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SUBSTITUENT EFFECT OF 4- AND 5-SUBSTITUTED 2-ARYL-METHYLIDENEINDANE-1,3-DIONES ON FORMATION OF 5-OXO-1H-4,5-DIHYDROINDENO[1,2-*b*]PYRIDINES

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The ratio of dihydroindenopyridine regioisomers formed from ethyl β-amino- crotonate and 4- or 5-monosubstituted 2-arylideneindane-1,3-dione depends on the total electronic and steric effects of the indanedione substituents.

Keywords: 7a,10-diazacyclohepta[*def*]fluorene**,** dihydroindenopyridines, regio- isomers, Michael addition.

During our previous investigations the dihydropyridine ring opening [1] and N- or C-alkylation [2] of 5-oxo-1H-4,5-dihydroindeno[1,2-*b*]pyridines were shown to be determined by the competitive reactivity of two endocyclic enamine fragments. Polarization of the enamine part N–C(2) = C(3) is efficiently achieved by the introduction of various substituents in position 3, whereas the alteration in electron distribution of the conjugated enamine fragment N–C(9b) = C(4a) could be influenced by the substituents at the indane moiety.

Condensation of 2-arylideneindane-1,3-diones with β-aminocrotonates or their analogues is the most convenient method for the preparation of 5-oxo-4,5-dihydro-1H-indeno[1,2-*b*]pyridines; nevertheless, indanediones bearing substituents at C(4) or/and C(5) atoms are seldom used for this purpose. Herein we wish to report studies on the substituent effect of such monosubstituted 2-arylideneindanediones **1** (R^1 or R^2 = H) on the formation of 5-oxo-4,5-dihydro- indeno[1,2-*b*]pyridine regioisomers **2**, **3**.

The formation of the dihydroindenopyridine ring proceeds *via* Michael addition of the ethyl 3-aminocrotonate to the ylidene **1** double bond followed by intramolecular condensation with participation of the amino function and one of indanedione carbonyl groups of the acyclic intermediate. The location of substituent R^1 or R^2 causes different reactivity of the carbonyl groups resulting in the formation of dihydroindenopyridine regioisomers. Thus, 4-substituted arylidene indanediones produce 6- and 9-substituted dihydroindenopyridine isomers, while indanedione derivatives, bearing a substituent at the C(5) atom, lead in their turn to 7- and 8-substituted indenopyridines.

The ratio of the indenopyridine regioisomers obtained is determined by total electronic and steric effects at the reactions last step. Thus, the yield of 9-halo-substituted indenopyridine is remarkably decreased in the halogen range from Cl to I, obviously due to the increased steric requirement of the substituent in the starting 4-substituted indanedione derivatives **1** (R^2 = H).

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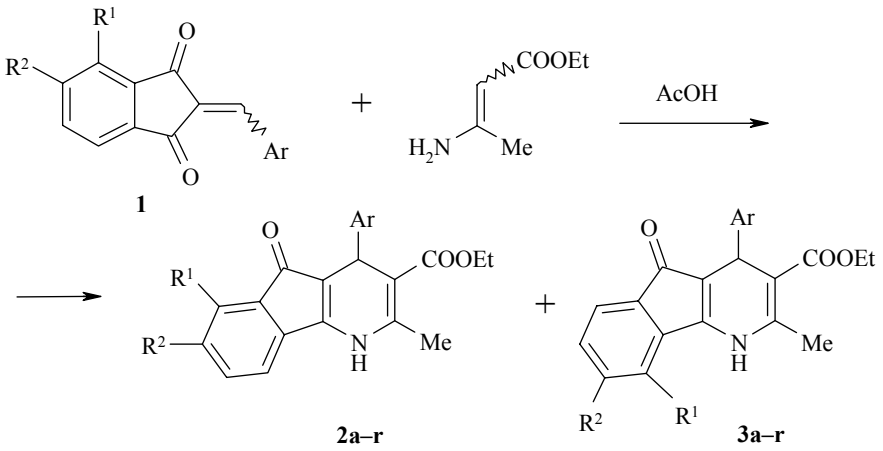

