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DERIVATIVES OF INDOLE. 143.* SYNTHESIS OF PHOTOCHROMIC DERIVATIVES OF 2-ARYLINDOLES

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New derivatives of 2-arylindoles containing (4-pyridyl)alkyl substituents at various positions of the pyrrole ring were synthesized. They react with 2,3-dimethoxycarbonylspirofluorenylcyclopropene with the formation of light-sensitive systems belonging to the photochromic dihydroindolizine class.

Keywords: 2-arylindoles, dihydroindolizines, pyridylindoles, photochromism.

Photochromic dihydroindolizines form a rich and varied class of light-sensitive compounds [2, 3]. Among the multitude of photochromic materials they are distinguished by high their efficiency, their cheapness, and their accessibility. This forms the basis of their prospective use in optical lenses, the recording and storage of data [4], and dental materials [5].

In the present work we describe the synthesis and photochromic characteristics of novel 2-arylindole systems containing a dihydroindolizine ring. It seemed to us important to couple the qualities of 2-arylindoles, which form the fundamental unit in many biologically active systems [6, 7], and those of photochromic molecules. Model systems of such a type are promising for use as marker molecules in the study of biological processes.

A standard and effective method for the production of photochromic dihydroindolizines is the addition of electron-excessive N-heterocyclic bases to spirocyclopropene. Such bases for us were the 1- and 3-(4-pyridyl)alkyl-substituted 2-arylindoles **4a-d** and **5a-c** that we had synthesized.

Indolepyridine is the main structural element of many natural products [8], among which there are antitumor [9] and antidiabetic [10] agents. On this basis compounds **4a-d** and **5a-c** are of interest in themselves as possible biologically active substances.

The initial bases **4a-d** and **5a-c** were produced by alkylation of the respective 2-arylindoles, obtained by the Fischer method [11] (Scheme 1).

The 1-(4-pyridylmethyl)-2-arylindoles **4a-d** were obtained by N-alkylation of 2-arylindoles (**1**) with 4-(chloromethyl)pyridine in the 50% aqueous potassium hydroxide–benzene two-phase system in the presence of tetrabutylammonium bromide.

It is known that 4-vinylpyridine in an acidic medium alkylates the indole ring at position 3 [12]. In our case too by boiling 2-arylindoles **1a-c** with 4-vinylpyridine **3** we obtained the corresponding 3-[2-(4-pyridyl)ethyl] derivatives **5a-c**.

* For Communication 142, see [1].

