Chemistry of Heterocyclic Compounds, Vol. 40, No. 1, 2004

ANOMALOUS BECKMANN REACTION IN A SERIES OF OXIMES OF 4-ARYL-2,7,7-TRIMETHYL-5-OXO-5,6,7,8-TETRAHYDROQUINOLINES IN POLYPHOSPHORIC ACID. 2*. UNEXPECTED SYNTHESIS OF 3'-ETHOXYCARBONYL-4',7',7'-TRIMETHYL-4-OXO-2',6',7',8'-TETRAHYDROSPIRO(CYCLOHEXA-2,5-DIENE-1,2'-PYRROLO[4,3,2-*d,e*]QUINOLINES)

S. V. Tolkunov[1], A. I. Khyzhan[1], S. V. Shishkina[2], O. V. Shishkin[2], and V. I. Dulenko[1]

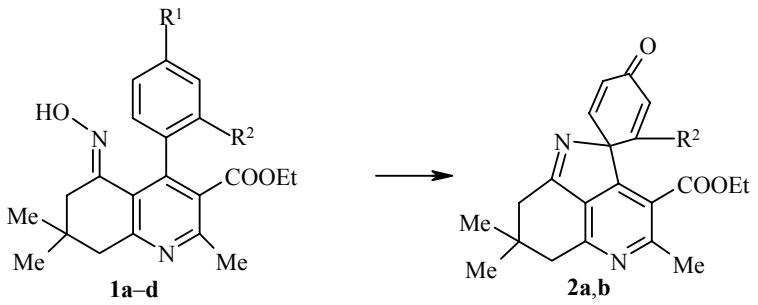
Oximes of 3-ethoxycarbonyl-4-halo(methoxy)phenyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinolines are converted in polyphosphoric acid (PPA) into 3'-ethoxycarbonyl-4',7',7'-trimethyl-4-oxo-2',6',7',8'-tetrahydrospiro(cyclohexa-2,5-diene-1,2'-pyrrolo[4,3,2-d,e]quinoline). An X-ray structural analysis has been carried out on one of the synthesized compounds.

Keywords: oximes of 4-aryl-3-ethoxycarbonyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinolines, 3'-ethoxycarbonyl-4',7',7'-trimethyl-4-oxo-2',6',7',8'-tetrahydrospiro(cyclohexa-2,5-diene-1,2'-pyrrolo-[4,3,2-*d,e*]quinolines), polyphosphoric acid.

We previously reported an anomalous Beckmann reaction in a series of oximes of 4-aryl-3-ethoxycarbonyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinolines in polyphosphoric acid (PPA) [1]. It was shown that, depending on the substituent in position 4 of the quinoline ring, the reaction may proceed in three directions: with aromatization of the saturated ring (Zemmler–Wolf aromatization), with the formation of azepinones, the normal Beckmann rearrangement products, and with the formation of pyridoacridines. While studying the rearrangement of oximes of 4-chloro(bromo, methoxy)phenyl-3-ethoxycarbonyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinolines in PPA we discovered a new route for the reaction process. As it turned out on heating oximes **1a-c** in PPA elimination of the substituent located at position 4 of the phenyl ring occurs and only one product is formed, *viz*. 3'-ethoxycarbonyl-4',7',7'-trimethyl-4-oxo-2',6',7',8'-tetrahydrospiro(cyclohexa-2,5-diene-1,2'-pyrrolo[4',3',2'-*d,e*]quinoline) (**2a**). When R^1 = Cl or Br hydrogen halide is evolved from the reaction mixture.

* For Part 1 see [1].

[1] L. M. Litvinenko Institute of Physical-Organic Chemistry and Coal Chemistry, National Academy of Sciences of Ukraine, Donetsk, 83114; e-mail: tolkunov@uvika.dn.ua. [2] Institute of Monocrystals, National Academy of Sciences of Ukraine, Kharkov 61001 Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 64-70, January, 2004. Original article submitted August 28, 2001; revision submitted January 31, 2002.