1–3 Ar = C_6H_4R-*p*; **1–3 a–h** R^2 = H; **a** R = H, $R^1 = NO_2$; **b** R = NO_2, $R^1 = NO_2$; **c** R = NO_2, R^1 = Cl; **d** R = OMe, R^1 = Cl; **e** R = H, R^1 = Br; **f** R = NO_2, R^1 = Br; **g** R = H, R^1 = I; **h** R = NO_2, R^1 = I; **i–r** R^1 = H; **i** R = H, $R^2 = NO_2$; **j** R = NO_2, R^2 = Cl; **k** R = OMe, R^2 = Cl; **l** R = H, R^2 = Br; **m** R = Cl, R^2 = Br; **n** R = NO_2, R^2 = Br; **o** R = Cl, R^2 = I; **p** R = OMe, R^2 = I; **r** R = Br, R^2 = I

On the contrary, the bulky nitro group does not significantly affect the reactivity of the neighboring carbonyl function and both 6- and 9-isomers are formed in equal yield. The lack of a 5-substituent steric influence on the arylindanedione **1** (R^1 = H) carbonyl group promotes the formation of indenopyridine isomers **2i-r** and **3i-r** in comparable yields (Table 1).

TABLE 1. Ethyl 4-Aryl-2-methyl-5-oxo-1H-4,5-dihydroindeno[1,2-*b*] pyridine 3-carboxylates **2** and **3**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, (isolated), %
		C	H	N		
1	2	3	4	5	6	7
2a	$C_{22}H_{18}N_2O_5$	67.85 / 67.69	4.56 / 4.65	7.01 / 7.18	218-220	41
3a	$C_{22}H_{18}N_2O_5$	67.34 / 67.69	4.47 / 4.65	6.98 / 7.18	187-188	41
2b	$C_{22}H_{17}N_3O_7$	60.45 / 60.69	3.47 / 3.94	9.98 / 9.65	217-219	43
3b	$C_{22}H_{17}N_3O_7$	60.78 / 60.79	4.15 / 3.94	9.51 / 9.65	177-179	43
2c	$C_{22}H_{17}ClN_2O_5$	62.43 / 62.20	4.27 / 4.03	6.78 / 6.59	228-230	66
3c	$C_{22}H_{17}ClN_2O_5$	62.13 / 62.20	3.87 / 4.03	6.42 / 6.59	224-226	24
2d	$C_{23}H_{20}ClNO_4$	67.21 / 67.40	4.77 / 4.92	3.48 / 3.42	250-252	73
3d	$C_{23}H_{20}ClNO_4$	67.53 / 67.40	5.18 / 4.92	3.25 / 3.42	195-197	24
2e	$C_{22}H_{18}BrNO_3$	62.34 / 62.28	4.16 / 4.28	3.16 / 3.30	265-266	76
3e	$C_{22}H_{18}BrNO_3$	62.57 / 62.28	4.42 / 4.28	3.51 / 3.30	170-172	11
2f	$C_{22}H_{17}BrN_2O_5$	56.56 / 56.31	3.73 / 3.65	5.93 / 5.97	239-241	78
3f	$C_{22}H_{17}BrN_2O_5$	56.08 / 56.31	3.84 / 3.65	5.65 / 5.97	220-222	13

TABLE 1. (continued)

