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CONDENSED PYRIDINE BASES. SYNTHESIS AND REACTIONS OF BENZOFURO[2,3-*c*]INDENO[2,1-*e*]-, BENZOTHIENO[2,3-*c*]INDENO[2,1-*e*]-, BENZOFURO-[3,2-*c*]INDENO[2,1-*e*]- AND THIENO[2,3:4',5']-THIENO[3,2-*c*]INDENO[2,1-*e*]PYRIDINES

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Condensation of hetarene carboxaldehydes with phthalide gave 2-(3-hydroxy-1-oxoinden-2-yl)benzo[b]furan and 2-(3-hydroxy-1-oxoinden-2-yl)-5-ethylthieno[2,3-b]thiophene. Starting from hetaryl acetic acids gave 3-(3-hydroxy-1-oxoinden-2-yl)benzo[b]furan and 3-(3-hydroxy-1-oxoinden-2-yl)benzo[b]thiophene. Acylation of 3-hydroxy-1-oxoinden-2-yl-substituted heterocycles using acetic anhydride in the presence of 70% $HClO_4$ leads to the formation of pentacyclic pyrilium salts. Pentacyclic indenopyridines are prepared by treating the pyrilium salts with ammonia. The reaction of the carbonyl group in the indenopyridines with hydroxylamine, hydrazine hydrate, and in reduction using $NaBH_4$ has been studied.

Keywords: benzo[*b*]thiophene, benzo[*b*]furan, indeno[2,1-*e*]pyridines, pyrilium salts, thieno[2,3-*b*]-thiophene, condensation.

The natural alkaloids harmine and harmane, which contain condensed indole and pyridine rings and ellipticine, which contains an indole and isoquinoline rings together with their synthetic analogs [1] are of interest from both a theoretical and a practical viewpoint.

By means of an acid catalyzed heterocyclization we were able to synthesize benzothieno- and benzofuro[2,3-*c*]pyrilium salts and the oxygen and sulphur analogs of β-carbolines [2, 3] based on them. Exchange of the indole nucleus for benzo[*b*]thiophene and benzo[*b*]furan in the tricyclic and tetracyclic analogs of the β-carbolines gives rise to a number of specific chemical and biological properties [4, 5]. Special interest in the study of biological activity can arise in the pentacyclic derivatives of benzothieno[2,3-*c*]- and benzofuro[2,3-*c*]pyridines containing an indene ring since it is known that a series of natural alkaloids contain an indenopyridine structural fragment [6-8]. We have based our synthesis of the pentacyclic pyridine bases on the use of a previously developed approach, according to which the corresponding pyrilium salt [9] is employed as the key intermediate. The latter were prepared by the acylation of the (3-hydroxy-1-oxoinden-2-yl)-substituted heterocycles **1-4**.

Compounds **1-4** were made using two methods. The first involves the condensation of the hetarene carboxaldehydes **5, 6** with phthalide **7** [10]. Using this method (Scheme 1), 2-formylbenzo[*b*]furan (**5**) and

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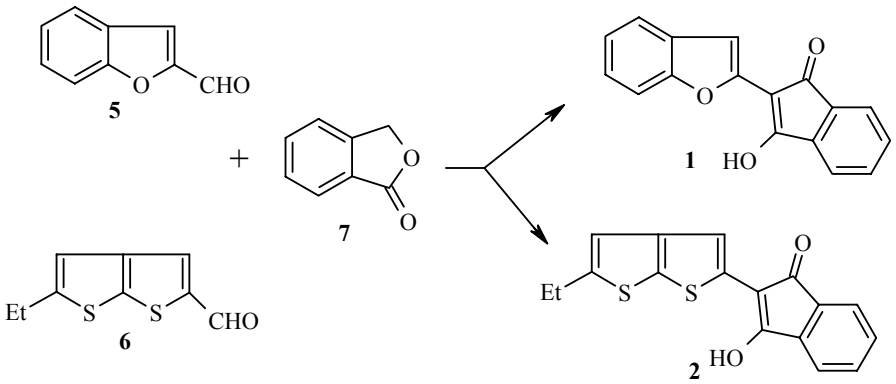
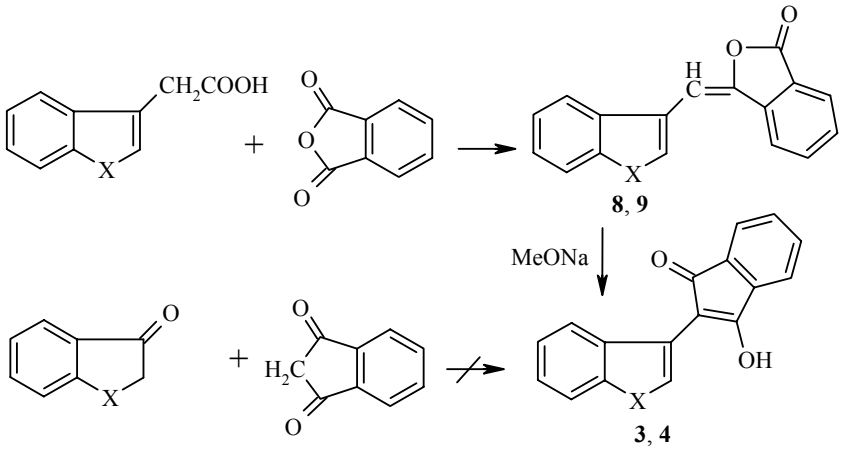
Scheme 1