1 a R^1 = Cl, **b** R^1 = Br, **c** R^1=OMe, **d** R^1 = Cl; **a-c** R^2 = H, **d** R^2 = Cl; **2 a** R^2 = H, **b** R^2 = Cl

The structure of compound **2a** was established by an X-ray structural investigation.

The tetrahydro ring is in a half-boat conformation. The deviation of the $C_{(3)}$ atom from the mean-square plane of the remaining ring atoms is 0.65 Å. One of the methyl substituents at $C_{(3)}$ has an axial orientation relative to the plane of the tetrahydro ring, the second is equatorial (torsion angle $C_{(1)}$–$C_{(2)}$–$C_{(3)}$–$C_{(20)}$ is 67.4(3)°, $C_{(1)}$–$C_{(2)}$–$C_{(3)}$–$C_{(21)}$ 172.9(2)°). Repulsion between the $H_{(20C)}$ atom and the ring atoms (shortened intramolecular contacts $H_{(20C)}\cdots C_{(1)}$ 2.79, $H_{(20C)}\cdots C_{(5)}$ 2.67, $H_{(20C)}\cdots C_{(6)}$ 2.73 Å (total of van der Waals radii 2.87 Å [2])) evidently leads to lengthening of the $C_{(3)}$–$C_{(4)}$ bond to 1.557(3) Å compared with a mean value of 1.538 Å [3].

The dihydro ring spiro-linked with the tricyclic fragment is planar with a precision of 0.02 Å and is folded practically perpendicularly to the plane of the rings (torsion angle $C_{(6)}$–$C_{(7)}$–$C_{(10)}$–$C_{(15)}$ is 113.4(2)°). The $C_{(13)}$–$O_{(3)}$ bond at 1.225(3) Å is extended somewhat compared with a mean value of 1.210 Å.

The $C_{(16)}$ atom of the ester substituent at the $C_{(8)}$ atom is somewhat out of the plane of the pyridine ring (torsion angle $C_{(6)}$–$C_{(7)}$–$C_{(8)}$–$C_{(16)}$ is -171.0(2)°), and the carbonyl group is folded practically perpendicularly to the plane of the tricyclic fragment (torsion angle $C_{(7)}$–$C_{(8)}$–$C_{(16)}$–$O_{(1)}$ is 118.1(3)°), which is probably explained by the repulsion between this substituent and the dihydro ring. The $C_{(18)}$ atom is randomized with an equally probable population at two positions ***A*** and ***B***. In conformer ***A*** the $C_{(18)}$ atom occupies an *as*-position relative to the $C_{(16)}$–$O_{(2)}$ bond and in conformer ***B*** a position close to *ar* (torsion angle $C_{(16)}$–$O_{(2)}$–$C_{(17)}$–$C_{(18)}$ 129.7(5)° in ***A*** and 163.4(4)° in ***B***).

Shortened intermolecular contacts were detected in the crystal of compound **2a** $O_{(1)}\cdots H_{(15)'}$ (0.5-*x*, *y*-0.5, 1.5-*z*) 2.43 and $O_{(3)}\cdots H_{(1b)'}$ (0.5-*x*, 0.5+*y*, 1.5-*z*) 2.43 Å (total of van der Waals radii 2.46 Å), which may hardly count as hydrogen bonds in view of the angles $C_{(15)}$–$H_{(15)}\cdots O_{(1)'}$ (105°) and $C_{(19)}$–$H_{(19b)}\cdots O_{(3)}$ (74°).