1	2	3	4	5	6	7
2g	$C_{22}H_{18}INO_3$	56.13 / 56.07	3.68 / 3.65	3.05 / 2.97	236-238	84
3g	$C_{22}H_{18}INO_3$	55.89 / 56.07	4.01 / 3.85	3.16 / 2.97	175-177	4
2h	$C_{22}H_{17}IN_2O_5$	51.32 / 51.18	3.15 / 3.32	5.65 / 5.43	238-240	86
3h	$C_{22}H_{17}IN_2O_5$	50.93 / 51.1	3.48 / 3.32	5.27 / 5.43	208-211	2
2i	$C_{22}H_{18}N_2O_5$	67.91 / 67.69	4.43 / 4.65	7.31 / 7.18	230-232	41
3i	$C_{22}H_{18}N_2O_5$	67.57 / 67.69	4.50 / 4.65	7.42 / 7.18	223-225	41
2j	$C_{22}H_{17}ClN_2O_5$	61.98 / 62.20	4.15 / 4.03	6.67 / 6.59	142-144	50
3j	$C_{22}H_{17}ClN_2O_5$	62.34 / 62.20	4.41 / 4.03	6.68 / 6.59	201-203	42
2k	$C_{23}H_{20}ClNO_4$	67.83 / 67.40	4.78 / 4.92	3.65 / 3.42	211-213	41
3k	$C_{23}H_{20}ClNO_4$	67.13 / 67.40	4.55 / 4.92	3.16 / 3.42	235-237	47
2l	$C_{22}H_{18}BrNO_3$	62.44 / 62.28	3.97 / 4.28	3.51 / 3.30	204-206	31
3l	$C_{22}H_{18}BrNO_3$	62.11 / 62.28	4.35 / 4.28	3.18 / 3.30	243-244	54
2m	$C_{22}H_{17}BrClNO_3$	57.71 / 57.60	3.33 / 3.74	3.11 / 3.05	182-184	33
3m	$C_{22}H_{17}BrClNO_3$	57.74 / 57.60	4.00 / 3.74	2.96 / 3.05	222-224	44
2n	$C_{22}H_{17}BrN_2O_5$	56.14 / 56.31	3.72 / 3.65	5.73 / 5.97	208-210	41
3n	$C_{22}H_{17}BrN_2O_5$	56.58 / 56.31	3.55 / 3.65	6.12 / 5.97	244-145	46
2o	$C_{22}H_{17}ClINO_3$	52.51 / 52.25	3.50 / 3.39	2.71 / 2.77	140-142	33
3o	$C_{22}H_{17}ClINO_3$	51.97 / 52.25	3.18 / 3.39	3.02 / 2.77	222-224	34
2p	$C_{23}H_{20}INO_4$	54.28 / 55.11	3.87 / 4.02	2.97 / 2.79	216-218	36
3p	$C_{23}H_{20}INO_4$	55.35 / 55.11	4.25 / 4.02	3.02 / 2.79	210-212	39
2r	$C_{22}H_{17}BrINO_3$	48.02 / 48.03	3.35 / 3.11	2.78 / 2.55	201-202	36
3r	$C_{22}H_{17}BrINO$	48.21 / 48.03	2.98 / 3.11	2.66 / 2.55	215-217	45

The structure of isolated dihydroindeno[1,2-*b*]pyridines was established by a thorough ^{1}H NMR spectra analysis including the NOE experiments.

Three sets of ^{1}H resonance signals corresponding to the 4-aryl substituent, indeno moiety, and pyridine unit are present in the spectra of indenopyridines **2**, **3**. Protons of indeno units of 6- and 9-substituted indenopyridine derivatives belong to ABK spin-coupling system, whereas protons of 7- and 8-substituted compounds – to the less complicated AMX type.

The relatively high difference (>1.0 ppm upfield) in the chemical shift values of NH protons of 9-substituted indenopyridine derivatives **3i-r** compared with other isomers may be a consequence of the 9-substituent "steric pressure" on the NH proton.

The analysis of proton chemical shifts using standard values of substituent increments for benzene was also applied for structure elucidation of indeno- pyridine regioisomers. Surprisingly, the chemical shift analysis of these considerably simple spin systems did not give an evident result for the assignments of proton resonances, and the application of NOE experiments was necessary. Observation of NOE cross-peaks of NH and

TABLE 2. ^{1}H NMR Characteristics of Ethyl 6- and 9-Substituted 4-Aryl-2-methyl-5-oxo-1H-4,5-dihydroindeno[1,2-*b*]pyridine-3-carboxylates **2a-h**, **3a-h** and Compounds **4, 7**

