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RECYCLIZATION OF 1-ALKYL-5-BENZOYL-3-ETHOXYCARBONYL-6-METHYLTHIO-1,2-DIHYDRO-PYRIDIN-2-ONES INTO 1,6-ANNELATED DERIVATIVES OF 3-ALKYLCARBAMOYL-5-BENZOYLPYRIDIN-2-ONE

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For the first time the possibility has been shown of recyclizing 1-alkyl-5-benzoyl-3-ethoxycarbonyl-6-methylthio-1,2-dihydropyridin-2-ones into 1,6-annelated bicyclic derivatives of 3-alkylcarbamoyl-5-benzoylpyridin-2-one, which takes place on reacting the former with 1,4- and 1,5-nitrogen-containing dinucleophiles. The structure of the recyclization products was demonstrated by spectral methods and X-ray structural analysis.

Keywords: alkylamines, 1-(alkylamino)phenylmethylidene-3-methylcarbamoyl-4-oxo-1,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridines, 1-alkyl-5-benzoyl-3-ethoxycarbonyl-6-methylthio-1,2-dihydropyridin-2-ones, 3-alkylcarbamoyl-1-benzoyl-4-oxo-4H-benzo[4,5][1,3]thiazolo[3,2-*a*]pyridines, 3-alkylcarbamoyl-1-benzoyl-4-oxo-4,10-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridines, 6-alkylcarbamoyl-8-benzoyl-5-oxo-1,2,3,5-tetrahydroimidazo[1,2-*a*]pyridines, 7-alkylcarbamoyl-9-benzoyl-6-oxo-1,2,3,5-tetrahydro-2H-pyrido[1,2-*a*]pyrimidines, 1-amino-2-mercaptoethane, 1,3-diaminopropane, *o*-aminothiophenol, diaminoethane, *o*-phenylenediamine, recyclization X-ray structural analysis.

We showed recently that 1-alkyl-5-benzoyl-3-ethoxycarbonyl-6-methylthio-1,2-dihydropyridin-2-ones **1a,b** are regiospecifically cyclocondensed with nitrogen-containing 1,2-, 1,3-, 1,4-, and 1,5-dinucleophiles [1-4]. In the last two cases the reaction proceeds as a recyclization [3,4].

The aim of the present work was to establish unequivocally the structure of the products of recyclization, to study the limits of its application, to investigate the effect of the ratio of starting materials on the direction of the reaction, and to clarify the sequence of formation of intermediate compounds.

It was discovered that 1-alkyl-5-benzoyl-3-ethoxycarbonyl-6-methylthio-1,2-dihydropyridin-2-ones **1a,b** react with an excess of diaminoethane **2a** and 1,3-diaminopropane **2b** nonselectively. The reaction products are therefore not derivatives of 5-benzoyl-3-heteryl-2H-2-pyranone, as we proposed previously [3, 4], but are 6-alkylcarbamoyl-8-benzoyl-5-oxo-1,2,3,5-tetrahydroimidazo[1,2-*a*]pyridines **3a,b**, 7-alkylcarbamoyl-9-benzo-yl-6-oxo-1,2,3,5-tetrahydro-2H-pyrido[1,2-*a*]pyrimidines **3c,d**, and 1-alkyl-6-(1-alkyl-5-benzoyl-

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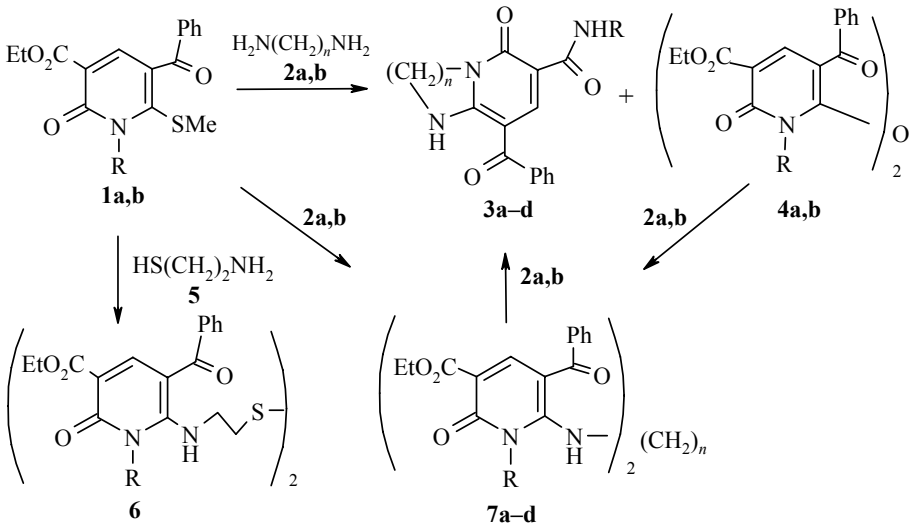
3-ethoxy-carbonyl-2-oxo-1,2-dihydropyrid-6-yl)oxy-5-benzoyl-3-ethoxycarbonyl-2-oxo-1,2-dihydropyridines **4a,b**. The latter are also formed on hydrolysis of the initial 1,2-dihydropyridin-2-ones **1a,b**, occurring under the action of water and triethylamine [3].