5-ethyl-2-formylthieno[2,3-*b*]thiophene (**6**) gave good yields of 2-(3-hydroxy-1-oxoinden-2-yl)benzo[*b*]furan (**1**) and 5-ethyl-2-(3-hydroxy-1-oxoinden-2-yl)thieno[2,3-*b*]thiophene (**2**). The reaction occurs readily when refluxing a mixture of the starting materials in the presence of sodium methylate.

The synthesis of 3-(3-hydroxy-1-oxoinden-2-yl)benzo[*b*]furan (**3**) and -benzo[*b*]thiophene (**4**) were performed by successive reactions of the corresponding hetaryl acetic acids to 3-(benzo[*b*]furyl-3-methylene)phthalide (**8**) and 3-(benzo[*b*]thienyl-3-methylene)phthalide (**9**) and then their recyclization to the indenones **3, 4** with sodium methylate using the method in [11] (Scheme 2). Attempts to prepare compounds **3** and **4** by condensation of benzo[*b*]furan(2H)-3-one and benzo[*b*]thiophen(2H)-3-one with 1,3-indanedione were unsuccessful. In contrast to a similar reaction with dimedone [5], there occurs in this case a condensation involving the methylene group of the benzo[*b*]furan(2H)-3-one and benzo[*b*]thiophen(2H)-3-one and not the indanedione.

