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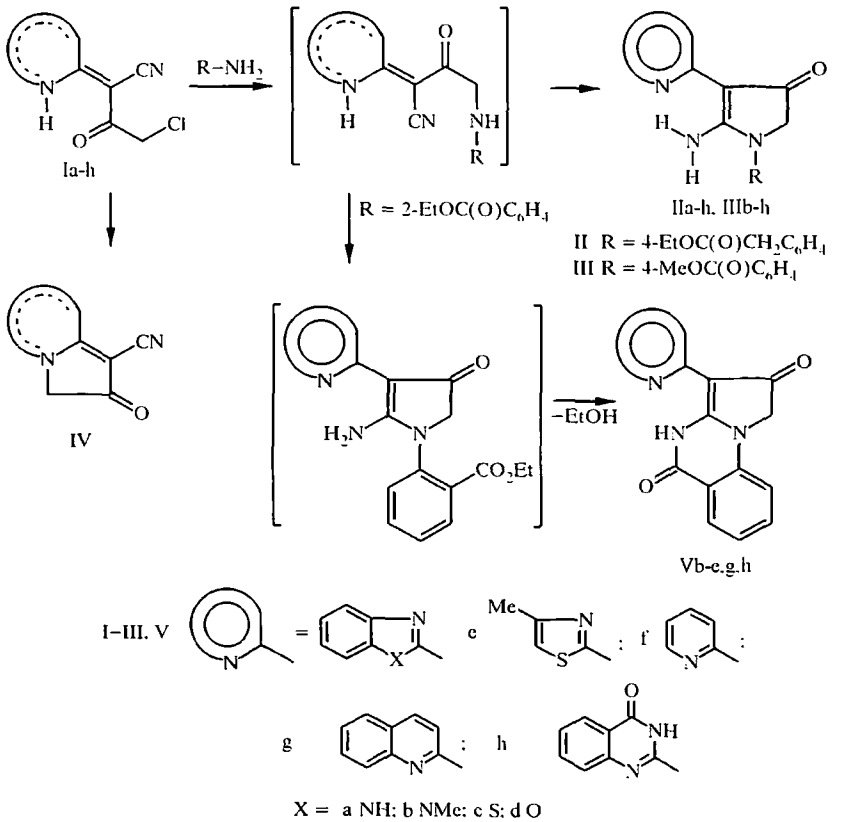
INTERACTION OF 2-(2-AZAHETARYL)-3-OXO-4-CHLOROBUTANE NITRILES WITH ESTERS OF AROMATIC AMINO ACIDS

E. V. Resnyanskaya, T. V. Shokol, Yu. M. Volovenko, and A. V. Tverdokhlebov

The reaction of 2-(2-azahetaryl)-3-oxo-4-chlorobutane nitriles with esters of aromatic acids was studied. A series of 1H,4H-3-(2-azahetaryl)pyrrolo[1,2-a]quinazoline-2,5-diones and 1-aryl-2-amino-3-(2-azahetaryl)-4-(5H)-oxopyrroles was obtained. The reaction of the latter with hydrazine and acetic anhydride was investigated.

The reaction of the 2-(2-azahetaryl)-3-oxo-4-chlorobutane nitriles Ia-c,e,h [1-3] with primary aliphatic amines was studied previously [4, 5]. It was shown [5] that it can proceed in two directions: the alkylation of the amine with the subsequent addition of the secondary amino group to the nitrile with the formation of the 1-alkyl-2-



Taras Shevchenko Kiev University, Kiev 252033, Ukraine. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1412-1418, October, 1999. Original article submitted June 4, 1998.

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amino-3-(2-azahetaryl)-4(5H)-oxopyrroles II, III (R = alkyl), or the intramolecular alkylation with the formation of pyrrolo[1,2-a]azaheterocycles IV.

The reaction of the compounds I with aromatic amines was studied less [6]. The majority of the 1-aryl derivatives of aminooxopyrroles II, III (R = aryl), described in the literature, were synthesized by an alternative method – the acylation of (het)arylacetonitriles with esters of N-aryl-α-amino acids [7-11]. However, such a path does not allow to prepare aminooxopyrroles II, III with the functionally substituted 1-aryl group. The given work studies the reaction of the compounds Ia-h with esters of aromatic amino acids, and also investigates some properties of the aminooxopyrroles II, III obtained.