1a, **3a**,**c**, **4a**, **6**, **7a**,**c** R = Me; **1b**, **3b**,**d**, **4b**, **7b**,**d** R = Et; **2a**, **3a**,**b**, **7a**,**b** *n* = 2; **2b**, **3c**,**d**, **7c**,**d** *n* = 3

The yields of compounds **3a-d** and **4a,b** were 39-69 and 24-49% respectively.

At the same time, at a ratio of initial reactants **1a,b** and **2a,b** equal to 2:1 the interaction occurs selectively with the formation of N,N'-di(1-alkyl-5-benzoyl-3-ethoxycarbonyl-2-oxo-1,2-dihydropyrid-6-yl)-1,2-diaminoethanes (1,3-diaminopropanes) **7a-d**. These same compounds are also obtained on reaction of dipyridyl oxides **4a,b** with equimolar amounts of diaminoalkanes **2a,b**. Compound **7a,** under the action of a threefold excess of diaminoalkane **2a,** is recyclized into 8-benzoyl-6-methylcarbamoyl-5-oxo-1,2,3,5-tetrahydroimidazo[1,2-*a*]pyridine (**3a**). Dipyridyl oxides **4a,b** and substituted diaminoalkanes **7a-d** are therefore intermediates in the recyclization of 1,2-dihydropyridin-2-ones **1a,b** into 5-oxo-1,2,3,5-tetrahydroimidazo-[1,2-*a*] pyridines **3a,b** and 6-oxo-1,2,3,5-tetrahydro-2H-pyrido[1,2-*a*]pyrimidines **3c,d**.

On using 1-amino-2-mercaptoethane **5** (generated *in situ* from its hydrochloride and triethylamine) as a 1,4-dinucleophilic reagent only di[2'-(5-benzoyl-3-ethoxycarbonyl-1-methyl-2-oxo-1,2-dihydropyrid-6-yl)-aminoethyl] disulfide (**6**) was isolated from the reaction mixture. This is probably explained both by the lower nucleophilicity of the mercapto group compared with the amino group, and by its ease of oxidation by air in the presence of bases [5].

Like the recyclization, interaction of 1,2-dihydropyridin-2-ones **1a,b** with the aromatic nitrogen-containing 1,4-dinucleophiles *o*-phenylenediamine (**8a**) and *o*-aminothiophenol (**8b**) also takes place. The products of this reaction were respectively, 3-alkylcarbamoyl-1-benzoyl-4-oxo-4,10-dihydrobenzo-[4,5]imidazo[1,2-*a*]pyridines **9a,b**, 3-alkylcarbamoyl-1-benzoyl-4-oxo-4H-benzo[4,5][1,3]thiazolo[3,2-*a*]pyridines **9c,d** and dipyridyl oxides **4a,b**. The yields of compounds **9a-d** and **4a,b** were 57-70 and 26-32%, respectively. The ability of *o*-aminothiophenol **8b**, unlike 1-amino-2-mercaptoethane **5**, to enter into recyclization with 1,2-dihydropyridin-2-ones **1a,b**, is, to all appearances, linked with its more rigid molecular structure and a lower inclination towards oxidation.

The yields, melting points, and data of elemental analysis of compounds **3a-d**, **6**, **7a-d**, and **9a-d** are given in Table 1, and the data of IR, ^{13}C, and ^{1}H NMR spectra in Tables 2-4. In difference to the reactions of

