carbamoylmethyl-3',3'-dimethyl-1',3'-dihydrospiro[2H-1-benzopyran-2,2'-[2H]indole] (4b). To a solution of 1-carbamoylmethyl-2,3,3-trimethyl-3H-indolium chloride **1a** and 2.21 g of 5-bromo-2-hydroxybenzaldehyde in 15 ml of ethanol [5 Drops of piperidine were added], and the mixture was refluxed for 3 h. The reaction mixture was poured into 100 ml of 1% sodium acetate and extracted with ether (2 x 20 ml). The extract was dried with calcium chloride, organic solvent evaporated and the residue crystallized from ethanol to yield 2.75 g (69 %) of compound **4b** with mp 182–183°C. ^{1}H NMR spectrum ($CDCl_3$): 1.20 (3H, s, 3'-CH_3), 1.35 (3H, s, 3'-CH_3), 3.86—3.96 (2H, AB-system, NCH_2), 5.73 (1H, d, ^3J = 10.2 Hz, H-3), 5.81 (1H, broad s, NH), 6.55 (1H, d, ^3J = 7.8 Hz, ArH), 6.74 (1H, br. s, NH), 6.81 (1H, d, ^3J = 10.2 Hz, H-4), 6.92—7.49 ppm (7H, m, ArH). ^{13}C NMR spectrum ($CDCl_3$): 21.03 (CH_3), 26.42 (CH_3), 47.96 (C-3'), 53.20 (NCH_2), 106.43, 107.54, 110.52, 113.23, 121.11, 121.49, 121.54, 122.46, 128.39, 129.16, 129.37, 135.64, 135.96, 145.51, 149.27 (C-2', C-3, C-4, 14 x Ar-C), 172.83 ppm (C=O). Found, %: C, 59.83; H, 5.01; N 7.14. $C_{20}H_{19}BrN_2O_2$ Calculated, %: C, 60.16; H 4.80; N, 7.02.

1-Carbamoylmethyl-2-[2-(2-hydroxyphenyl)ethenyl]-3,3-dimethyl-3H-indolium perchlorate (5). To a solution of 3.20g (10 mmol) of the compound **4a** in 12 ml of ethanol 60 % perchloric acid was added until pH 2. The mixture was kept at –5°C for 12 h, the crystalline compound filtered off and recrystallized from ethanol. Yield of perchlorate **5** 2.27 g (54 %), mp 203—204°C. IR spectrum: 3475 (N–H), 3260 (N–H), 1688 (C=O), 1100 and 624 cm^{-1} (ClO_4^-). ^{1}H NMR spectrum (CF_3COOH): 1.40 (6H, s, 3,3-CH_3), 4.58 (2H, s, NCH_2), 6.30 (1H, d, J = 16.0 Hz, C**H**=CH), 6.18—7.61 ppm (11H, m, ArH, $CONH_2$, CH=C**H**). Found, %: C, 56.78; H, 5.32; Cl 8.66; N, 6.69. $C_{20}H_{21}ClN_2O_6$. Calculated, %: C, 57.08; H, 5.03, Cl 8.42; N, 6.66.

9a-[2-(2-Benzyloxyphenyl)ethenyl]-3,3-dimethyl-1,2,3,9a-tetrahydro-9H-imidazo[1,2-*a*]-indol-2-one (6). To a solution of 3.20 g (10 mmol) of compound **5a** and 1.90 g (1.56 ml, 15 mmol) of benzylchloride in 10 ml of ethanol (2.24 g (40 mmol) of powdered potassium hydroxide were added), and the mixture was refluxed for 3 h. The reaction mixture was cooled until r.t., crystalline compound filtered off, washed with 2 ml of ethanol and recrystallized from acetone. Yield, mp and ^{1}H NMR spectra data of compound **6** are presented in Tables 1, 2.

9,9-Dimethyl-9a-[2-(2-thienyl)ethenyl]-1,2,3,9a-tetrahydro-9H-imidazo[1,2-a]indol-2-one (7). A solution of 2.53g (10 mmol) of chloride **1a** and 1.12 g (10 mmol) of thiophene-2-carboxaldehyde in 12 ml of acetic acid was heated at 100°C for 5 h, after which the mixture was poured into 150 ml of water, treated with 5% hydroxide until alkaline, and extracted with 20 ml of ether. After 18 h, the precipitated substance was removed by filtration, dried, and crystallized from acetone to give 1.18 g (38%) of a product with mp183–184°C. ^{1}H NMR spectrum (DMSO-d_6): 1.06 (3H, s, CH_3), 1.35 (3H, s, CH_3), 3.57–3.76 (2H, AB-q, J = 15.0 Hz, NCH_2), 6.20 (1H, d, J = 15.9 Hz, C**H**=C**H**), 6.89—7.47 (7H, m, ArH, CH=C**H**), 8.80 ppm (1H, br.s, NH). Found, %: C 69.45; H 6.03; N 8.90. $C_{18}H_{18}N_2OS$. Calculated, %: C 69.65; H 5.84; N 9.02.

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