The reaction of the halonitriles Ia-h with ethyl 4-aminophenylacetate proceeds smoothly in *n*-butanol in the presence of the equivalent amount of N,N-dimethylaniline. This results in the formation of the 1-[4-(ethoxycarbonylmethyl)phenyl]-2-amino-3-(2-azahetaryl)-4-oxopyrroles IIa-h with yields of 60-85%. Under the same conditions, the reaction of the compounds Ib-h with methyl 4-aminobenzoate proceeds analogously and leads to the 1-(4-methoxycarbonylphenyl)-2-amino-3-(2-azahetaryl)-2(5H)-oxopyrroles IIIb-h. Utilization of bases stronger than N,N-dimethylaniline favors intramolecular alkylation and the formation of the compounds IV.

The PMR spectra (DMSO-d_6) of the compounds II and III contain the two-proton singlet of the pyrrole ring methylene group at 4.2-4.4 ppm. Signals of the primary amino group protons are observed at 8.0-10.5 ppm as two single-proton singlets, owing to their nonequivalence, or a broad two-proton signal due to rapid exchange. It is interesting that the chemical shifts of the 3'- and 5'-protons of the pyridyl substituent in the PMR spectra of the 3-(2-pyridyl) derivatives IIf, IIIf differ by 1.5 ppm. Thus, the 5'-H signal is observed at 6.98 ppm (dd, J = 8 Hz, J = 6 Hz) whereas the 3'-H signal occurs at 8.50 ppm (d, J = 8 Hz). The latter even resonates at lower field than the 6'-H (8.35 ppm , d, J = 6 Hz). Such a high chemical shift for the 3'-H is explained by the deshielding action of the carbonyl group in the pyrrole ring, which indicates the coplanarity of the pyrrole and pyridine rings in the compounds IIf and IIIf. An analogous effect is noted for the 3'-H in the quinolyl derivatives IIg and IIIg. The signals of the remaining protons of the aminooxypyrroles II and III are observed in their characteristic regions.

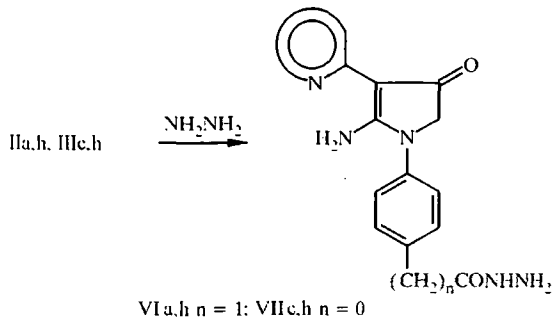
The IR spectra of the amino derivatives IIa-h, IIIb-h contain two strong absorption bands of the stretching vibrations of the primary amino group at 3340-3300 cm^{-1} and 3150-3100 cm^{-1}, as well as a strong absorption band of the stretching vibrations of the ester CO group at 1735-1710 cm^{-1}. The stretching vibrations of the carbonyl group of the pyrrole ring are not observed in the IR spectra of the compounds IIa-h, IIIb-h, which conforms with known data [3, 4, 12].

The reaction of the halogenonitriles Ia-h with ethyl anthranilate proceeds differently. In this case, the reaction does not stop at the stage of formation of the aminooxypyrrole, but is accompanied by intramolecular acylation of the primary amino group by the ester resulting in the formation of the 1H,4H-3-(2-azahetaryl)pyrrolo[1,2-*a*]quinazoline-2,5-diones Va-h. The preparation of the benzimidazolyl and pyridyl derivatives Va,f by such a method was described previously [6]. We managed to extend the range of the 2-(2-azahetaryl)-3-oxo-4-chlorobutane nitriles I introduced into the reaction, and to obtain the new derivatives of this series Vb-e,g,h.