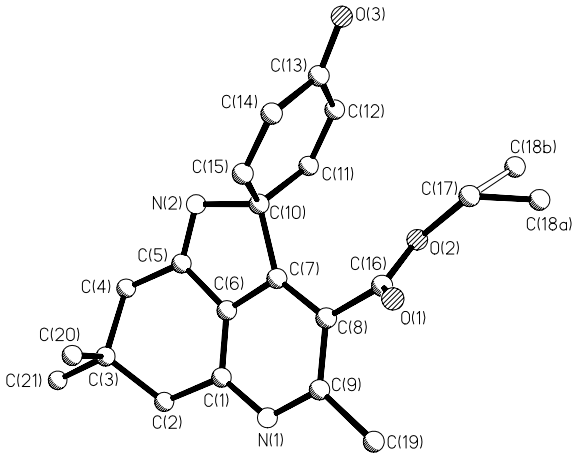
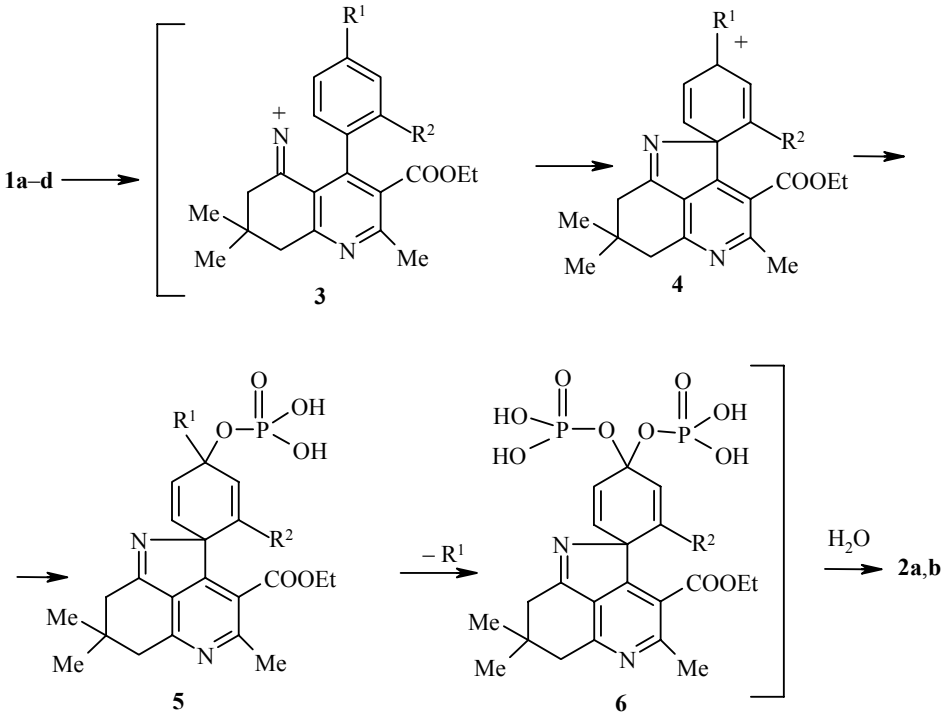


Fig. 1. Structure of compound **2a**.

The ^{1}H NMR spectra were in complete agreement with structures **2a,b**. However attention is attracted by the special features of the ^{1}H NMR spectrum of pyrroloquinoline **2b** (R^2 = Cl) compared with the spectrum of **2a**. The protons of the CH_2 group in the carboxyethyl fragment are magnetically nonequivalent and are displayed as a multiplet of ten lines. The protons of the 8-CH_2 group are also magnetically nonequivalent, which is caused by the different spatial orientation of the C–H bonds and by the displacement of one of them due to the influence of the magnetic anisotropy of the chlorine atom.

The formation of such a condensed system is explained by the uncoordinated orientation in the substituted phenyl ring and as a result attack by the nitrene cation **3** occurs at position 1 of the phenyl substituent with the formation of cation **4**, which is then converted as a result of the usual addition–fission reactions into pyrroloquinolines **2a,b**.



The formation of small quantities of 1-ethoxycarbonyl-2,5,5-trimethyl-5,6-dihydro-4H-pyrrolo[2,3,4-*k,l*]-acridine (**7**), in addition to pyrroloquinoline **2a,** was discovered in the reaction of 4-(4-bromophenyl)-3-ethoxycarbonyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinoline oxime (**1b**).