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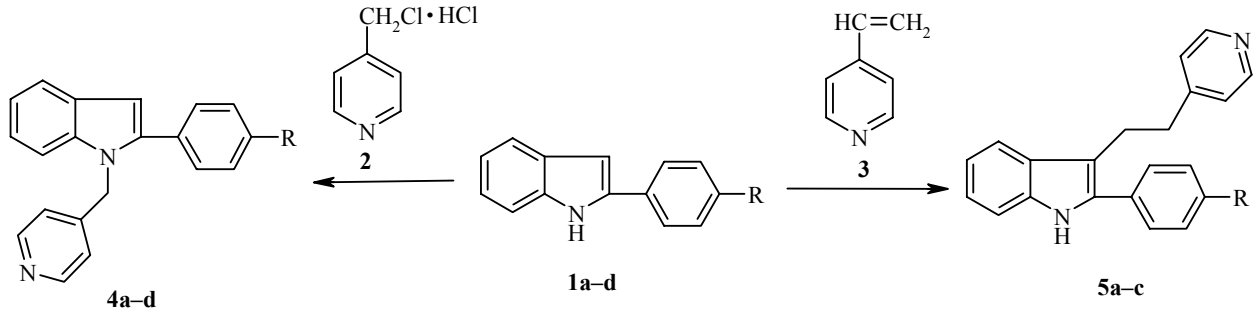
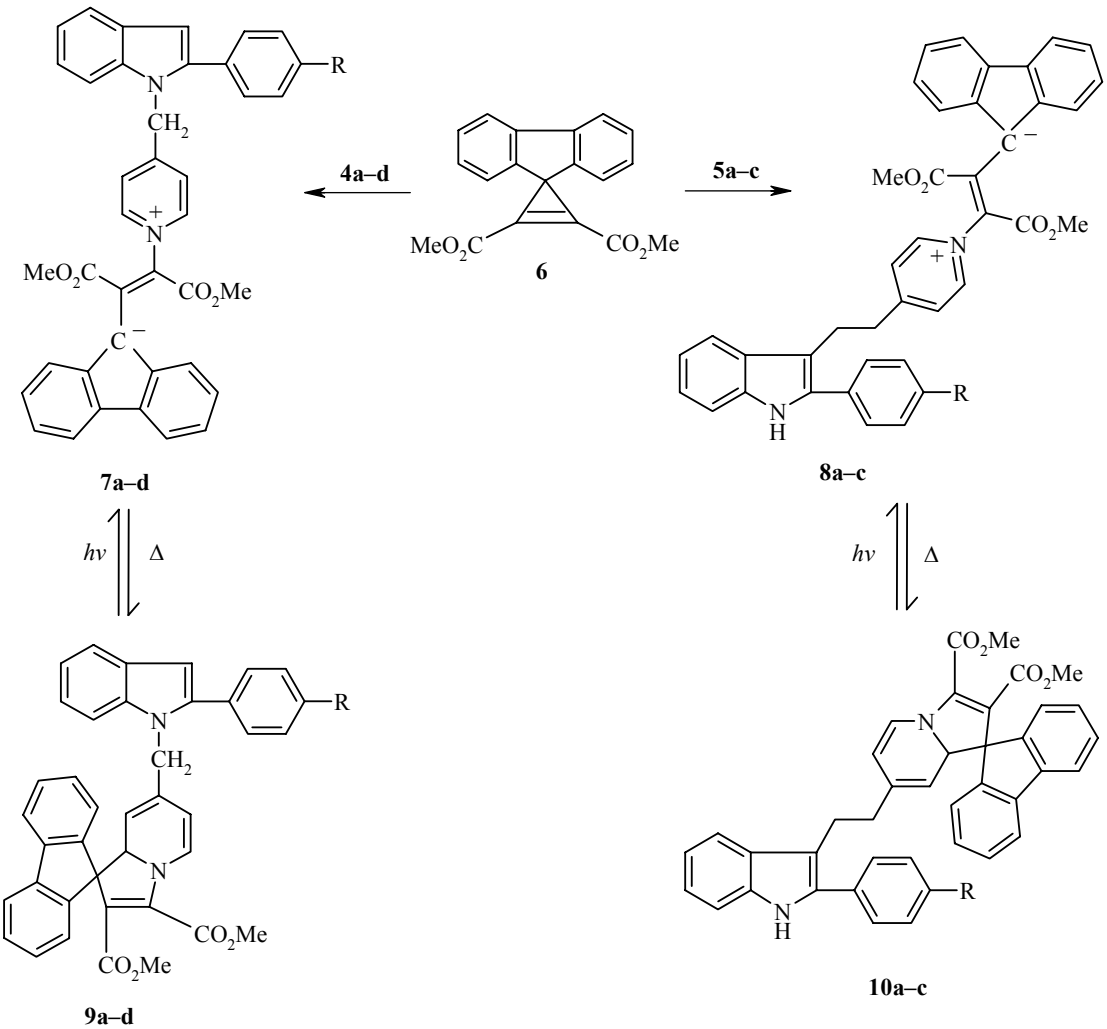
Scheme 1



1, 4, 5 a R = H, **b** R = Ph, **c** R = Br; **1**, **4 d** R = NO_2

The bases **4a-d** and **5a-c** react with 2',3'-dimethoxycarbonylspirofluorenylcyclopropene **6** in the dark at room temperature with the formation of the light-sensitive compounds **9a-d** and **10a-c** (Scheme 2).

Scheme 2



7-10 a R = H, **b** R = Ph, **c** R = Br; **7**, **9 d** R = NO_2

During exposure to UV light the light-yellow solutions of compounds **9a-d** and **10a-c** become dark-green as a result of opening of the dihydroindolizine ring and transformation into the betaine forms **7a-d** and **8a-c**. In the dark the color of the solutions is restored as a result of 1,5-electrocyclization of the betaines with the formation of the initial dihydroindolizines **9a-d** and **10a-c**.