Scheme 2

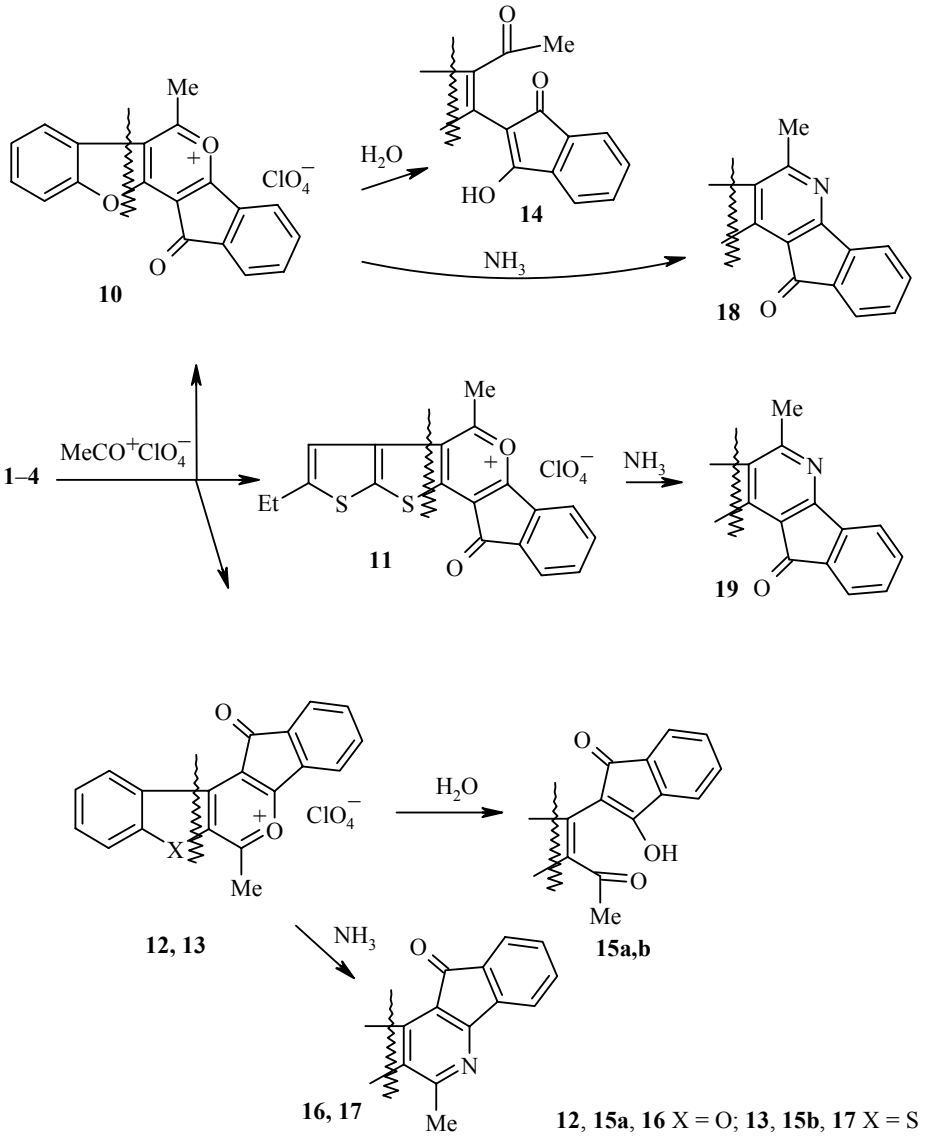


3, 8 X = O; **4, 9** X = S

The IR spectra of compounds **1-4** show a group of absorption bands for the C=O bond at 1680, 1660 cm^{-1} and C=C at 1640 and 1620 cm^{-1}. This shows that the indicated compounds exist in the enol form. The ^1H NMR spectra also only show bands for the absorption of the corresponding enol form.

Acylation of compounds **1-4** using acetic anhydride in the presence of 70% perchloric acid gives the indenopyrilium pentacyclic salts **10-13**, the IR spectra of which show absorption bands for the pyrilium and aromatic rings at 1505-1640 cm^{-1} together with absorption for a carbonyl group at 1710 cm^{-1} (Scheme 3).

Scheme 3



The presence of an oxo group in the pyrilium salts **10, 12, 13** destabilizes them, as a result of which they are readily hydrolyzed in aqueous alcoholic solutions to the corresponding 3(2)-acetyl-2(3)-(inden-2-yl)-benzo[*b*]furan or -benzo[*b*]thiophene (**14, 15**).

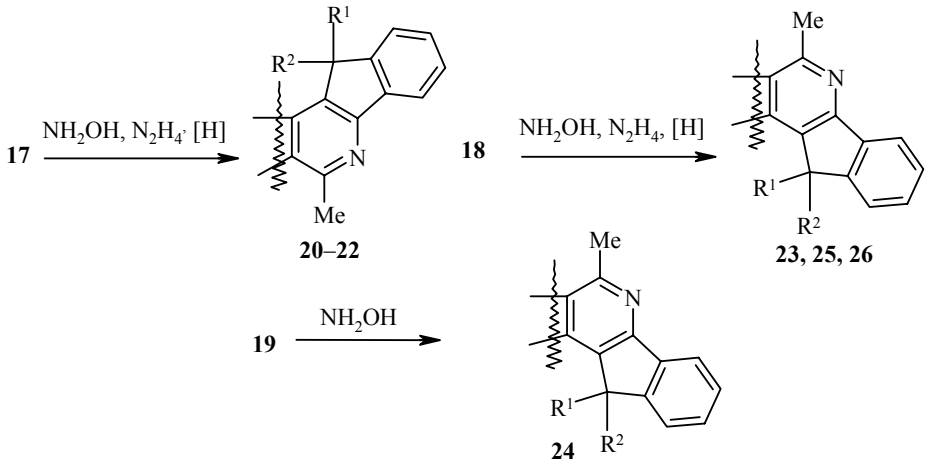
The ^{1}H NMR spectra of compounds **14, 15** show a double set of signals for the methyl groups corresponding to the enol and keto form. According to the ratio of integrated intensities of the methyl group signals and also the signal for the CH proton of the keto form (5.92 ppm) it is evident that compounds **14, 15** contain up to 30% of the keto form.