The PMR spectra of the compounds Vb-e,g,h, measured in DMSO-d_6, contain the two-proton singlet of the CH_2 group at 4.5-4.7 ppm. If the PMR spectra of these compounds are measured in CF_3COOD, then the signal of the methylene group is slowly reduced, completely disappearing after 1-2 h. This indicates the deuteration of the compounds Vb-e,g,h at the position 1, which evidently proceeds *via* the enol form.

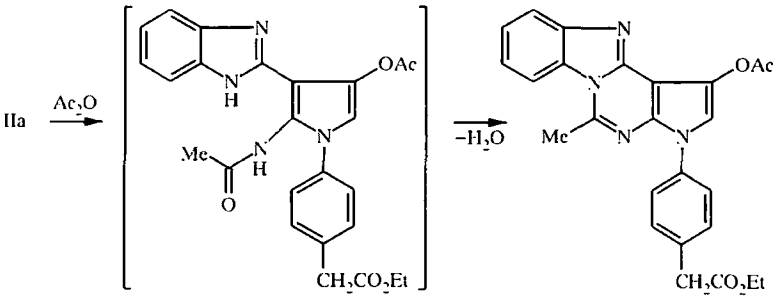
The IR spectra of the pyrrolo[1,2-*a*]quinazolines VIb-e,g,h contain two strong bands of the carbonyl groups stretching vibrations at 1720-1700 cm^{-1} (2-CO) and 1670-1650 cm^{-1} (5-CO). The stretching vibrations of the NH bond are observed as weak bands at 3400-3200 cm^{-1}.

We studied the reaction of the esters IIa,h, IIIc,h with hydrazine hydrate. The reaction with excess hydrazine hydrate proceeds selectively at the ester group, not affecting the carbonyl group in the pyrrole ring, with the formation of the hydrazides VIa,h and VIIc,h. Their PMR spectra, measured in DMSO-d_6, lack the signals of the alkoxyl groups, and contain the averaged signal of the hydrazine fragment protons in the form of a broad three-proton singlet at 4.2-5.0 ppm. The remaining protons resonate in the same regions as in the initial esters IIa,h, IIIc,h. The IR spectra of the hydrazides VIa,h, VIIc,h contain strong absorption at 3400-3100 cm^{-1}, determined by the stretching vibrations of the NH bonds.



VIa,h n = 1; VIIc,h n = 0

Reaction of compound IIa with acetic anhydride does not stop at the stage of the diacetyl derivative formation, but is accompanied by cyclization leading to 1-acetoxy-5-methyl-3-[4-(ethoxycarbonylmethyl)phenyl]-pyrrolo[3',2':5,6]pyrimido[3,4-*a*]benzimidazole (VIIIa), which conforms with known data [12].



VIIIa

The PMR spectrum of compound VIIIa, measured in DMSO-d_6, lacks signals of the available protons and the two-proton singlet of the methylene group of the pyrrole ring. Two three-proton signals of methyl groups are observed at 2.45 ppm ($OCOCH_3$) and 3.14 ppm ($5\text{-}CH_3$), and a one-proton singlet of the 2-H is observed at 7.70 ppm. The 0.7 ppm low-field shift of the proton at $C_{(7)}$ should be noted in relation to its position in compound IIa (from 7.56 ppm to 8.21 ppm) as the internal proton of the angular heterocyclic system.

The IR spectrum of compound VIIIa lacks appreciable absorption in the region above 3050 cm^{-1}. Two bands of the stretching vibrations of the the ester C=O groups are observed (1750 cm^{-1} and 1730 cm^{-1}).

EXPERIMENTAL

The monitoring of the course of all reactions was accomplished utilizing TLC on plates of Silufol UV-254 in the 9:1 system of chloroform–methanol. The IR spectra were recorded on the Pye Unicam SP 3-300 instrument using KBr tablets. The PMR spectra were measured in DMSO-d_6 or CF_3CO_2D on the Bruker WP-100 SY instrument with the working frequency of 100 MHz.