Fig. 1 shows as an example the electronic absorption spectra of compound **8b** before (*a*) and after (*b*) exposure. In spectrum (*a*) strong absorption bands appear at 248 and 307 nm with a comparatively weak band at 383 nm. After exposure the peak at 383 nm, assigned to the dihydroindolizine fragment, disappears, and two new absorption bands appear in the visible region at 450 and 600 nm, which correspond to the colored open form.

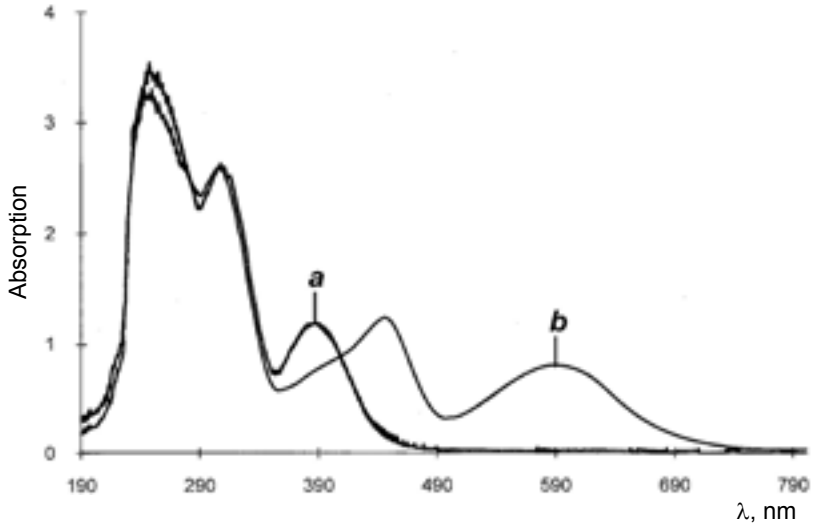


Fig. 1. The electronic absorption spectra of compound **8b** before (*a*) and after (*b*) exposure.

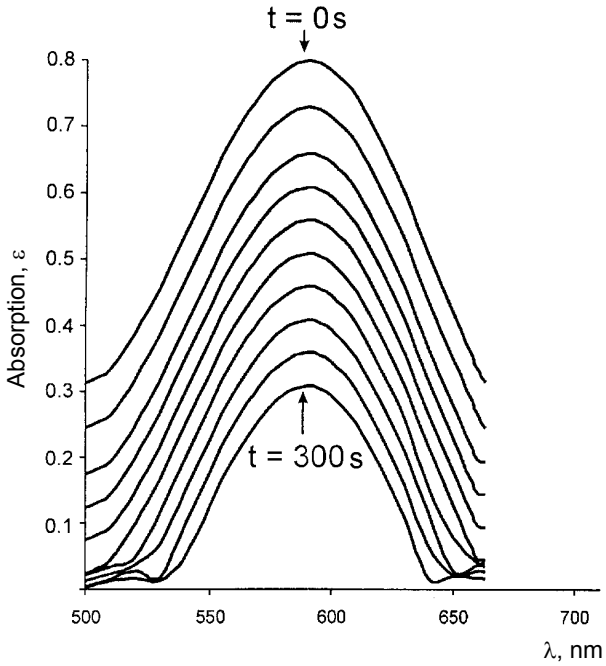


Fig. 2. The spectrum for the thermal decolorization of compound **10b** with the formation of the betaine **8b** in methylene chloride solution. Time interval 15 sec.

Fig. 2 shows the electronic absorption spectra of the exposed solutions of compound **8b** recorded in the dark for 5 min at intervals of 15 sec. The decrease in the intensity of the absorption bands in the visible region and their final disappearance and also the increase in the intensity of the peak at 383 nm clearly indicate electrocyclization of the betaine form. The half-conversion times $t_{1/2}$ of the betaines (Table 4), which vary in the range of 0.5-1 min, were determined on the basis of the kinetic data.

The physicochemical and spectral characteristics of compounds **4a-d**, **5a-c**, **9a-d**, and **10a-c** are given in Tables 1-4.