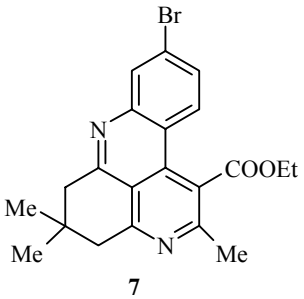


TABLE 1. Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) of Non-hydrogen Atoms in Structure **2a**

Atom	*x*	*y*	*z*	U_{eq}
$N_{(1)}$	1425(2)	-1138(2)	10764 (2)	53(1)
$N_{(2)}$	3210(3)	2071(2)	11184(2)	61(1)
$O_{(1)}$	3122(2)	-664(2)	8271(1)	77(1)
$O_{(2)}$	1772(2)	675(2)	8017(1)	65(1)
$O_{(3)}$	4517(2)	3372(2)	8194(2)	95(1)
$C_{(1)}$	1789(2)	-372(2)	11386(2)	45(1)
$C_{(2)}$	1770(3)	-428(2)	12442(2)	55(1)
$C_{(3)}$	2858(3)	249(2)	13087(2)	55(1)
$C_{(4)}$	2743(3)	1354(2)	12709(2)	62(1)
$C_{(5)}$	2754(3)	1382(2)	11658(2)	52(1)
$C_{(6)}$	2235(3)	514(2)	11076(2)	46(1)
$C_{(7)}$	2374(3)	658(2)	10150(2)	47(1)
$C_{(8)}$	2056(2)	-142(2)	9502(2)	47(1)
$C_{(9)}$	1547(3)	-1021(2)	9847(2)	50(1)
$C_{(10)}$	3044(3)	1694(2)	10153(2)	51(1)
$C_{(11)}$	2205(3)	2439(2)	9477(2)	58(1)
$C_{(12)}$	2669(3)	2965(2)	8846(2)	61(1)
$C_{(13)}$	4051(3)	2848(2)	8747(2)	63(1)
$C_{(14)}$	4873(3)	2077(2)	9342(2)	61(1)
$C_{(15)}$	4428(3)	1563(2)	9995(2)	57(1)
$C_{(16)}$	2372(3)	-95(2)	8531(2)	51(1)
$C_{(17)}$	2183(3)	850(3)	7112(2)	93(1)
$C_{(18a)}$	914(6)	944(8)	6274(4)	93(3)
$C_{(18b)}$	1089(7)	1540(6)	6504(6)	76(2)
$C_{(19)}$	1105(4)	-1917(2)	9200(2)	72(1)
$C_{(20)}$	4256(3)	-156(3)	13107(2)	77(1)
$C_{(21)}$	2652(4)	251(3)	14117(2)	79(1)

TABLE 2. Bond Lengths (*l*) in the Structure of Pyrroloquinoline **2a**

Bond	*l*, Å	Bond	*l*, Å	Bond	*l*, Å
$N_{(1)}$–$C_{(1)}$	1.339(2)	$C_{(8)}$–$C_{(16)}$	1.494(3)	$C_{(3)}$–$C_{(20)}$	1.519(4)
$N_{(2)}$–$C_{(5)}$	1.288(3)	$C_{(10)}$–$C_{(11)}$	1.495(4)	$C_{(3)}$–$C_{(4)}$	1.555(4)
$O_{(1)}$–$C_{(16)}$	1.197(3)	$C_{(11)}$–$C_{(12)}$	1.314(4)	$C_{(5)}$–$C_{(6)}$	1.441(4)
$O_{(2)}$–$C_{(17)}$	1.466(3)	$C_{(13)}$–$C_{(14)}$	1.457(4)	$C_{(7)}$–$C_{(8)}$	1.391(4)
$C_{(1)}$–$C_{(6)}$	1.371(3)	$C_{(17)}$–$C_{(18b)}$	1.538(1)	$C_{(8)}$–$C_{(9)}$	1.412(4)
$C_{(2)}$–$C_{(3)}$	1.545(4)	$N_{(1)}$–$C_{(9)}$	1.348(3)	$C_{(9)}$–$C_{(19)}$	1.503(4)
$C_{(3)}$–$C_{(21)}$	1.531(4)	$N_{(2)}$–$C_{(10)}$	1.519(3)	$C_{(10)}$–$C_{(15)}$	1.494(4)
$C_{(4)}$–$C_{(5)}$	1.498(4)	$O_{(2)}$–$C_{(16)}$	1.317(3)	$C_{(12)}$–$C_{(13)}$	1.460(4)
$C_{(6)}$–$C_{(7)}$	1.373(3)	$O_{(3)}$–$C_{(13)}$	1.229(3)	$C_{(14)}$–$C_{(15)}$	1.319(4)
$C_{(7)}$–$C_{(10)}$	1.534(4)	$C_{(1)}$–$C_{(2)}$	1.509(4)	$C_{(17)}$–$C_{(19a)}$	1.538(1)