The target heteroindeno[2,1-*e*]pyridines **16-19** were prepared by treating the pyrilium salts **10-13** or the tricarbonyl compounds **14, 15** with aqueous alcoholic ammonia solution.

Some features of the ^{1}H NMR spectra of the pyrilium salts **12, 13** and the corresponding pyridine bases **16, 17** should be noted. The observed low field shift of the 11-H aromatic proton signal to 9.4 ppm, as in the case of an analogously constructed tetracyclic pyridine base [5], is related to its structural characteristics. Calculation of compounds **16, 17** using the AM1 (MOPAC 6.0) method shows that the distance between H-11 and the C=O group is 2.19 Å for X = O and 2.12 Å for X = S. Because it is placed at a small distance from the CO group and is fixed by the overall rigidity of the molecule the H-11 proton must experience the marked low field shift *via* magnetic anisotropy. A similar effect is absent in the ^{1}H NMR spectra of compounds **10, 18**, isomers of compounds **12, 16**. Calculation shows the presence of significant steric hindrances in the starting molecules **16, 17**, in particular towards the products of reaction at the carbonyl group. On this basis it can be proposed that the reactivity of the carbonyl group in the indenopyridines **16, 17** will be lowered [5].

With the aim of checking these ideas we carried out reactions at the oxo group of 6-methyl-12-oxobenzothieno[2,3-*c*]indeno[2,1-*e*]pyridine (**17**) using hydroxylamine, hydrazine hydrate, and sodium borohydride (Scheme 4).

Scheme 4



20, **23**, **24** $R^1 - R^2$ = NOH; **21** $R^1 = R^2$ = H, **22**, **26** R^1 = OH, R^2 = H, **25** R^1–R^2 = N–NH_2

When refluxing compound **17** with hydroxylamine hydrochloride in acetic acid for 20 h, the starting indenopyridine **17** is always present in the reaction mixture. The yield of the oxime **20** does not exceed 50%. The indenopyridine does not react with hydrazine hydrate in alcohol and acetic acid even after refluxing for 20 h. Prolonged heating of the indenopyridine **17** with hydrazine hydrate in ethylene glycol leads to reduction of the C=O group to give the 6-methyl-(12H)-benzothieno[2,3-*c*]indeno[2,1-*e*]pyridine (**21**). Reduction of **17** with sodium borohydride gives a high yield of the corresponding hydroxy derivative **22**. In contrast, 6-methyl-12-oxobenzofuro[3,2-*c*]indeno[2,1-*e*]pyridine (**18**) and 8-ethyl-6-methylthieno[2,3:4',5']thieno[3,2-*c*]indeno[2,1-*e*]-pyridine (**19**) react with hydroxylamine after 1 h under these conditions to give the corresponding oximes **23, 24**. Heating the indenopyridine **18** with hydrazine hydrate in alcohol gave the hydrazone **25**. Attention was paid to a number of features of their ^{1}H NMR spectra. In place of the expected single signal to low field for the amino group there were observed two exchangeable signals of intensity 1H at 8.60 and 8.80 ppm which were markedly different in half width. With increase in temperature (18-50°C) the broadened signal at 8.60 ppm reacted more strongly and shifted by 0.15 ppm to high field whereas the signal at 8.80 ppm shifted by 0.05 ppm. While there is good agreement in the integrated intensities of the aliphatic and aromatic parts of the spectrum, the aromatic region shows multiplets at 8.0 and 8.3 ppm for 0.5H which are assigned to the H-1 proton and are due to the existence of a mixture of geometric isomers which differ in the position of the amino group relative to