TABLE 1. The ^{1}H NMR Spectra of Compounds **4a-d**, **5a-c**, **9a-d**, and **10a-c**

Com-pound	Chemical shifts, δ, ppm (*J*, Hz)
1	2
4a	5.50 (2H, s, CH_2); 6.69 (1H, s, H-3); 6.85 (2H, d, $J_{\alpha\beta}$ = 5.3, β-H); 7.08-7.10 (2H, m, H-5, H-6); 7.34 (1H, d, J_o = 8.0, H-7); 7.39-7.49 (5H, m, Ar-H); 7.62 (1H, dd, J_m = 1.3, J_o = 7.1, H-4); 8.41 (2H, dd, $J_{\alpha\alpha}$ = 1.3, $J_{\alpha\beta}$ = 5.7, α-H)
4b	5.56 (2H, s, CH_2); 6.76 (1H, s, H-3); 6.89 (2H, d, $J_{\beta\alpha}$ = 5.7, β-H); 7.12 (2H, q, J_m = 1.8, J_o =7.5, H-5, H-6); 7.34 (1H, d, J_o= 8.0, H-7); 7.38 (1H, t, J_o = 7.5, H-1"); 7.48 (2H, t, J_o = 8.0, H-2", H-6"); 7.57 (2H, d, J_o= 8.0, H-3", H-5"); 7.64 (1H, dd, J_m = 1.8, J_o = 6.6, H-4); 7.71 (2H, d, J_o= 7.1, H-2', H-6'); 7.76 (2H, d, J_o= 8.4, H-3', H-5'); 8.43 (2H, dd, $J_{\alpha\alpha}$ = 1.3, $J_{\alpha\beta}$ = 5.8, α-H)
4c	5.50 (2H, s, CH_2); 6.73 (1H, s, H-3); 6.84 (2H, dd, $J_{\beta\beta}$ = 1.7, $J_{\beta\alpha}$ = 5.72, β-H); 7.09-7.17 (2H, m, H-5, H-6); 7.36 (1H, d, J_o= 8.4, H-7); 7.43 (2H, d, J_o = 9.3, A-H); 7.65 (3H, d, J_o = 8.4, B-H, H-4); 8.42 (2H, dd, $J_{\alpha\alpha}$ = 1.8, $J_{\alpha\beta}$ = 6.2, α-H)
4d	5.59 (2H, s, CH_2); 6.85 (2H, d, $J_{\beta\alpha}$ = 5.7, β-H); 6.93 (1H, s, H-3); 7.14 (1H, t, J_o = 7.5, H-5); 7.21 (1H, t, J_o = 7.5, H-6); 7.43 (1H, d, J_o = 8.0, H-7); 7.69 (1H, d, J_o = 7.5, H-4); 7.78 (2H, d, J_o = 8.4, B-H); 8.27 (2H, d, J_o = 8.8, B-H); 8.41 (2H, d, $J_{\alpha\beta}$ = 5.7, α-H)
5a	2.94 (2H, m, *J* = 10.6, *J* = 8.8, 1'-CH_2); 3.14 (2H, m, *J* = 10.2, *J* = 8.8, 2'-CH_2); 7.02 (1H, t, J_o = 8.0, H-5); 7.11 (1H, t, J_o = 7.1, H-6); 7.21 (2H, d, $J_{\beta\alpha}$ = 5.8, β-H); 7.37 (2H, t, J_o=7.5, H-7, Ar-H); 7.49 (2H, t, J_o = 7.8, Ar-H); 7.55 (2H, d, J_o=7.8, Ar-H); 7.61 (1H, d, J_o = 8.0, H-4); 8.40 (2H, d, $J_{\alpha\beta}$ = 5.7, α-H); 11.15 (1H, s, NH)