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-300 instrument (300 MHz) and on a Gemini-200 instrument (200 MHz), internal standard was TMS. A check on the purity of the compounds obtained was carried out by TLC on Silufol UV-254 plates. Visualization was with UV light or iodine vapor.

TABLE 3. Valence Angles (ω) in Structure **2a**

Angle	ω, deg.	Angle	ω, deg.
$C_{(1)}$–$N_{(1)}$–$C_{(9)}$	118.4(2)	$C_{(5)}$–$N_{(2)}$–$C_{(10)}$	107.6(2)
$C_{(16)}$–$O_{(2)}$–$C_{(17)}$	114.6(2)	$N_{(1)}$–$C_{(1)}$–$C_{(6)}$	119.9(2)
$N_{(1)}$–$C_{(1)}$–$C_{(2)}$	123.5(2)	$C_{(6)}$–$C_{(1)}$–$C_{(2)}$	116.6(2)
$C_{(1)}$–$C_{(2)}$–$C_{(3)}$	112.4(2)	$C_{(20)}$–$C_{(3)}$–$C_{(21)}$	109.2(2)
$C_{(20)}$–$C_{(3)}$–$C_{(2)}$	110.1(2)	$C_{(21)}$–$C_{(3)}$–$C_{(2)}$	108.8(2)
$C_{(20)}$–$C_{(3)}$–$C_{(4)}$	109.4(2)	$C_{(21)}$–$C_{(3)}$–$C_{(4)}$	108.3(2)
$C_{(2)}$–$C_{(3)}$–$C_{(4)}$	111.0(2)	$C_{(5)}$–$C_{(4)}$–$C_{(3)}$	110.5(2)
$N_{(2)}$–$C_{(5)}$–$C_{(6)}$	113.3(2)	$N_{(2)}$–$C_{(5)}$–$C_{(4)}$	129.2(3)
$C_{(6)}$–$C_{(5)}$–$C_{(4)}$	117.5(2)	$C_{(1)}$–$C_{(6)}$–$C_{(7)}$	123.2(2)
$C_{(1)}$–$C_{(6)}$–$C_{(5)}$	127.2(2)	$C_{(7)}$–$C_{(6)}$–$C_{(5)}$	109.4(2)
$C_{(6)}$–$C_{(7)}$–$C_{(8)}$	117.9(2)	$C_{(6)}$–$C_{(7)}$–$C_{(10)}$	105.7 (2)
$C_{(8)}$–$C_{(7)}$–$C_{(10)}$	135.8(2)	$C_{(7)}$–$C_{(8)}$–$C_{(9)}$	116.4(2)
$C_{(7)}$–$C_{(8)}$–$C_{(16)}$	120.8(2)	$C_{(9)}$–$C_{(8)}$–$C_{(16)}$	122.5(2)
$N_{(1)}$–$C_{(9)}$–$C_{(8)}$	124.0(2)	$N_{(1)}$–$C_{(9)}$–$C_{(19)}$	114.7(2)
$C_{(8)}$ –$C_{(9)}$–$C_{(19)}$	121.3(2)	$C_{(11)}$–$C_{(10)}$–$C_{(15)}$	113.3(2)
$C_{(11)}$–$C_{(10)}$–$N_{(2)}$	108.4(2)	$C_{(15)}$–$C_{(10)}$ –$N_{(2)}$	107.2(2)
$C_{(11)}$–$C_{(10)}$–$C_{(7)}$	113.8(2)	$C_{(15)}$–$C_{(10)}$–$C_{(7)}$	109.5(2)
$N_{(2)}$–$C_{(10)}$–$C_{(7)}$	104.1(2)	$C_{(12)}$–$C_{(11)}$–$C_{(10)}$	123.0(3)
$C_{(11)}$–$C_{(12)}$–$C_{(13)}$	121.8(3)	$O_{(3)}$–$C_{(13)}$–$C_{(14)}$	120.7(3)
$O_{(3)}$–$C_{(13)}$–$C_{(12)}$	122.3(3)	$C_{(14)}$–$C_{(13)}$–$C_{(12)}$	117.0(2)
$C_{(15)}$–$C_{(14)}$–$C_{(13)}$	121.5(3)	$C_{(14)}$–$C_{(15)}$–$C_{(10)}$	123.1(3)
$O_{(1)}$–$C_{(16)}$–$O_{(2)}$	124.3(2)	$O_{(1)}$–$C_{(16)}$–$C_{(8)}$	123.9(3)
$O_{(2)}$–$C_{(16)}$–$C_{(8)}$	111.7(2)	$O_{(2)}$–$C_{(17)}$–$C_{(18b)}$	105.3(4)
$O_{(2)}$–$C_{(17)}$–$C_{(18a)}$	109.1(4)	$C_{(18b)}$–$C_{(17)}$–$C_{(18a)}$	32.4(4)