TABLE 1. Characteristics of the Synthesized Compounds

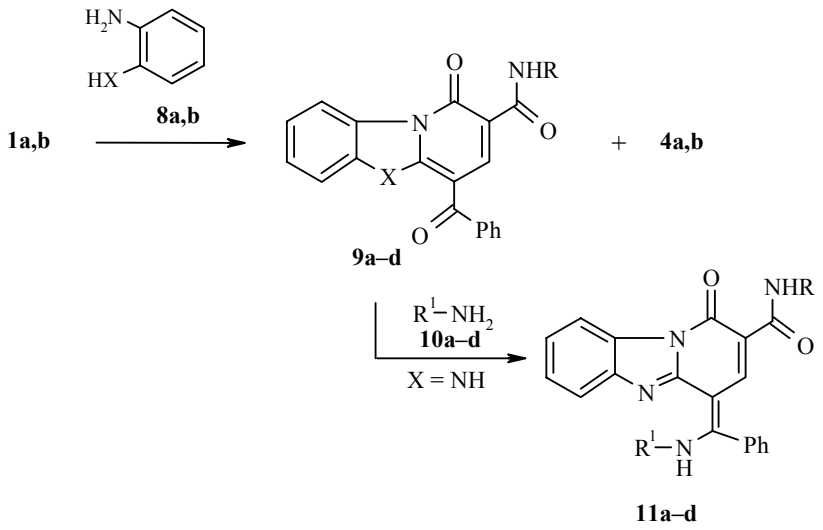
Compound	Empirical formula	Found, % / Calculated, %				mp, °C*	Yield, %
		C	H	N	S		
3a	$C_{16}H_{15}N_3O_3$	64.37 / 64.64	4.98 / 5.09	14.30 / 14.13		335-337	69
3b	$C_{17}H_{17}N_3O_3$	65.60 / 65.58	5.58 / 5.50	13.61 / 13.50		300-303	63
3c	$C_{17}H_{17}N_3O_3$	65.73 / 65.58	5.32 / 5.50	13.74 / 13.50		253-256	43
3d	$C_{18}H_{19}N_3O_3$	66.64 / 66.45	5.68 / 5.89	13.15 / 12.91		257-259	39
4b*[2]	$C_{34}H_{32}N_2O_9$	66.43 / 66.66	4.99 / 5.26	4.86 / 4.57		75-77	45
6	$C_{36}H_{38}N_4O_8S_2$	59.88 / 60.15	5.59 / 5.33	7.93 / 7.79	8.81 / 8.92	185-187	61
7a	$C_{34}H_{34}N_4O_8$	65.32 / 65.17	5.22 / 5.47	9.07 / 8.94		220-222	73
7b	$C_{36}H_{38}N_4O_8$	65.83 / 66.04	6.02 / 5.85	8.65 / 8.56		155-158	69
7c	$C_{35}H_{36}N_4O_8$	65.45 / 65.61	5.84 / 5.66	9.02 / 8.74		215-218	67
7d	$C_{37}H_{40}N_4O_8$	66.25 / 66.45	5.92 / 6.03	8.50 / 8.38		123-125	62
9a	$C_{20}H_{15}N_3O_3$	69.74 / 69.56	4.31 / 4.38	12.13 / 12.17		283-285	70
9b	$C_{21}H_{17}N_3O_3$	69.89 / 70.18	4.56 / 4.77	11.85 / 11.69		272-275	63
9c	$C_{20}H_{14}N_2O_3S$	66.02 / 66.29	4.15 / 3.89	7.48 / 7.73	8.64 / 8.85	250-252	61
9d	$C_{21}H_{16}N_2O_3S$	66.75 / 67.01	4.42 / 4.28	7.29 / 7.44	8.40 / 8.52	241-243	57
11a	$C_{22}H_{20}N_4O_3$	68.22 / 68.03	5.03 / 5.19	14.30 / 14.42		232-234	73
11b	$C_{23}H_{22}N_4O_3$	68.62 / 68.64	5.72 / 5.51	13.97 / 13.92		210-212	77
11c	$C_{28}H_{24}N_4O_2$	75.11 / 74.98	5.40 / 5.39	12.72 / 12.49		214-217	82
11d	$C_{25}H_{20}N_4O_3$	70.49 / 70.74	5.00 / 4.75	13.03 / 13.20		210-212	69

* Compounds **3a-d, 9a-d, 7a,b** were recrystallized from DMSO, compound **4b** from 2-propanol, compounds **6 and7a-d** from nitromethane, compounds **11a-d** from ethanol.

*[2]The mp of compound **4a** corresponded to that given in [3].

3-cyano-5-ethoxycarbonyl-4-methyl-6-methylthio-1-phenyl-1,2-dihydropyridin-2-one with diaminoethane and 1,3-diaminopropane [6], the recyclization reaction investigated by us of compounds **1a,b** into 1,6-annelated derivatives of 3-alkylcarbonyl-5-benzoylpyridin-2-one **3a-d** and **9a-d** were effected with the participation of the ethoxycarbonyl group and without elimination of the alkylamino group. This recyclization therefore has a general character and permits the synthesis of the series of bicyclic derivatives of 3-benzoylpyridin-2-one **3a-d**, **9a-d**, containing an alkylcarbamoyl group in their structures.