Compound*	δ, ppm; *J*, Hz, in DMSO-d_6																
	Indeno moiety protons									4-Aryl group protons		Pyridine ring protons					NOE cross peak NH–H(9)
	H-6	H-7	H-8	H-9	$J_{6,7}$	$J_{6,8}$	$J_{7,8}$	$J_{7,9}$	$J_{8,9}$	H-2',6'	H-3',5'	H-4	2-Me	3-COOEt		NH	
2a		7.68	7.69	7.86			8.3	0.7	7.7	7.11-7.28		4.79	2.44	1.05	3.97; 3.95	10.41	7.86
2b		7.71	7.71	7.90			8.4	1.56	6.6	7.51	8.14	4.94	2.48	1.04	3.96; 3.95	10.55	—*[2]
2c		7.31	7.46	7.62			8.3	0.9	7.2	7.50	8.14	4.94	2.48	1.05	3.96; 3.95	10.31	—*[2]
2d		7.28	7.43	7.58			8.2	0.8	7.2	7.10	6.80	4.72	2.42	1.09	3.98; 3.96	10.11	7.58
2e		7.44	7.36	7.63			8.3	0.8	7.2	7.10-7.27		4.78	2.44	1.06	3.97; 3.95	10.17	7.63
2f		7.47	7.38	7.66			8.3	0.7	7.1	7.50	8.14	4.94	247	1.05	3.95	10.31	—*[2]
2g		7.68	7.17	7.64			8.2	0.9	7.2	7.10-7.28		4.79	2.43	1.06	3.97; 3.95	10.13	—*[2]
2h		7.68	7.19	7.70			8.2	0.7	7.3	7.50	8.14	4.94	2.47	1.05	3.96; 3.95	10.28	7.70
4		6.61	7.07	6.84			8.5	0.6	6.9	7.07-7.25		4.75	2.41	1.06	3.95; 3.94	9.76	6.84
3a	7.61	7.63	8.04		7.1	0.9	8.6			7.12-7.30		4.89	2.45	1.09	4.01; 3.99	8.78	
3b	7.65	7.63	8.06		7.0	1.1	8.4			7.53	8.17	5.05	2.49	1.08	3.99	8.89	
3c	7.27	7.39	7.44		7.1	1.0	8.3			7.52	8.15	4.96	2.53	1.07	3.98	8.59	
3d	7.25	7.37	7.42		7.2	0.9	8.3			7.12	6.81	4.75	2.47	1.11	3.99	8.44	
3e	7.29	7.29	7.56		7.1	1.1	7.9			7.11-7.27		4.81	2.49	1.08	4.00; 3.98	8.29	
3f	7.31	7.31	7.59		7.1	0.8	8.4			7.55	8.15	4.96	2.52	1.07	3.98	8.39	
3g*[3]	7.32	7.12	7.79		6.8	1.4	7.9			7.20-7.30		4.80	2.46	1.08	3.99	8.27	
3h*[3]	7.10	6.91	7.58		6.6	1.1	7.6			7.33	7.94	4.73	2.47	1.08	3.76	8.13	
5	6.55	7.00	6.69		6.8	1.1	8.5			7.07-7.25		4.73	2.45	1.08	3.97	8.91	

* δ, ppm OCH_3 3.68 (**2d**); NH_2 6.01 (**4**); OCH_3 3.69 (**3d**) and NH_2 5.73 (**5**).

*[2] Cross-peak not observed.

*[3] Chemical shifts (from 90 MHz spectra) without iteration.

TABLE 3. ^{1}H NMR Data of Ethyl 7- and 8-Substituted 4-Aryl-2-methyl-5-oxo-1H-4,5-dihydroindeno[1,2-*b*]pyridine-3-carboxylates **2i-r** and **3i-r**