X-Ray Structural Investigation. The crystals of compound **2a** were monoclinic, $C_{21}H_{22}N_2O_3$, and at 20°C: a = 10.212(4), b = 13.258(5), c = 14.226(5) Å; β = 104.04(2)°; V = 1869(1) Å^3; M = 349.40; Z = 4, space group $P2_1/n$; d_{calc} = 1.242 g/cm^3; μ(MoKα) = 0.084 mm^{-1}; F(000) = 740. Unit cell parameters and the intensities of 3174 reflections (3001 independent, R_{int} = 0.025) were measured on a Siemens P3/PC automatic four-circle diffractometer (MoKα, graphite monochromator, 2θ/θ scanning, $2\theta_{max}$ = 50°).

The structure was solved by the direct method with the SHELX97 [4] set of programs. The positions of the hydrogen atoms were made apparent from an electron density difference synthesis and were refined by a riding model with U_{iso}-nU_{eq} (n = 1.5 for a methyl group and n = 1.2 for the remaining hydrogen atoms). When refining the structure, limits were imposed on the bond lengths in the randomized fragment (C(sp^3)–C(sp^3) 1.54(1) Å). The structure was refined on F^2 by the full-matrix least-squares method in an anisotropic approach for the nonhydrogen atoms to wR_2 = 0.155 for the 3001 reflections (R_1 = 0.052 for 1827 reflections with $F > 4\sigma(F)$, S = 0.971).

The 4-aryl-3-ethoxycarbonyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinolines were obtained by the procedure of [5,6].

General Procedure for Obtaining Oximes of 4-Aryl-3-ethoxycarbonyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinolines (1a-d). Hydroxylamine hydrochloride (6.9 g, 100 mmol) and pyridine (8 ml) were added to a solution of the appropriate tetrahydroquinoline (10 mmol) in ethanol (50 ml). The mixture was boiled for 6 h, poured into water, neutralized with dilute hydrochloric acid to a neutral reaction, and the product was filtered off.

4-(4'-Chlorophenyl)-3-ethoxycarbonyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinoline Oxime (1a). Yield 56.6%; mp 170°C (alcohol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.95 (3H, t, *J* = 7.1, $COOCH_2C\underline{H}_3$); 1.02 (6H, s, 7- ,7-CH_3); 2.45 (3H, s, 2-CH_3); 2.55 (2H, s, 8-CH_2); 2.78 (2H, s, 6-CH_2); 3.96 (2H, q, *J* = 7.1, $COOC\underline{H}_2CH_3$); 7.18 (2H, d, $J_{2,3}$ = 8.2, 3'- ,5'-H); 7.50 (2H, d, $J_{5,6}$ = 8.2, 2' -,6'-H): 10.90 (1H, s, NOH). Found, %: C 65,33; H 6.05; Cl 9.23: N 7.35. $C_{21}H_{23}ClN_2O_3$. Calculated, %: C 65.20; H 5.99; Cl 9.16; N 7.24.