5b	2.98 (2H, t, *J* = 5.8, 1'-CH_2); 3.18 (2H, t, *J* = 5.8, 2'-CH_2); 7.03 (1H, t, J_o = 7.0, H-5'); 7.12 (1H, t, J_o = 7.1, H-6); 7.26 (2H, dd, $J_{\beta\beta}$ = 1.8, $J_{\beta\alpha}$ = 6.2, β-H); 7.39 (2H, t, J_o = 7.5, H-7, H-1"); 7.50 (2H, t, J_o = 8.0, H-2", H-6"); 7.62 (1H, d, J_o = 7.5, H-4); 7.67 (2H, d, J_o = 8.4, H-3", H-5"); 7.76 (2H, dd, J_m = 1.3, J_o = 7.1, H-2', H-6'); 7.82 (2H, d, J_o = 8.4, H-3', H-5'); 8.42 (2H, dd, $J_{\alpha\alpha}$ = 1.8, $J_{\alpha\beta}$ = 6.2, α-H); 11.23 (1H, br. s, NH)
5c	2.92 (2H, m, *J* = 8.8, 1'-CH_2); 3.12 (2H, m, *J* = 8.4, 2'-CH_2); 7.02 (1H, t, J_o = 7.5, H-5); 7.13 (1H, t, J_o= 8.0, H-6); 7.21 (2H, d, $J_{\beta\alpha}$ = 5.8, β-H); 7.37 (1H, d, J_o = 8.4, H-7); 7.50 (2H, d, *J* = 8.4, A-H) 7.62 (1H, d, J_o = 8.0, H-4); 7.69 (2H, m, *J* = 8.6, B-H); 8.40 (2H, d, $J_{\alpha\beta}$ = 5.8, α-H); 11.21 (1H, s, NH)
9a	3.18 (3H, s, 2'-$COOCH_3$); 3.91 (3H, s, 3'-$COOCH_3$); 3.98 (1H, s, H-8'a); 4.50 (2H, br. s, CH_2); 4.91 (1H, dd, $J_{8'6'}$ = 1.4, $J_{8'8'a}$ = 7.5, H-8'); 5.45 (1H, br. s, H-6'); 6.43 (1H, br. s, H-5'); 6.67 (1H, d, J_o = 7.5, Ar-H); 6.91 (1H, d, J_o = 7.5, Ar-H); 7.00-7.04 (2H, td, J_o = 7.0, J_m = 1.3, Ar-H); 7.24-7.45 (11H, m, Ar-H); 7.58 (1H, d, J_o = 7.5, Ar-H); 7.75 (2H, t, J_o = 7.5, Ar-H)
9b	3.19 (3H, s, 2'-$COOCH_3$); 3.92 (3H, s, 3'-$COOCH_3$); 4.04 (1H, s, H-8'); 4.56 (2H, br. s, CH_2); 4.96 (1H, d, $J_{6'5'}$ = 5.8, H-6'); 5.49 (1H, s, H-8'a); 6.50 (1H, s, H-3); 6.71 (1H, d, $J_{5'6'}$ = 5.8, H-5'); 6.94 (1H, d, J_o = 6.6, Ar-H); 7.00-7.06 (2H, m, Ar-H); 7.24 (1H, t, J_o = 5.8, Ar-H); 7.30-7.43 (7H, m, Ar-H); 7.47 (1H, d, J_o = 6.6, Ar-H); 7.52 (2H, t, J_o = 6.2, Ar-H) 7.58 (1H, d, J_o = 5.8, Ar-H); 7.72-7.77 (6H, m, Ar-H)
9c	3.18 (3H, s, 2'-$COOCH_3$); 3.92 (3H, s, 3'-$COOCH_3$); 3.97 (1H, s, H-8'a); 4.50 (2H, br. s, CH_2); 4.80 (1H, d, $J_{8'8'a}$ = 7.5, H-8'); 5.45 (1H, br. s, H-6'); 6.47 (1H, br. s, H-5'); 6.92-7.06 (3H, m, Ar-H); 7.18 (2H, d, J_o = 7.5, A-H); 7.25-7.41 (6H, m, Ar-H); 7.47 (1H, d, Ar-H); 7.57 (1H, d, Ar-H); 7.61 (2H, d, J_o = 8.4, B-H); 7.77 (2H, t, Ar-H)