Compound	δ, ppm; *J*, Hz, in $CDCl_3$																
	Indeno moiety protons									4-Aryl group protons		Pyridine ring protons					NOE cross-peak NH–H(9)
	H-6	H-7	H-8	H-9	$J_{6,7}$	$J_{6,8}$	$J_{6,9}$	$J_{7,9}$	$J_{8,9}$	H-2',6'	H-3',5'	H-4	2-Me	3-COOEt		NH	
2i	7.84		8.43	7.85		2.2	0.0		8.04	7.11-7.28		4.85	2.44	1.07	3.98; 3.96	10.41	7.85*
2j	7.23		7.53	7.63		2.0	-0.1		7.81	7.50	8.13	4.94	2.47	1.05	3.96	10.39	7.63
2k*[2]	7.21		7.51	7.59		2.0	0.0		7.81	7.10	6.79	4.73	2.41	1.09	3.97	10.18	7.59
2l	7.32		7.67	7.54		1.9	0.2		7.82	7.10-7.26		4.79	2.43	1.06	3.97; 3.95	10.21	7.54
2m	7.34		7.61	7.55		1.9	0.1		8.12	7.22	7.30	4.79	2.43	1.07	3.96; 3.96	10.29	—*[3]
2n	7.34		7.69	7.57		1.9	0.1		7.88	7.49	8.13	4.94	2.46	1.05	3.95	10.27	7.57
2o	7.48		7.87	7.40		1.7	0.2		7.69	7.20	7.29	4.77	2.42	1.06	3.97; 3.96	10.25	7.40
2p*[2]	7.46		7.85	7.39		1.5	0.2		7.63	7.09	6.79	4.18	2.40	1.09	3.97	10.14	7.39
2r	7.47		7.87	7.40		1.7	0.2		7.57	7.15	7.43	4.76	2.42	1.07	3.97; 3.96	10.24	—*[3]
3i	7.86	8.39		8.47	8.1		0.1	2.1		7.11-7.27		4.83	2.44	1.07	3.98; 3.96	10.47	—*[3]
3j	7.25	7.41		7.72	7.6		0.1	1.8		7.50	8.13	4.95	2.46	1.05	3.96	10.28	7.79
3k*[2]	7.23	7.38		7.68	7.7		0.0	1.9		7.10	6.79	4.73	2.40	1.09	3.97	10.08	7.68
3l	7.17	7.54		7.84	7.6		0.1	1.7		7.09-7.26		4.79	2.48	1.07	3.97; 3.96	10.12	7.84
3m	7.17	7.55		7.84	8.2		0.1	1.8		7.22	7.30	4.79	2.42	1.07	3.97	10.16	7.84
3n	7.18	7.56		7.87	7.6		0.0	1.6		7.49	8.13	4.94	2.46	1.05	3.95	10.27	7.87
3o	7.02	7.74		8.01	7.5		0.2	1.5		7.21	7.29	4.78	2.42	1.07	3.97; 3.96	10.14	8.01
3p*[2]	7.06	7.73		7.99	7.4		0.0	1.5		7.09	6.79	4.72	2.39	1.09	3.97	10.05	7.99
3r	7.02	7.74		8.01	7.6		0.0	1.5		7.15	7.43	4.77	2.41	1.07	3.97; 3.96	10.14	8.01

* Determined at 313 K.

*[2] Chemical shifts: δ OCH_3 3.68 ppm.

*[3] Cross-peak not determined.

H-9 protons resulted in the undoubted identification of H-9 proton signals (Tables 2, 3). Final structure establishment of indenopyridine isomers was done taking into consideration both spin-spin coupling constants and multiplicity of other protons of the indeno moiety.

The substituent increments for the dihydroindenopyridine system were calculated in accordance with the formula

$$S_{ij} = \delta_i - \delta_{i_0},$$

where δ_i and δ_{i0} are the proton chemical shifts of the substituted and non-substituted indenopyridines. The calculated increments (Table 4) differ remarkably from such values for benzene and depend on the disposition of both substituent and proton affected. For example, increments calculated for *ortho* protons (H-6 and H-8) of 7-NO_2