4-(4'-Bromophenyl)-3-ethoxycarbonyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinoline Oxime (1b). Yield 61.5%; mp 213°C (alcohol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.95 (3H, t, *J* = 7.1, $COOCH_2C\underline{H}_3$); 1.02 (6H, s, 7-, 7-CH_3); 2.45 (3H, s, 2-CH_3); 2.55 (2H, s, 8-CH_2); 2.78 (2H, s, 6-CH_2); 3.96 (2H, q, *J* = 7.1, $COOC\underline{H}_2CH_3$); 7.15 (2H, d, $J_{2,3}$ = 8.2, 3'-, 5'-H); 7.57 (2H, d, $J_{5,6}$ = 8.2, 2'-, 6'-H); 10.90 (1H, s, NOH). Found, %: C 58.61; H 5.31; Br 18.60; N 6.30. $C_{21}H_{23}BrN_2O_3$. Calculated, %: C 58.48; H 5.37; Br 18.52; N 6.49.

3-Ethoxycarbonyl-4-(4'-methoxyphenyl)-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinoline Oxime (1c). Yield 77.47%; mp 190-192°C (alcohol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.95 (3H, t, *J* = 7.1, $COOCH_2C\underline{H}_3$); 1.02 (6H, s, 7-, 7-CH_3); 2.45 (3H, s, 2-CH_3); 2.55 (2H, s, 8-CH_2); 2.78 (2H, s, 6-CH_2); 3.79 (3H, s, 4'-OCH_3); 4.01 (2H, q, *J* = 7.1, $COOC\underline{H}_2CH_3$); 6.92 (2H, d, $J_{2,3}$ = 8.6, 3'-, 5'-H); 7.05 (2H, d, $J_{5,6}$ = 8.6, 2'-,6'-H); 10.92 (1H, s, NOH). Found, %: C 69.37; H 6.67; N 7.21. $C_{22}H_{26}N_2O_4$. Calculated, %: C 69.09; H 6.85; N 7.32.

4-(2',4'-Dichlorophenyl)-3-ethoxycarbonyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinoline Oxime (1d). Yield 57.5%; mp 158-159°C (alcohol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.90 (3H, t, *J* = 7.1, $COOCH_2C\underline{H}_3$); 0.92 (3H, s, 7-CH_3); 1.03 (3H, s, 7-CH_3); 2.46 (3H, s, 2-CH_3); 2.50 (2H, s, 8-CH_2); 2.78 (2H, s, 6-CH_2); 3.93 (2H, q, *J* = 7.1, $COOC\underline{H}_2CH_3$); 7.15 (1H, d, $J_{5,6}$ = 8.2, 6'-H); 7.41 (1H, dd, $J_{5,6}$ = 8.2, $J_{3,5}$ = 2.2, 5'-H); 7.57 (1H, d, $J_{3,5}$ = 2.1, 3'-H); 10.88 (1H, s, NOH). Found, %: C 59.91; H 5.15; Cl 16.75; N 6.45. $C_{21}H_{22}Cl_2N_2O_3$. Calculated, %: C 59.87; H 5.26; Cl 16.83; N 6.65.

General Procedure for Obtaining Compounds 2a,b, 7. A mixture of PPA (10 g) and the appropriate oxime **1a-d** (1 g) was kept at 100°C for 1 h. The reaction mixture was poured into water (100 ml), neutralized with aqueous ammonia solution, and the precipitated solid extracted with chloroform. Purification was by chromatography on silica gel. The eluent was chloroform–alcohol, 10:0.5 for **2a** and toluene–chloroform–alcohol, 5:1:0.4 for **2b**.