2-(2-Benzoxazolyl)-3-oxo-4-chlorobutane Nitrile (Id). Chloroacetyl chloride (3.95 g, 0.035 mol) was added slowly with stirring to the solution of 2-benzoxazolylacetonitrile (4.74 g, 0.03 mol) and triethylamine (3.54 g, 0.035 mol) in 50 ml of dry dioxane at the temperature of 50-60°C, whereby strong warming of the mixture was observed. The resulting suspension was heated for 2 h on a water bath. After the cooling of the mixture, the precipitated residue was filtered off and washed with dioxane and then water. Recrystallization was performed from acetonitrile. The yield of the nitrile Id is 75%.

3-(2-Azahetaryl)-2-amino-4(5H)-oxo-1-(4-ethoxycarbonylmethylphenyl)pyrroles (IIa-h). The suspension of 2-(2-azahetaryl)-3-oxo-4-chlorobutane nitrile (I) (3 mmol), ethyl 4-aminophenylacetate (0.63 g, 3.5 mmol), and N,N-dimethylaniline (0.42 g, 3.5 mmol) in *n*-butanol (10 ml) was boiled for 4-6 h until the

TABLE 1. Characteristics of the Compounds Id, IIa-h, IIIb-h, Vb-e,g,h, VIa,h, VIIc,h, and VIIIa

Compound	Empirical formula	Found, % / Calculated, %		mp, °C	Solvent for recrystallization	Yield, %
		N	S			
Id*	$C_{11}H_7ClN_2O_2$	11.89 / 11.94		242	MeCN	75
IIa	$C_{21}H_{20}N_4O_3$	15.15 / 14.89		217	MeCN	81
IIb	$C_{22}H_{22}N_4O_3$	14.30 / 14.35		205	MeCN	74
IIc	$C_{21}H_{19}N_3O_3S$	10.85 / 10.68	8.34 / 8.14	209	MeCN	72
IId	$C_{21}H_{19}N_3O_4$	11.01 / 11.14		215	MeCN	79
IIe	$C_{18}H_{19}N_3O_3S$	11.97 / 11.76	9.20 / 8.96	170	MeCN	84
IIf	$C_{19}H_{19}N_3O_3$	12.56 / 12.46		159	MeCN	58
IIg	$C_{23}H_{21}N_3O_3$	10.89 / 10.85		198	MeCN	56
IIh	$C_{22}H_{20}N_4O_4$	14.09 / 13.86		225	MeCN	80
IIIb	$C_{20}H_{18}N_4O_3$	15.23 / 15.47		>300	*n*-Butanol	75
IIIc	$C_{19}H_{15}N_3O_3S$	11.77 / 11.51	8.73 / 8.77	279	*n*-Butanol	66
IIId	$C_{19}H_{15}N_3O_4$	12.13 / 12.03		>300	DMF	54
IIIe	$C_{16}H_{15}N_3O_3S$	12.96 / 12.76	9.91 / 9.73	288	*n*-Butanol	67
IIIf	$C_{17}H_{15}N_3O_3$	13.76 / 13.59		276	Dioxane	60
IIIg	$C_{21}H_{17}N_3O_3$	11.78 / 11.70		>300	*n*-Butanol	52
IIIh	$C_{20}H_{16}N_4O_4$	14.97 / 14.89		287	DMF	73
Vb	$C_{19}H_{14}N_4O_2$	17.13 / 16.97		>300	DMF	65
Vc	$C_{18}H_{11}N_3O_2S$	12.80 / 12.61	9.80 / 9.61	>300	DMF	50
Vd	$C_{18}H_{11}N_3O$	13.14 / 13.25		>300	DMF	76
Ve	$C_{15}H_{11}N_3O_2S$	14.02 / 14.14	10.93 / 10.77	>300	DMF	82
Vg	$C_{20}H_{13}N_3O_2$	12.97 / 12.84		>300	DMF	55
Vh	$C_{19}H_{12}N_4O_3$	16.10 / 16.28		>300	DMF	83
VIa	$C_{19}H_{13}N_6O_2$	23.01 / 23.20		265	DMF	87
VIh	$C_{20}H_{18}N_6O_3$	21.80 / 21.54		270	DMF	70
VIIc	$C_{18}H_{15}N_5O_2S$	19.31 / 19.18	8.91 / 8.77	306	DMF	85
VIIh	$C_{19}H_{16}N_6O_3$	22.51 / 22.34		>300	DMF	90
VIIIa	$C_{25}H_{22}N_4O_4$	12.49 / 12.67		220	Ac_2O	65