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Empirical formula	Found, % / Calculated, %					mp, °C	Yield, %
		C	H	Cl	N	S		
1	$C_{17}H_{10}O_3$	77.78 / 77.86	3.94 / 3.84	—	—	—	174	71
2	$C_{17}H_{12}O_2S_2$	65.55 / 65.36	4.04 / 3.87	—	—	20.24 / 20.53	200	41
3	$C_{17}H_{10}O_3$	77.31 / 77.86	3.48 / 3.84	—	—	—	140	80
4	$C_{17}H_{10}O_2S$	73.67 / 73.36	3.35 / 3.62	—	—	11.60 / 11.52	166	77
8	$C_{17}H_{10}O_3$	77.62 / 77.86	4.15 / 3.84	—	—	—	272	38
9	$C_{17}H_{10}O_2S$	73.49 / 73.36	3.74 / 3.62	—	—	11.15 / 11.52	272	40
10	$C_{19}H_{11}ClO_7$	58.62 / 59.01	3.00 / 2.87	9.34 / 9.14	—	—	260	84
11	$C_{19}H_{13}ClO_6S_2$	52.48 / 52.24	3.17 / 2.97	8.39 / 8.12	—	14.67 / 14.64	220	83
12	$C_{19}H_{11}ClO_7$	59.26 / 59.01	2.27 / 2.87	9.41 / 9.14	—	—	235	92
13	$C_{19}H_{11}ClO_6S$	56.81 / 56.65	2.84 / 2.75	8.47 / 8.80	—	7.74 / 7.94	223	94
14	$C_{19}H_{12}O_4$	75.78 / 74.99	3.76 / 3.97	—	—	—	190	74
15a	$C_{19}H_{12}O_4$	74.80 / 74.99	3.81 / 3.97	—	—	—	167	54
15b	$C_{19}H_{12}O_3S$	71.58 / 71.23	3.81 / 3.78	—	—	10.28 / 10.01	178	63
16	$C_{19}H_{11}NO_2$	80.15 / 79.99	4.02 / 3.89	—	4.67 / 4.91	—	224	90
17	$C_{19}H_{11}NO_2S$	75.80 / 75.72	3.41 / 3.68	—	4.55 / 4.65	10.88 / 10.64	200	91
18	$C_{19}H_{11}NO_2$	79.86 / 79.99	3.53 / 3.89	—	4.67 / 4.91	—	280	89
19	$C_{19}H_{13}NOS_2$	68.55 / 68.03	4.06 / 3.91	—	4.34 / 4.18	19.04 / 19.12	218	86
20	$C_{19}H_{12}N_2OS$	72.31 / 72.13	3.97 / 3.82	—	9.02 / 8.85	10.37 / 10.13	307	64
21	$C_{19}H_{13}NS$	79.55 / 79.41	4.25 / 4.56	—	5.02 / 4.87	11.34 / 11.16	185	83
22	$C_{19}H_{13}NOS$	75.28 / 75.22	4.43 / 4.32	—	4.51 / 4.62	10.47 / 10.57	190	85
23	$C_{19}H_{12}N_2O_2$	76.18 / 75.99	4.23 / 4.03	—	9.51 / 9.33	—	330	71
24	$C_{19}H_{14}N_2OS_2$	84.35 / 65.12	4.20 / 4.03	—	7.82 / 7.99	18.47 / 18.30	138	88
25	$C_{19}H_{13}N_3O$	76.38 / 76.24	4.21 / 4.38	—	14.12 / 14.04	—	243	70
26	$C_{19}H_{13}NO_2$	79.55 / 79.43	4.25 / 4.56	—	5.05 / 4.87	—	190	50

the C=N bond [12]. In addition, in the *anti* isomer (NH_2 8.8, H-1 8.0 ppm) the protons of the amino group can interact with the electron pair of the benzofuran oxygen atom to form an intramolecular hydrogen bond. The calculated distances between these atoms are fully in agreement with this possibility. The temperature experiment and the absence of spin-spin coupling between the protons in the NH_2 in a 2M COSY experiment confirm our interpretation.

Reduction of the indenopyridine **18** with sodium borohydride gives 12-hydroxybenzofuro-6-methyl-[3,2-*c*]indeno[2,1-*e*]pyridine (**26**). Attempts to carry out a Beckmann reaction with the oximes **23, 24** in PPA at 140°C gave the starting oximes.