To obtain derivatives of compound **9** suitable for establishing the structure by X-ray structural analysis we carried out the amination of 4-oxo-4,10-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine **9a** with alkylamines **10a-d**. The reactions of compound **9a** with a threefold excess of reactants **10a-d** at 120-140°C were completed after 10-20 min, while benzimidazo[1,2-*a*]pyridine **9a** was completely stable to the action of a sixfold excess of boiling aniline after 6 h. Evidently the determining factor enabling the reaction to be effected at an acceptable rate is the high nucleophilicity of alkylamines **10a-d**.



9a,**c**, **11a–d** R = Me, **9b**,**d** R = Et, **8a**, **9a**,**b** X = NH, **8b**, **9c**,**d** X = S;
10a, **11a** $R^1 = (CH_2)_2OH$, **10b**, **11b** $R^1 = (CH_2)_3OH$, **10c**, **11c** $R^1 = Ph(CH_2)_2$,
10d, **11d** R^1 = 2-furfuryl

It was found that the products of the amination of 4-oxo-4,10-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine **9a** with alkylamines **10a-d** are 1-(alkylamino)phenylmethylidene-3-methylcarbamoyl-4-oxo-1,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridines **11a-d** and the reaction takes place in preparative yield (69-82%). 3-Alkylcarbamoyl-1-benzoyl-4-oxo-4H-benzo[4,5][1,3]thiazolo[3,2-*a*]pyridines **9c,d** did not take part in similar reactions with alkylamines **10a-d**. A convincing sign of the accomplishment of this interaction is the absence

TABLE 2. IR Spectra of the Synthesized Compounds

Compound	ν, cm^{-1}
3a	3380, 3300, 3050, 2970, 1680, 1640, 1600, 1580, 1500
3b	3400, 3300, 3100, 3000, 1680, 1640, 1610, 1580, 1500, 1450, 1380, 1330
3c	3300, 3100, 2950, 1670, 1640, 1590, 1550, 1510, 1440, 1400, 1380
3d	3300, 3100, 3000, 1670, 1640, 1580, 1540, 1510, 1470, 1380
4b*	3100, 3000, 1720, 1680, 1610, 1530, 1450, 1400, 1370, 1320
6	3000, 1720, 1650, 1570, 1500, 1450, 1400, 1380, 1320
7a	3400, 3200, 3050, 1720, 1680, 1660, 1540, 1580, 1500, 1440
7b	3300, 3100, 3000, 1720, 1660, 1620, 1590, 1520, 1460, 1420
7c	3400, 3200, 3000, 1720, 1660, 1580, 1520, 1450, 1370
7d	3300, 3050, 3000, 1720, 1650, 1630, 1590, 1510, 1460, 1410
9a	3330, 3000, 1675, 1620, 1600, 1560, 1540, 1470, 1450, 1390, 1370
9b	3330, 3000, 1685, 1610, 1560, 1470, 1440, 1390, 1370, 1340, 1320, 1260
9c	3350, 3000, 1670, 1615, 1560, 1490, 1460, 1420, 1380, 1330
9d	3300, 3000, 1690, 1620, 1570, 1500, 1470, 1385, 1310
11a	3400, 3270, 2900, 1660, 1620, 1590, 1530, 1450, 1430, 1350, 1330, 1295
11b	3400, 3300, 3000, 1690, 1660, 1620, 1570, 1470, 1440, 1360, 1350
11c	3300, 3000, 2900, 1680, 1600, 1570, 1540, 1430
11d	3350, 2900, 1690, 1660, 1620, 1560, 1470, 1440

*The IR spectrum of compound **4a** corresponded to that given in [3].