* Calculated, %: Cl 15.14. Found, %: Cl 15.40.

disappearance of the initial nitrile I from the reaction mixture according to TLC. The mixture was cooled, and the precipitated residue was filtered off and washed with *n*-butanol and water. The residue was dried and recrystallized from a suitable solvent (Table 1). The mother liquor, obtained after the filtration of the reaction mixture, was

TABLE 2. Spectral Characteristics of the Compounds Id, IIa-h, IIIb-h, Vb-e,g,h, VIa,h, VIIc,h, and VIIIa

Compound	IR spectrum, ν, cm^{-1}	PMR spectrum (DMSO-d_6), δ, ppm
1	2	3
Id	3210 (NH), 2200 (CN)	4.50 (2H, s, CH_2); 7.4-7.8 (4H, m, arom.)
IIa	3300, 3100 (NH_2), 1735 (CO)	1.22 (3H, t, J = 13 Hz, CH_3); 3.72 (2H, s, $ArCH_2CO$); 4.10 (2H, q, J = 13 Hz, CH_2–CH_3); 4.34 (2H, s, CH_2 in ring); 7.07 (2H, m, benzimidazole); 7.43-7.51 (6H, m, benzimidazole and $H_{arom}R$); 8.50 (2H, s, NH_2)
IIb	3300, 3100 (NH_2), 1730 (CO)	1.24 (3H, t, J = 13 Hz, CH_3); 3.75 (2H, s, $ArCH_2CO$); 4.01 (3H, s, CH_3–N); 4.12 (2H, q, J = 13 Hz, CH_2–CH_3); 4.31 (2H, s, CH_2 in ring); 7.16-7.60 (4H, m, benzimidazole); 7.45 (4H, s, $H_{arom}R$); 8.4 (2H, s, NH_2)
IIc	3320, 3100 (NH_2), 1720 (CO)	1.21 (3H, t, J = 13 Hz, CH_3); 3.73 (2H, s, $ArCH_2CO$); 4.09 (2H, q, J = 13 Hz, CH_2–CH_3); 4.34 (2H, s, CH_2 in ring); 7.15-7.40 (2H, m, benzothiazole); 7.45 (4H, s, $H_{arom}R$); 7.80-7.95 (2H, m, benzothiazole); 8.34 (1H, s, NH); 8.79 (1H, s, NH···N)
IId	3350, 3150 (NH_2), 1780	1.21 (3H, t, J = 13 Hz, CH_3); 3.73 (2H, s, $ArCH_2CO$); 4.11 (2H, q, J = 13 Hz, CH_2–CH_3); 4.27 (2H, s, CH_2 in ring); 7.2-7.9 (8H, m, arom.); 8.29 (2H, s, NH_2)
IIe	(CO) 3320, 3150 (NH_2) 1725 (CO)	1.21 (3H, t, J = 12 Hz, CH_2–CH_3); 2.32 (3H, s, CH_3); 3.70 (2H, s, $ArCH_2CO$); 4.10 (2H, q, J = 12 Hz, CH_2–CH_3); 4.24 (2H, s, CH_2 in ring); 6.82 (1H, s, 5'-H thiazole); 7.40 (4H, s, $H_{arom}R$); 8.31 (2H, s, NH_2)
IIf	3300, 3100 (NH_2), 1730 (CO)	1.21 (3H, t, J = 13 Hz, CH_3); 3.70 (2H, s, $ArCH_2CO$); 4.08 (2H, q, J = 13 Hz, CH_2–CH_3); 4.16 (2H, s, CH_2 in ring); 6.98 (1H, dd, J = 6, J = 8 Hz, 5'-H); 7.39 (4H, s, $H_{arom}R$); 7.80 (1H, t, J = 8 Hz, 4'-H); 8.35 (1H, d, J = 6 Hz, 6'-H); 8.50 (1H, d, J = 8 Hz, 3'-H); 8.30 (2H, s, NH_2)
IIg	3320, 3100 (NH_2), 1725 (CO)	1.21 (3H, t, J = 12 Hz, CH_3); 3.72 (2H, s, $ArCH_2CO$); 4.10 (2H, q, J = 12 Hz, CH_2–CH_3); 4.24 (2H, s, CH_2 in ring); 7.40 (4H, s, $H_{arom}R$); 7.5-8.0 (4H, m, 5'-H, 6'-H, 7'-H, 8'-H); 8.13 (1H, d, J = 10 Hz, 4'-H); 8.70 (1H, d, J = 10 Hz, 3'-H); 10.44 (2H, s, NH_2)