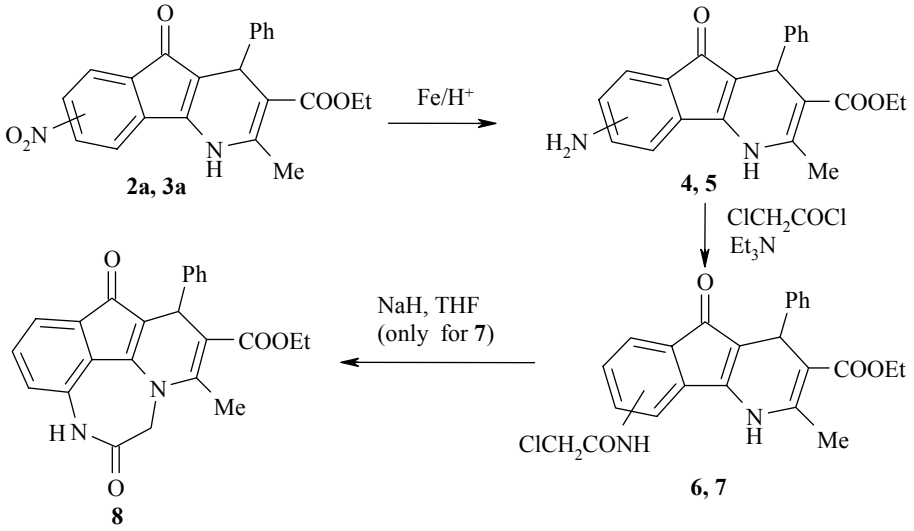

TABLE 4. Substituents Increments Calculated for Indeno Unit of 5-Oxo-1H-4,5-dihydroindeno[1,2-*b*]pyridine

Substituent		Increments S_{ij}				
Type	Position (j)	6	7	8	9	Benzene
NO_2	6	—	0.40	0.30	0.31	*o* 0.95
	7	0.66	—	1.03	0.28	*m* 0.26
	8	0.70	1.09	—	0.90	*p* 0.38
	9	0.45	0.33	0.65	—	
Cl	6	—	-0.01	0.05	0.03	*o* 0.03
	7	0.03	—	0.12	0.04	*m* -0.02
	8	0.06	0.08	-0.03	0.15	*p* -0.09
	9	0.08	0.08		—	
Br	6	—	0.16	-0.03	0.08	*o* 0.18
	7	0.16	-0.25	0.28	0.00	*m* -0.08
	8	-0.01	0.00	—	0.28	*p* -0.04
	8	0.12		0.18	—	
I	6	–	0.38	-0.21	0.10	*o* 0.39
	7	0.29	—	0.47	-0.17	*m* -0.21
	8	-0.16	0.44	—	0.42	*p* 0.00
	9					
NH_2	6	–	-0.70	-0.33	-0.74	*o* -0.75
	9	-0.71	-0.30	-0.63	–	*m* -0.25
						p -0.65

derivative **2i** are 0.66 and 1.03, respectively, while the corresponding value for *ortho* proton of benzene is 0.95. Obviously it is due to the smaller delocalization of C=C bonds caused by the influence of the pyridine moiety. The substituents in an indeno unit influence the values of spin-spin coupling constants of the neighboring protons; besides, *ortho* and *meta* couplings are more affected, resembling that of other aromatic systems [3].

The chemical transformations of 6- and 9-nitroindenopyridines **2a** and **3a** also confirms the structures determined. Both nitro compounds **2a** and **3a** can be reduced into amino derivatives **4**, **5** and converted into the corresponding chloroacetoamides **6**, **7**, but only the 9-substituted compound **7** is capable of intramolecular alkylation upon treatment with NaH/THF to afford 7a, 10-di-azacyclohepta[*def*]fluorene **8**.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AM-360 (360 MHz) in DMSO-d_6 solutions using TMS as internal standard. 2D proton NOE spectra were obtained using standard pulse sequences and data processing procedures: 1.5 kHz spectral width, 512 or 1024 data points, 128 or 256 t_1 increments and 3s relaxation delay. Simulations of indeno moiety proton shifts were calculated using the PANIC program. Melting points were determined on a Boetius table.

4-Aryl-5-oxo-4,5-dihydroindeno[1,2-*b*]pyridines 2,3 (General Method). Ethyl β-aminocrotonate (2.8 mmol) was added to a boiling solution of arylideneindane-1,3-dione **1** (2.5 mmol) in acetic acid (15 ml). The reaction mixture refluxed for 3-5 min was cooled and diluted with water. A red colored mixture of dihydroindenopyridine isomers was filtered off, dried, and chromatographed (Silasorb 30 μ, 50×460 mm, $CHCl_3$–EtOAc, 5:1, flow 30-35 ml/min for separation of 6- and 9-substituted pyridines **2a-h** and **3a-h** and 15-18 ml/min for 7- and 8-substituted compounds **2i-r** and **3i-r**). Yields and mp of the compounds obtained are summarized in Table 1, ^{1}H NMR data – in Tables 2 and 3.