TABLE 2. Spectroscopic Characteristics of Compounds **1-4, 8-26**

Com-pound	IR spectrum, ν, cm^{-1}, C=O and C=C	^{1}H NMR spectrum, δ, ppm (*J*, Hz)	
		H arom and other protons	CH_3 (3H, s), (C_2H_5) (3H, t, 2H, q)
1	2	3	4
1	1680, 1640, 1620, 1530	7.10 (1H, s, H-3'); 7.16-7.23 (2H, m, H-5',6'); 7.40-7.61 (6H, m)	—
2	1660, 1650, 1625, 1570	6.80 (1H, s, H-4'); 7.00 (1H, s, H-3'); 7.45-7.62 (4H, m)	(1.34, 2.90, *J* = 7.0)
3	1680, 1550	7.32-7.41 (2H, m, H-5' and H-6'); 7.52 (1H, s, H-2'); 7.55-7.78 (6H, m)	—
4	1710-1640, 1580	7.32-7.41 (2H, m, H-5',6'); 7.41-7.53 (3H, m, H-4',5,6); 7.61 (1H, s, H-2'); 7.71-8.08 (3H, m, H-4,7',7)	—
8	1770, 1700, 1610, 1570	7.12 (1H, s, H-2'); 7.46-8.07 (7H, m); 8.14 (1H, d, *J* = 8.0, H-4); 8.27 (1H, s, CH=)	—
9	1750, 1640, 1450	7.37 (1H, s, H-2'); 7.46-8.07 (7H, m); 8.29 (1H, s, CH=); 8.33 (1H, d, *J* = 8.0, H-4)	—
10	1710, 1580, 1500, 1450	7.30-7.78 (7H, m); 8.10 (1H, d, *J* = 8.0, H-1)	2.98
11	1710, 1610, 1580	7.36 (1H, t, *J* = 7.9, 3-H); 7.39 (1H, s, H-7); 7.52-7.62 (2H, m, H-2,4); 7.70 (1H, d, *J* = 8.0, H-1)	2.98, (1.36, 3.00, *J* = 7.5)
12	1715, 1610, 1580	7.20-7.60 (6H, m); 8.05 (1H, d, *J* = 8.0, H-1); 9.30 (1H, d, *J* = 8.0, H-11)	2.75
13	1715, 1610, 1580	7.40-7.70 (6H, m); 8.05 (1H, d, *J* = 8.0, H-1); 9.40 (1H, d, *J* = 8.0, H-11)	2.70
14	1700, 1690, 1650, 1615	5.51 (HO- enol in exchange with H_2O); 5.76 (1H, CH enol form); 7.40-8.20 (8H, m)	2.30 (keto form); 2.40 (enol form)
15b	1700, 1690, 1650, 1615	5.20 (HO-enol in exchange with H_2O); 5.96 (1H, CH enol form); 7.40-8.20 (8H, m)	2.41 (keto form); 2.43 (enol form)
16	1710, 1605, 1590, 1560	7.20-7.60 (6H, m); 8.0 (1H, d, *J* = 8.0, H-1); 9.30 (1H, d, *J* = 8.0, H-11)	2.75
17	1700, 1605-1560	7.40-7.70 (6H, m); 8.05 (1H, d, *J* = 8.0, H-1); 9.40 (1H, d, *J* = 8.0, H-11)	2.70
18	1710, 1635, 1605, 1585, 1570	7.40-7.61 (4H, m, H-2,3,8,9); 7.76 (1H, *J* = 8.0, H-4); 7.94 (1H, *J* = 8.0, H-7); 8.09 (1H, *J* = 8.0, H-10); 8.39 (1H, d, *J* = 8.0, H-1)	2.98
19	1705, 1610, 1575, 1550	7.36 (1H, t, *J* = 7.9, H-3); 7.39 (1H, s, H-7); 7.52–7.62 (2H, m, H-2,4); 7.71 (1H, d, *J* = 8.0, H-1)	2.98 (1.36, 3.00, *J* = 7.5)
20	1660 (C=NOH), 1615, 1590	7.42-7.80 (4H, m, H-2,3,9,10); 8.17 (1H, d, *J* = 8.0, H-8); 8.43 (1H, d, *J* = 8.0, H-4); 8.50 (1H, d, *J* = 8.0, H-1); 9.83 (1H, d, *J* = 8.0, H-11); 13.1 (1H, s, HON=)	2.83
21	1620, 1590, 1570	4.19 (2H, s, 12-CH_2); 7.42–7.64 (5H, m, H-2,3,4,9,10); 7.65 (1H, d, *J* = 7.8, H-8); 8.18 (1H, d, *J* = 7.8, H-11); 8.24 (1H, d, *J* = 7.8, H-1)	2.87
22	3400 (C–OH), 1620, 1585, 1550	3.40 (OH in exchange with H_2O); 6.00 (1H, s, C<u>H</u>–OH); 7.15-8.20 (7H, m); 8.91 (1H, d, *J* = 8.0, H-1)	2.83