IIh	3400, 3130 (NH_2) 1730, 1670 (CO)	1.21 (3H, t, J = 13 Hz, CH_3); 3.72 (2H, s, $ArCH_2CO$); 4.10 (2H, q, J = 13 Hz, CH_2–CH_3); 4.38 (2H, s, CH_2 in ring); 7.43 (4H, s, $H_{arom}R$); 7.2-7.8 (3H, m, 6'-H, 7'-H, 8'-H); 8.10 (1H, d, J = 8 Hz, 5'-H); 8.29 (1H, s, NH); 9.10 (1H, s, NH···N); 11.92 (1H, s, NH)
IIIb	3300, 3150 (NH), 1710, 1650 (CO)	3.90 (3H, s, CH_3); 4.01 (3H, s, CH_3–N); 4.36 (2H, s, CH_2 in ring); 7.1-7.6 (4H, m, benzimidazole); 7.63 (2H, d, J = 8.5 Hz, 2'-and 6'-$H_{arom}R$); 8.1 (2H, d, J = 8.5 Hz, 3'- and 5'-$H_{arom}R$); 8.59 (2H, s, NH_2)
IIIc	3350, 3160 (NH_2), 1710 (CO)	3.88 (3H, s, CH_3); 4.41 (2H, s, CH_2); 7.2-7.5 (2H, m, benzothiazole); 7.63 (2H, d, J = 8.5 Hz, 2'- and 6'-$H_{arom}R$); 7.8-8.0 (2H, m, benzothiazole); 8.1 (2H, d, J = 8.5 Hz, 3'- and 5'-$H_{arom}R$); 8.2 (2H, s, NH_2)
IIId	3290, 3100 (NH_2), 1720 (CO)	3.88 (3H, s, CH_3); 4.28 (2H, s, CH_2); 7.2-7.4 (2H, m, benzoxazole); 7.60 (2H, d, J = 8.5 Hz, 2'- and 6'- $H_{arom}R$); 8.09 (2H, d, J = 8.5 Hz, 3'- and 5'-Harom); 8.47 (2H, s, NH_2)
IIIe	3350, 3180 (NH_2), 1720 (CO)	2.35 (3H, s, CH_3); 3.88 (3H, s, OCH_3); 4.32 (2H, S, CH_2); 6.83 (1H, s, 5'-H thiazole); 7.56 (2H, d, J = 8 Hz, 2'- and 6'-$H_{arom}R$); 8.09 (2H, d, J = 8 Hz, 3'- and 5'-$H_{arom}R$); 8.54 (2H, s, NH_2)
IIIf	3320, 3100 (NH_2), 1710 (CO)	3.88 (3H, s, CH_3); 4.28 (2H, s, CH_2); 7.00 (1H, t, J = 6 Hz, 5'-H pyridine); 7.55 (2H, d, J = 9 Hz, 2'- and 6-$H_{arom}R$); 7.75 (1H, dd, J = 6, J = 8 Hz, 4'-H pyridine); 8.06 (2H, d, J = 9 Hz, 3'- and 5'-$H_{arom}R$); 8.50 (1H, d, J = 6 Hz, 6'-H pyridine); 8.60 (1H, d, J = 6 Hz, 3'-H pyridine)
IIIg	3310, 3120 (NH_2), 1710 (CO)	3.88 (3H, s, CH_3); 4.28 (2H, s, CH_2); 7.2-7.8 (4H, m, 5'-H, 6'-H, 7'-H, 8'- quinoline); 7.60 (2H, d, J = 9 Hz, 2'- and 6'-$H_{arom}R$); 8.05 (2H, d, J = 9 Hz, 3'- and 5'-$H_{arom}R$); 8.20 (1H, d, J = 9 Hz, 4'-H quinoline); 8.70 (1H, d, J = 9 Hz, 3'-H quinoline); 9.40 (2H, s, NH_2)
IIIh	3370, 3150 (NH), 1715, 1670 (CO)	3.89 (3H, s, CH_3); 4.45 (2H, s, CH_2); 7.2-7.8 (3H, m, 6'-H, 7'-H, 8'-H quinozoline); 7.6 (2H, d, J = 9 Hz, 2'-, 6'-$H_{arom}R$); 8.05 (3H, d, J = 9 Hz, 3'- and 5'-H_{arom} + d, 5'-H quinozoline); 9.02 (2H, s, NH_2); 11.8 (IH, s, NH)
Vb	1700 (CO), 1650 (CO)	4.10 (3H, s, CH_3); 4.57 (2H, s, CH_2); 7.2-7.8 (7H, m, all arom. protons except 6-H); 8.07 (1H, d, J = 8.5 Hz, 6-H)
Vc	1720 (CO), 1660 (CO)	4.58 (2H, s, CH_2); 7.2–8.0 (7H, m, all arom. protons except 6-H); 8.2 (1H, d, J = 9 Hz, 6-H)
Vd*	1720 (CO), 1670 (CO)	5.15 (~1H, s, CH_2); 7.6-8.4 (7H, m, all arom. protons except 6-H); 8.56 (1H, d, J = 8 Hz, 6-H)