TABLE 1 (continued)

1	2
9d	3.18 (3H, s, 2'-$COOCH_3$); 3.91 (3H, s, 3'-$COOCH_3$); 3.93 (1H, s, H-8'a); 4.58 (1H, d, J_{gem} = 17.2, CH_2); 4.63 (1H, d, J_{gem} = 17.7, CH_2); 4.88 (1H, dd, $J_{8'6'}$ = 1.3, $J_{8'8'a}$ = 7.5, H-8'); 5.40 (1H, d, $J_{6'8'}$ = 1.3, H-6'); 6.68 (2H, t, $J_{5'6'}$ = 7.5, H-5', H-3); 7.02-7.19 (3H, m, Ar-H); 7.23-7.38 (5H, m, Ar-H); 7.51-7.56 (4H, m, Ar-H); 7.72-7.75 (2H, m, J_o = 7.5, J_m = 1.3, Ar-H); 8.32 (2H, dd, J_o = 7.7, Ar-H)
10a	2.10 (2H, m, 2'-CH_2); 2.65 (1H, m, 1'-CH_2); 2.79 (1H, m, 1'-CH_2); 3.20 (3H, s, 2'-$COOCH_3$); 3.95 (3H, s, 3'-$COOCH_3$); 4.01 (1H, s, H-8'); 5.26 (1H, dd, $J_{6'8'}$ = 1.3, $J_{6'5'}$ = 7.5, H-6'); 5.38 (1H, s, H-8'a); 6.67 (1H, d, $J_{5'6'}$ = 7 .5, H-5'); 6.95 (1H, t, J_o = 8.0, H-5); 7.07 (1H, t, J = 8.0, H-6); 7.28-7.44 (4H, m, Ar-H); 7.52-7.59 (5H, m, Ar-H); 7.69-7.75 (4H, m, J_o = 8.4, Ar-H); 7.82 (2H, d, J_o = 7.5, Ar-H); 11.12 (1H, s, NH)
10b	2.09 (2H, m, 2'-CH_2); 2.63 (1H, m, 1'-CH_2) 2.72 (1H, m, 1'- CH_2); 3.20 (3H, s, 2'-$COOCH_3$); 3.98 (3H, s, 3'-$COOCH_3$); 4.01 (1H, s, H-8'); 5.15 (1H, d, $J_{6'5'}$ = 7.0, H-6'); 5.36 (1H, s, H-8'a); 6.66 (1H, d, $J_{5'6'}$ = 6.6, H-5'); 6.91 (1H, t, J_o = 7.5, H-5); 7.06 (1H, t, J_o = 7.0, H-6); 7.10-7.61 (17H, m, Ar-H); 7.84 (2H, d, J_o = 7.1, Ar-H); 11.05 (1H, s, NH)
10c	2.08 (2H, m, 2'-CH_2); 2.56 (1H, m, 1'-CH_2); 2.72 (1H, m, 1'-CH_2); 3.21 (3H, s, 2'-$COOCH_3$); 3.96 (3H, s, 3'-$COOCH_3$); 4.01 (1H, s, H-8'); 5.23 (1H, d, $J_{6'5'}$ = 7.5, H-6'); 5.36 (1H, s, H-8'a); 6.66 (1H, d, $J_{5'6'}$ = 7.5, H-5'); 6.94 (1H, t, J_o = 8.0, H-5); 7.07 (1H, t, J_o = 8.0, H-6); 7.20 (2H, m, Ar-H); 7.29-7.37 (7H, m, Ar-H); 7.57-7.61 (3H, m, J = 8.8, Ar-H); 7.84 (2H, d, J = 7.6, Ar-H); 11.10 (1H, br. s, NH)

TABLE 2. The Data from Elemental Analysis of Compounds **4a-d**, **5a-c**, **9a-d**, and **10a-c**

Compound	Empirical formula	Found, % / Calculated, %			
		C	H	N	Br
4a	$C_{20}H_{16}N_2$	84.28 / 84.51	5.85 / 5.63	9.85 / 9.86	
4b	$C_{26}H_{20}N_2$	86.46 / 86.67	5.39 / 5.55	8.00 / 7.77	
4c	$C_{20}H_{15}Br\ N_2$	66.40 / 66.11	4.41 / 4.13	7.55 / 7.71	21.02 / 22.04
4d	$C_{20}H_{15}N_3O_2$	72.86 / 72.95	4.56 / 4.60	12.90 / 12.76	
5a	$C_{21}H_{18}N_2$	84.00 / 84.56	5.73 / 6.04	9.80 / 9.39	
5b	$C_{27}H_{22}N_2$	86.82 / 86.63	5.28 / 6.88	8.00 / 7.48	
5c	$C_{21}H_{17}BrN_2$	66.75 / 66.84	4.38 / 4.51	7.49 / 7.43	21.08 / 21.22
9a	$C_{39}H_{30}N_2O_4$	79.52 / 79.32	5.40 / 5.08	4.48 / 4.74	
9b	$C_{45}H_{34}N_2O_4$	80.00 / 81.08	5.08 / 5.10	4.00 / 4.20	
9c	$C_{39}H_{29}BrN_2O_4$	69.17 / 70.95	4.60 / 4.33	3.91 / 4.18	11.52 / 11.96
9d	$C_{39}H_{29}N_3O_6$	73.75 / 73.70	4.31 / 4.57	6.50 / 6.61	
10a	$C_{40}H_{32}N_2O_4$	79.80 / 79.47	5.00 / 5.30	4.60 / 4.63	
10b	$C_{46}H_{36}N_2O_4$	81.00 / 81.18	5.20 / 5.29	4.08 / 4.12	
10c	$C_{40}H_{36}BrN_2O_4$	70.20 / 70.28	4.52 / 4.54	4.05 / 4.10	11.69 / 11.71