6-Amino- and 9-Amino-3-ethoxycarbonyl-2-methyl-4-phenyl-5-oxo-1H-4,5-dihydroindeno-[1,2-*b*]pyridines (**4**, **5**). To a solution of nitro compound **2a** or **3a** (0.2 g, 0.51 mmol) in ethanol (30 ml) 0.4 g of Fe was added with stirring at 60°C. After addition of 15 ml of acetic acid, the stirring was continued for 3-4 h (TLC checking for residual nitro compound). The reaction mixture, diluted with water (50 ml) was extracted with chloroform (3×40 ml). The extract, washed with water (3×10 ml), saturated $NaHCO_3$ solution (2×3ml), and dried, was evaporated and the resulting residue was crystallized from ethanol. 6-Amino isomer **4** scinters at 122-124°C and melts at 233-235°C. 9-Amino isomer **5**, mp 200-202°C. See ^{1}H NMR data in Table 2.

6- and 9-(Chloroacetylamino)-3-ethoxycarbonyl-2-methyl-4-phenyl-5-oxo-4,5-dihydroindeno-pyridine (**6**, **7**). To a solution of amino compound **4** or **5** (0.16 g, 0.45 mmol) in chloroform (12 ml for **7** or 40 ml for **6**) triethylamine (0.07 ml) and chloroacetylchloride (0.04 ml) were added sequentially. The reaction mixture was stirred at room temperature for 4 h. The solvent was evaporated; the residue was triturated with water and the formed solid afforded chloroacetyl derivatives **6** and **7** after recrystallization from ethanol.

6-(Chloroacetylamino)indenopyridine 6. Mp 225–227°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.09 (3H, t, *J* = 7.1, $CH_2C\underline{H}_3$); 2.46 (3H, s, 2-CH_3); 3.99 (2H, q, *J* = 7.1, $C\underline{H}_2CH_3$); 4.39 (2H, s, CH_2Cl); 4.82 (1H, s, H-4); 7.06-7.39 (9H, m, aromatic protons); 8.54 (1H, s, H-1); 10.21 (1H, s, N<u>H</u>CO). Found, %: C 65.77; H 4.89; N 6.30. $C_{24}H_{21}ClN_2O_4$. Calculated, %: C 65.98; H 4.84; N 6.41.

9-(Chloroacetylamino)indenopyridine 7. Mp 112-114°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.06 (3H, t, *J* = 7.1, $CH_2C\underline{H}_3$); 2.40 (3H, s, 2-CH_3); 3.92 (2H, q, *J* = 7.1, $C\underline{H}_2CH_3$); 4.36 (2H, s, CH_2Cl); 4.72 (1H, s, H-4); 7.16 (5H, s, 4-C_6H_5); 7.36 (2H, m) and 8.11 (2H, m) protons at C(6)–C(9); 10.17 (1H, s, N<u>H</u>CO); 10.33 (1H, s, H-1). Found, %: C 65.77; H 4.89; N 6.30. $C_{24}H_{21}ClN_2O_4$. Calculated, %: C 65.98; H 4.84; N 6.41.

Ethyl 7-methyl-4,9-dioxo-5-phenyl-4,5,7a,8,9,10-hexahydro-7a,10-diaza-cyclo- hepta[*def*]fluorene-6-carboxylate (**8**). To a solution of 9-chloroacetylamino compound **7** (0.15 g, 0.34 mmol) in THF 0.02 g of NaH (0.5 mmol, 60 % suspension in oil) was added. The reaction mixture, stirred for 2 h, was diluted with 5 ml

of ethanol, evaporated, and treated with water. The solid filtered off and recrystallized from ethanol afforded 0.12 g (87 %) of compound **8**; mp 199-202°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.10 (3H, t, *J* = 7.1, $CH_2C\underline{H}_3$); 2.64 (3H, s, 7-CH_3); 4.00 (2H, q, *J* = 7.1, $C\underline{H}_2CH_3$); 4.51 (1H, d, *J* = 17.0) and 4.64 (1H, d, *J* = 17.0, 8-CH_2); 4.81 (1H, s, H-5); 7.04 (2H, m) and 7.26 (6H, m, aromatic protons). Found, %: C 71.63; H 5.16; N 7.07. $C_{24}H_{20}N_2O_4$. Calculated, %: C 71.99; H 5.03; N 7.00.

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