TABLE 2 (continued)

1	2	3
Ve*	1720 (CO), 1650 (CO)	2.70 (3H, s, CH_3); 7.30 (1H, s, 5'-H thiazole); 7.55 (1H, d, J = 9 Hz, 9-H); 7.70 (1H, t, J = 9 Hz, 7-H); 8.10 (1H, t, J = 9 Hz, 8-H); 8.50 (1H, d, J = 9 Hz, 6-H)
Vg	1720 (CO), 1660 (CO)	4.55 (2H, s, CH_2); 7.2-8.0 (7H, m, 8-, 9- and 10-H + 5'-, 6'-, 7'-, 8'-H quinoline); 8.10 (1H, d, J = 9 Hz, 4'-H quinoline); 8.35 (1H, d, J = 8 Hz, 6-H); 8.60 (1H, d, J = 9 Hz, 3'-H quinoline)
Vh	3400, 3200 (NH), 1700, 1760 (CO)	4.67 (2H, s, CH_2); 7.2-8.0 (8H, m, arom.); 11.2 (2H, s, NH)
VIa	3300-3100 (NH), 1620 (CO)	3.40 (2H, s, $ArCH_2CO$); 4.29 (2H, s, CH_2 in ring); 4.21 (3H, s, $NHNH_2$); 7.01 (2H, m, benzimidazole); 7.39 (6H, m, p-phenylene + benzimidazole); 8.30 (1H, s, NH); 9.20 (1H, s, NH···N); 11.67 (1H, s, NH benzimidazole)
VIh	3300-3100 (NH), 1670 (CO)	3.40 (2H, s, $ArCH_2CO$); 4.38 (2H, s, CH_2 in ring); 4.95 (~4H, s, NH, $NHNH_2$); 7.3-7.7 (7H, m, 6'-, 7'-, 8'-H quinazoline + p-phenylene); 8.04 (1H, d, J = 8 Hz, 5'-H quinazoline); 9.30 (2H, s, NH_2)
VIIc	3250-3100 (NH), 1720 (CO)	4.39 (2H, s, CH_2); 5.0 (~5H, br. s, NH); 7.2-7.5 (2H, m, benzothiazole); 7.65 (2H, d, J = 9 Hz, 2'-H and 6'-H p-phenylene); 7.80 (2H, m, benzothiazole protons); 8.00 (2H, d, J = 9 Hz, 3'-H and 5'-H p-phenylene)
VIIh	3300-3100 (NH), 1650 (CO)	4.44 (5H, distorted s, CH_2 + $NHNH_2$); 7.2-8.0 (8H, m, quinoline + p-phenylene); 9.16 (1H, s, NH); 9.81 (1H, s, NH···N); 11.8 (1H, s, NH quinozoline)
VIIIa	1730, 1750 (CO)	1.23 (3H, t, J = 13 Hz, CH_3); 2.45 (3H, s, CH_3CO); 3.14 (3H, s, 5-CH_3); 3.77 (2H, s, $ArCH_2CO$); 4.15 (2H, q, J = 13 Hz, CH_2–CH_3); 7.3-7.8 (4H, m, 2-, 8-, 9-, 10-H); 7.5 (2H, d, J = 9 Hz, 2'-H, 6'-H, p-phenylene); 7.69 (2H, d, J = 9 Hz, 3'-H and 5'-H p-phenylene); 8.21 (1H, d, J = 8 Hz, 7-H)