TABLE 2 (continued)

1	2	3	4
23	1670 (C=NOH), 1620, 1585, 1550	7.40-7.60 (4H, m, H-2,3,8,9); 7.78 (1H, d, *J* = 8.0, H-4); 7.90 (1H, d, *J* = 7.8, H-7); 8.10 (1H, d, *J* = 7.8, H-10); 8.38 (1H, d, *J* = 8.0, H-1); 13.1 (1H, s, HON=)	2.99
24	1670 (C=NOH), 1610, 1599, 1550	7.40 (1H, s, H-7); 7.40-7.53 (2H, m, H-2,3); 7.82 (1H, d, *J* = 8.0, H-4); 8.27 (1H, d, *J* = 8.0, H-1); 12.91 (1H, s, HON=)	2.96 (1.25, 3.25, *J* = 7.5)
25	3350 (NH_2), 1650, 1620, 1585, 1550	7.45-7.65 (5H, m, H-2,3,4,8,9); 7.78 (1H, d, *J* = 8.0, H-7); 8.13 (1H, d, *J* = 8.0, H-1); *syn* isomer: 8.30 (1H, d, *J* = 8.0, H-1); 8.60 (2H, s, NH_2); *anti* isomer: 8.00 (1H, d, *J* = 8.0, H-1); 8.80 (2H, s, NH_2)	3.04
26	3400 (OH), 1615, 1590, 1550	3.40 (OH in exchange with H_2O); 6.00 (1H, s, CH–O); 7.40-8.20 (8H, m)	2.99

EXPERIMENTAL

IR spectra were taken on a UR-20 instrument using KBr and ^{1}H NMR spectra on a Gemini-200 instrument (200 MHz) with TMS internal standard and DMSO-d_6 solvent. Elemental analytical data for the compounds synthesized agreed with those calculated. The characteristics of the compounds prepared are given in Tables 1 and 2.

2-(3-Hydroxy-1-oxoinden-2-yl)benzo[*b*]furan (1) and 5-Ethyl-2-(3-hydroxy-1-oxoinden-2-yl)thieno-[2,3-*b*]thiophene (2) (General Method). A mixture of 2-formylbenzo[*b*]furan **5** or 2-formyl-5-ethylthieno-[2,3-b]thiophene (**6**) (0.1 mol), phthalide **7** (14.7 g, 0.11 mol), sodium methylate (prepared from sodium (7 g, 0.3 mol) and methanol (100 ml)), and ethyl acetate (8.8 ml) was refluxed for 2 h. Water (500 ml) was added to the solution which was then filtered and acidified with hydrochloric acid to pH 1.0. The precipitate was filtered off and recrystallized from acetonitrile.

3-(3'-Benzo[*b*]furyl-3-methylene)phthalide (8) and 3-(Benzo[*b*]thienyl-3-methylene)phthalide (9). Triethylamine (10.5 ml, 0.075 mol) was added slowly to a mixture of the benzofuran-3- or benzothiophen-3-acetic acids (0.025 mol) and phthalic anhydride (3.75 g, 0.025 mol) in acetic anhydride (16 ml) and the mixture was heated for 1 h at 100°C. The reaction product was cooled and poured into a mixture of ice (30 g) and hydrochloric acid (10 ml). The precipitate was filtered off and crystallized from acetonitrile.

3-(3-Hydroxy-1-oxoinden-2-yl)benzo[*b*]furan (3) and 3-(3-Hydroxy-1-oxoinden-2-yl)benzo-[*b*]thiophene (4) (General Method). A mixture of compound **8** or **9** (0.1 mol) and sodium methylate (prepared from sodium (3.7 g, 0.16 mol) and methanol (100 ml)) was refluxed for 2 h. Methanol was evaporated off in vacuo and the residue was dissolved in water and acidified to pH 1.0. The product was filtered off, washed with water, and crystallized from acetonitrile.