TABLE 3. The Physicochemical and Spectral Characteristics of Compounds **4a-d**, **5a-c**, **9a-d**, and **10a-c**

Com-pound	mp, °C	R_f*	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	Yield, %
4a	114-115	0.28	1530 (C=N arom.), 1530 (C=C)	248 (4.27), 294 (4.36)	53
4b	165-167	0.45	1580 (C=N arom.), 1610 (C=C)	240 (4.34), 303 (4.19)	56
4c	142-142.5	0.36	1590 (C=C), 1595 (C=N arom.)	235 (4.35), 300 (4.20)	50
4d	183-184	0.30	1375 (NO_2), 1410 (C=C), 1590 (C=N arom.)	259 (4.38)	48
5a	191-192	0.27	1580 (C=N arom.), 3270 (NH)	232 (4.35), 240 (4.34), 305 (4.10)	63
5b	214-216	0.59	1590 (C=N arom.), 1465 (C=C), 3120 (NH)	229 (4.32), 257 4.25), 317 (4.27)	39
5c	225-227	0.36	1590 (C=N arom.), 1630 (C=C), 3310 (NH)	230 (5.59), 244 (5.41), 307 (4.31)	37
9a	104-105	0.30	1600 (C=C), 1695, 1735 (CO ester)	384 (4.44)	44
9b	124-126	0.44	1560 (C=N arom.), 1690, 1740 (CO ester)	231 (2.88), 260 (3.50), 262 (3.52), 310 (2.36), 388 (0.87)	42
9c	162-163	0.37	1590 (C=C), 1680, 1740 (CO ester)	247 (3.65), 303 (2.66), 388 (4.13)	45
9d	135-136	0.26	1510 (NO_2), 1590 (C=N arom.), 1690, 1740 (CO ester)	428 (4.40)	53
10a	120-121	0.23	1695, 1735 (CO ester), 3310 (NH)	235 (4.43), 265 sh. (4.37), 305 (4.30), 362 (4.09)	32
10b	125-127	0.59	1685, 1740 (CO ester), 3250 (NH)	234 (4.43), 259 (4.49), 319 (4.38)	48
10c	190-190.5	0.36	1590 (C=N arom.), 1695, 1740 (CO ester), 3460 (NH)	248 (4.51), 307 (2.57), 383 (4.06)	35

* Solvent systems: 1:1 benzene–ether for compounds **4a-d**, benzene for **5a-c**, 1:5 hexane–ether for **9a-d**, 1:1 hexane–ether for **10a-c**.

TABLE 4. The Kinetic Data for the Thermal Reverse Reaction – the Transformation of the Betaines into Cyclic Structures **7a-d** → **9a-d** and **8a-c** → **10a-c**

Compound	**7a-c**, **8a-c**, λ_{max}, nm	**9a-d**, **10a-c**, λ_{max}*, nm	k, 1/s (**7a-c** → **9a-d**) (**8a-c** → **10a-c**)	$t_{1/2}$, s (**7a-c** → **9a-d**) (**8a-c** → **10a-c**)
7a/**9a**	603	384	1.26×10^{-2}	55
7b/**9b**	612	388	0.80×10^{-2}	52
7c/**9c**	605	388	2.17×10^{-2}	32
7d/**9d**	609	428	1.58×10^{-2}	44
8a/**10a**	587	362	1.27×10^{-2}	50
8b/**10b**	590	319	1.37×10^{-2}	54
8c/**10c**	588	383	1.03×10^{-2}	67

* $T = 24°C$, $c = 10^{-4}$ mol·l^{-1} in CH_2Cl_2.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument in vaseline oil, and the electronic absorption spectra were recorded on an FT-UV/VIS HP 8453 spectrophotometer in methylene chloride. The ^{1}H NMR spectra were recorded on a Bruker AM-400 instrument at 400 MHz in DMSO-d_6 with TMS as internal standard. Elemental analysis was performed on an LECO CHNS-932 analyzer. The melting points were determined on Buchi spm-20 apparatus.