* The PMR spectra were measured in CF_3CO_2D.

concentrated to dryness in vacuo. The residue was flushed with water, triturated, filtered off, and recrystallized from the same solvent prior to the addition to the first portion. The yields of the pyrroles IIa-h are shown in Table 1.

3-(2-Azahetaryl)-2-amino-4(5H)-oxo-1-(4-methoxycarbonylphenyl)pyrroles (IIIb-h). A suspension of 2-(2-azahetaryl)-3-oxo-4-chlorobutane nitrile (I) (3 mmol), methyl 4-aminobenzoate (0.53 g, 3.5 mmol), and N,N-dimethylaniline (0.42 g, 3.5 mmol) in *n*-butanol (15 ml) was heated with the boiling for 10-14 h until the disappearance of the initial nitrile I from the reaction mixture according to TLC. The preceding method was then followed. The yields of the pyrroles IIIb-h are shown in Table 1.

1H,4H-3-(2-Azahetaryl)pyrrolo[1,2-*a*]quinazoline-2,5-diones (Vb-e,g,h). A suspension of 2-(2-azahetaryl)-3-oxo-4-chlorobutane nitrile (I) (3 mmol) and ethyl anthranilate (1.16 g, 7 mmol) in *n*-butanol (15 ml) was boiled for 14-20 h until the disappearance of the initial nitrile I from the reaction mixture according to TLC. The preceding method was then followed. The yields of the quinazolinediones Vb-e,g,h are shown in Table 1.

Hydrazides of 2-[4-{3-(2-azahetaryl)-2-amino-4(5H)-oxopyrrol-1-yl}phenyl]acetic Acid (VIa,h) and 4-[3-(2-azahetaryl)-2-amino-4(5H)-oxopyrrol-1-yl]benzoic Acid (VIIc,h). A suspension of 1-R-2-amino-3-(2-azahetaryl)-4(5H)-oxopyrrole (IIa,h), (IIIc,h) (2 mmol) in hydrazine hydrate (1 ml, 0.02 mol) was boiled for 10 min. Dioxane (10 ml) was added, and the mixture was heated for 1-2 h more until the disappearance of the initial oxopyrrole from the reaction mixture according to TLC. After cooling the mixture, the precipitated residue was filtered off and washed with dioxane, and then water. It was recrystallized from DMF. The yields of the hydrazides VIa,h and VIIc,h are shown in Table 1.

1-Acetoxy-5-methyl-3-[4-(ethoxycarbonylmethyl)phenyl]pyrrolo[3',2':5,6]pyrimido[3,4-*a*]benzimidazole (VIIIa). A solution of compound IIa (0.752 g, 2 mmol) in acetic anhydride (1 ml, 0.01 mol) was boiled for 3 h. After cooling the mixture, the precipitated residue was filtered off and washed with acetic anhydride, and then water. It was recrystallized from acetic anhydride. The yield of the benzimidazole VIIIa is 65%.

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