6-Methyl-12-oxobenzofuro[3,2-*c*]indeno[2,1-*e*]pyrilium (10), 8-Ethyl-6-methylthieno[2,3:4',5']-thieno[3,2-*c*]indeno[2,1-*e*]pyrilium (11), and 6-Methyl-12-oxobenzofuro(benzothieno)[2,3-*c*]indeno[2,1-*e*]-pyrilium (12, 13) Perchlorate Salts (General Method). Perchloric acid (0.5 ml, 70%) was added to a suspension of the hetaryliden-1-one **1-4** (0.005 mol) in acetic anhydride (5 ml). The mixture became warm and the starting compounds **1-4** dissolved. The reaction mixture was held for 1 h at room temperature and the precipitated pyrilium salt was filtered off, washed with isopropanol and ether, and crystallized from acetic acid.

3-Acetyl-2-(3-hydroxy-1-oxoinden-2-yl)benzo[*b*]furan (14), 2-Acetyl-3-(3-hydroxy-1-oxoinden-2-yl)benzo[*b*]furan (15a), and 2-Acetyl-3-(3-hydroxy-1-oxoinden-2-yl)benzo[*b*]thiophene (15b) (General Method). A suspension of the corresponding pyrilium salt **10, 12, 13** (0.005 mol) in 70% aqueous alcohol

(50 ml) was heated to the salt dissolving. It was filtered and the product was precipitated with water. For purification, the product was dissolved in a 5% solution of $NaHCO_3$, filtered, and precipitated using hydrochloric acid. It was crystallized from alcohol.

Indenopyridines 16-19 (General Method). Concentrated ammonia solution (10 ml) was added to a suspension of the perchlorates **10-13** (0.005 mol) in methanol (20 ml). The mixture was refluxed for 0.5 h, cooled, water (20 ml) was added, and the precipitate was filtered off and crystallized from DMF.

12-Hydroximino-6-methylbenzothieno[2,3-*c*]indeno[2,1-*e*]pyridine (20), 12-Hydroximino-6-methylbenzofuro[3,2-*c*]indeno[2,1-*e*]pyridine (23), and 8-Ethyl-11-hydroximino-6-methylthieno-[2,3:4',5']thieno[3,2-*c*]indeno[2,1-*e*]pyridine (24) (General Method). A mixture of the indenopyridine **17, 18,** or **19** (0.005 mol) and hydroxylamine hydrochloride (1.4 g, 0.02 mol) in acetic acid (40 ml) was refluxed for 1 h for compounds **18** and **19** or for 20 h for compound **17**. Sodium acetate (1.64 g, 0.02 mol) was added to the reaction mixture and heating was continued for a further 0.5 h. The product was cooled and the precipitate was filtered off, washed with water, and crystallized from DMF.

6-Methyl-(12H)-benzothieno[2,3-*c*]indeno[2,1-*e*]pyridine (21) (General Method). Hydrazine hydrate (5 ml, 85%) was added to a suspension of the indenopyridine **17** (1.5 g, 0.005 mol) in ethylene glycol (40 ml) and the mixture was refluxed for 15 h. After cooling, the precipitate was filtered off, washed with water, and crystallized from alcohol.

6-Methyl-12-oxobenzofuro[3,2-*c*]indeno[2,1-*e*]pyridine Hydrazone (25). Hydrazine hydrate (5 ml, 85%) was added to a suspension of the indenopyridine **18** (1.43 g, 0.005 mol) in methanol (100 ml) and the mixture was refluxed for 3 h. After cooling, the precipitate was filtered off, washed with water, and crystallized from DMSO.

12-Hydroxy-6-methyl-(12H)-benzothieno[2,3-*c*]indeno[2,1-*e*]pyridine (22) and 12-Hydroxy-6-methyl-(12H)-benzofuro[3,2-*c*]indeno[2,1-*e*]pyridine (26) (General Method). Sodium borohydride (0.19 g, 0.005 mol) was added in small portions to a suspension of the indenopyridine **17** or **18** (1.50 g, 0.005 mol) in methanol (20 ml). The mixture obtained was stirred for 3 h and left overnight. It was diluted with water (20 ml) and the precipitate formed was filtered off, washed with water, and crystallized from acetone.

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