3'-Ethoxycarbonyl-4',7',7'-trimethyl-4-oxo-2',6',7',8'-tetrahydrospiro(cyclohexa-2,5-diene-1,2'-pyrrolo[4',3',2'-*d,e*]quinoline) (2a). Yield 28.4%; mp 110-112°C (hexane). R_f 0.60. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.07 (6H, s, 7-, 7-CH_3); 1.16 (3H, t, *J* = 7.1, $COOCH_2C\underline{H}_3$); 2.62 (3H, s, 2-CH_3); 2.72 (2H, s, 6-CH_2); 2.86 (2H, s, 8-CH_2); 4.08 (2H, q, *J* = 7.1, $COOC\underline{H}_2CH_3$); 6.43 (4H, s, CH=CH). ^{1}H NMR spectrum (pyridine-d_5), δ, ppm (*J*, Hz): 0.98 (6H, s, 7-, 7-CH_3); 1.21 (3H, t, *J* = 7.1, $COOCH_2C\underline{H}_3$); 2.72 (3H, s, 2-CH_3); 2.89 (4H, s, 6-, 8-CH_2); 4.25 (2H, q, *J* = 7.1, $COOC\underline{H}_2CH_3$); 6.55 (2H, d, $J_{2,3}$ = 10, 2,6-CH=CH); 6.75 (2H, d, $J_{5,6}$ = 10, 3,5-CH=CH). Found, %: C 71.79; H 6.45; N 7.80. $C_{21}H_{22}N_2O_3$. Calculated, %: C 71.98; H 6.33; N 7.99.

2-Chloro-3'-ethoxycarbonyl-4',7',7'-trimethyl-4-oxo-2',6',7',8'-tetrahydrospiro(cyclohexa-2,5-diene-1,2'-pyrrolo[4',3',2'-*d,e*]quinoline) (2b). Yield 31.4%; mp 110°C (hexane). R_f 0.33. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.02 (3H, s, 7-CH_3); 1.16 (3H, s, 7-CH_3); 1.19 (3H, t, *J* = 7.1, $COOCH_2C\underline{H}_3$); 2.71 (3H, s, 2-CH_3); 2.78 (2H, s, 6-CH_2); 2.90 and 2.91 (2H, s, 8-CH_2); 4.14 (2H, m, *J* = 7.1, $COOC\underline{H}_2CH_3$); 6.48 (2H, s, 2,3-CH=CH); 6.80 (1H, s, 5-CH=). Found, %: C 65.67; H 5.65; Cl 9.05; N 7.41. $C_{21}H_{21}ClN_2O_3$. Calculated, %: C 65.54; H 5.50; Cl; 9.21; N 7.28.

9-Bromo-1-ethoxycarbonyl-2,5,5-trimethyl-5,6-dihydro-4H-pyrido[2,3,4-*k,l*]acridine (7). Yield 7%; mp 178°C (alcohol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.05 (6H, s, 5-, 5-CH_3); 1.34 (3H, t, *J* = 7.1, $COOCH_2C\underline{H}_3$); 2.58 (3H, s, 2-CH_3); 3.04 (4H, s, 4- and 6-CH_2); 4.40 (2H, q, *J* = 7.1, $COOC\underline{H}_2CH_3$); 7.17 (1H, dd, $J_{10,11}$ = 9.2, $J_{8,10}$ = 2.8, 10-H); 7.32 (1H, d, $J_{8,10}$ = 2.8, 8-H); 7.95 (1H, d, $J_{10,11}$ = 9.2, 11-H). Found, %: C 61.36; H 5.27; Br 19.08; N 6.67. $C_{21}H_{21}BrN_2O_2$. Calculated, %: C 61.03; H 5.12; Br 19.33; N 6.78.

REFERENCES

1. S. V. Tolkunov, A. I. Khizhan, and V. I. Dulenko, *Khim. Geterotsikl. Soedin.*, 1849 (2003).
2. Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.*, **58**, 713 (1989).
3. H.-B. Burgi and J. D. Dunitz, *Structure Correlation, Vol. 2*, VCH, Weinheim (1994), p. 741.
4. G. M. Sheldrick, *SHELX97. PC Version, A System of Computer Programs for Crystal Structure Solution and Refinement*, 1998, Rev. 2.
5. H. J. Antaki, *J. Chem. Soc.*, 4877 (1973).
6. E. E. Grinshtein, E. I. Stankevich, and G. Ya. Dubur, *Khim. Geterotsikl. Soedin.,* 1118 (1966).