The reaction and the purity of the compounds were monitored and the R_f values were determined on Silufol-254 plates. Silica gel 100/250 μ was used as sorbent for column chromatography.

2-Phenyl-1-(4-pyridylmethyl)indoles 4a-d (General Procedure). To the two-phase system consisting of 50% aqueous potassium hydroxide (10 ml) and benzene we added 4-(chloromethyl)pyridine hydrochloride (**2**) (3.5 mmol). The mixture was stirred vigorously at 0°C for 15 min, and tetrabutylammonium bromide (0.15 mmol) and a solution of the respective 2-phenylindole **1** (3 mmol) were added. The mixture was boiled for 4 h, cooled, and extracted with benzene. The extract was washed with water and dried with anhydrous calcium chloride. The product was chromatographed on a column of silica gel with the following eluents: 7:1 chloroform–ether (**4a**), 4:1 carbon tetrachloride–ether (**4b**,**c**), and 5:1 benzene–ether (**4d**). The products were recrystallized from benzene, and compound **4a** from hexane. Colorless crystals were obtained, and compound **4d** was isolated in the form of yellow needles.

2-Aryl-3-[2-(4-pyridyl)ethyl]indoles 5a-c (General Procedure). To a solution of 2-phenylindole **1a** (5 mmol) in acetic acid (15 ml) we added a solution of 4-vinylpyridine **3** (10 mmol) in acetic acid (10 ml), and we boiled the mixture for 2 h. After cooling the reaction mixture was poured in a stream into iced water and neutralized with an aqueous solution of potassium hydroxide to pH 7. The precipitate was filtered off and recrystallized from isopropyl alcohol. Colorless crystals were obtained.

Dihydroindolizines 9a-d and 10a-c (General Procedure). To a solution of 2',3'-dimethoxycarbonyl-spirofluorenylcyclopropene (**6**) (0.5 mmol) in absolute ether (40 ml) we added the compound **4a-d** or **5a-c** (0.5 mmol). The mixture was stirred in the dark at room temperature for 24 h. The solvent was evaporated, and the residue was chromatographed on a column in the following systems: 20:1 benzene–ether for **9a**,**b**, 1:2 benzene–hexane for **9c**, benzene for **9d**, 3:2 hexane–ether for **10a**, 5:3 hexane–ether for **10b**, and 2:1 hexane–ether for **10c**. Yellow crystals were obtained.

2',3'-Dimethoxycarbonyl-7'-(2-phenyl-1-indolylmethyl)spiro[fluorene[9,1']-1',8'a-dihydroindolizine] (9a). Yield 0.13 g.

2',3'-Dimethoxycarbonyl-7'-[2-(4'-biphenylyl)-1-indolylmethyl]spiro[fluorene[9,1']-1',8'a-dihydro-indolizine] (9b). Yield 0.17 g.

2',3'-Dimethoxycarbonyl-7'-[2-(*p*-bromophenyl)-1-indolylmethyl]spiro[fluorene[9,1']-1',8'a-dihydro-indolizine] (9c). Yield 0.14 g.

2',3'-Dimethoxycarbonyl-7'-[2-*p*-nitrophenyl)-1-indolylmethyl]spiro[fluorene[9,1']-1',8'a-dihydro-indolizine] (9d). Yield 0.136 g.

2',3'-Dimethoxycarbonyl-7'-[2-(*p*-nitrophenyl)-1-indolylmethyl]spiro[fluorene[9,1']-1',8'a-dihydro-indolizine] (10a). Yield 0.098 g.

2',3'-Dimethoxycarbonyl-7'-{2-[2-(4'-biphenylyl)-3-indolyl]ethyl}spiro[fluorene[9,1']-1',8'a-dihydro-indolizine (10b). Yield 0.20 g.

2',3'-Dimethoxycarbonyl-7'-[2-(2-*p*-bromophenyl-3-indolyl)ethyl]spiro[fluorene-[9,1']-1',8'a-dihydro-indolizine] (10c). Yield 0.069 g.

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