TABLE 3. ^{13}C NMR Spectra of the Synthesized Compounds

Compound	Chemical shifts (DMSO-d_6), δ, ppm
3b	14.8 ($NCH_2\underline{C}H_3$); 33.2 (C-2); 43.1 ($N\underline{C}H_2CH_3$); 43.4 (C-3); 97.7, 106.5, 127.8, 128.3, 130.7, 138.8, 146.4, 156.3; 160.3 (C=O); 162.8 (C=O); 191.3 (Ph–<u>C</u>=O)
3c	18.7 (3-CH_2); 26.1 (NCH_3); 38.7 (C-2); 39.9 (4-CH_2); 98.8, 104.6, 128.5, 128.9, 131.1, 140.0, 146.8, 155.0; 161.4 (C=O); 164.4 (C=O); 194.1 (C_6H_5–<u>C</u>=O)
7a	14.7 ($OCH_2\underline{C}H_3$); 33.4 (N CH_3); 48.0 (NCH_2); 60.1 ($O\underline{C}H_2Me$); 101.5, 104.5, 128.8, 129.1, 132.0, 138.9, 148.2, 159.0, 160.2; 164.6 (C=O); 193.1 (C_6H_5–<u>C</u>=O)
9a	25.7 (NMe); 99.4, 105.6, 113.0, 116.4, 123.5, 126.8, 126.9, 128.4, 128.5, 131.2, 131.5, 138.5, 144.1, 144.9; 159.4 (C=O); 163.8 (C=O); 191.2 (C_6H_5–<u>C</u>=O)
11b	26.2 (NCH_3); 32.6 (CH_2); 44.3 (CH_2NH); 58.4 (CH_2OH); 97.3, 107.1, 116.0, 118.2, 122.9, 125.7, 128.9, 129.5, 129.8, 130.2, 131.4, 142.8, 145.0, 149.8; 161.5; 164.5 (C=O); 169.6 (C=O
11d	26.3 (NCH_3); 43.2 (CH_2Het); 97.5, 109.3, 111.4, 116.0, 118.2, 123.2, 125.8, 129.2, 129.5, 129.7, 129.8, 131.6, 142.6, 144.1, 145.4, 149.3, 149.8, 161.6; 164.4 (C=O); 169.4 (C=O)

from the ^{13}C NMR spectra of the extremely characteristic signals of the carbonyl group carbon atom of the benzoyl fragment which, in the ^{13}C NMR spectra of 1,6-annelated derivatives of 5-alkylcarbamoyl-3-benzoyl-pyridin-2-one **3b,c**, **9a**, are observed in the region of 191.2-194.1 ppm.

TABLE 4. ^{1}H NMR Spectra of the Synthesized Compounds

Compound	Chemical shifts (DMSO-d_6) δ, ppm (SSCS, *J*, Hz)*
1	2
3a	2.75 (3H, d, *J* = 4.2, $NHC\underline{H}_3$); 3.91 (2H, m, H-2); 4.14 (2H, t, *J* = 9.3, H-3); 7.52 (5H, m, C_6H_5); 8.31 (1H, s, H-7); 8.90 (1H, br. s, N<u>H</u>Me); 9.39 (1H, br. s, 1-NH)
3b	1.08 (3H, t, *J* = 7.2, $NHCH_2C\underline{H}_3$); 3.21 (2H, m, $NHC\underline{H}_2CH_3$); 3.92 (2H, m, H-2); 4.13 (2H, t, *J* = 9.0, H-3); 7.52 (5H, m, C_6H_5); 8.32 (1H, s, H-7); 9.02 (1H, br. s, N<u>H</u>Et); 9.37 (1H, br. s, 1-NH)
3c	2.04 (2H, m, H-3); 2.75 (3H, d, *J* = 4.5, $NHC\underline{H}_3$); 3.52 (2H, m, H-2); 3.99 (2H, m, H-4); 7.39-7.65 (5H, m, C_6H_5); 8.31 (1H, s, H-8); 8.92 (1H, q, *J* = 4.5, N<u>H</u>Me); 10.88 (1H, br. s, 1-NH)
3d	1.07 (3H, t, *J* = 6.6, $NCH_2C\underline{H}_3$); 2.06 (2H, m, H-3); 3.47 (2H, m, $NC\underline{H}_2CH_3$); 3.53 (2H, m, H-2); 3.98 (2H, m, H-4); 7.40-7.61 (5H, m, C_6H_5); 8.32 (1H, s, H-8); 9.05 (1H, br. t, $N\underline{H}CH_2CH_3$); 10.87 (1H, br. s, 1-NH)
4b*[2]	1.28 (12H, m, $4CH_2C\underline{H}_3$), 4.18 (4H, q, *J* = 7.1, $2NC\underline{H}_2Me$), 4.37 (4H, q, *J* = 6.4, $2OC\underline{H}_2Me$), 7.52-7.65 (10H, m, $2C_6H_5$), 8.17 (2H, s, 4-2H)
6	1.30 (6H, t, *J* = 6.6, $2OCH_2C\underline{H}_3$); 2.96 (4H, t, *J*= 6.0, $2CH_2S$); 3.59 (6H, s, $2NCH_3$); 3.85 (4H, m, $2CH_2$); 4.26 (4H, q, *J* = 6.6, $2OC\underline{H}_2Me$); 7.45-7.54 (5H, m, C_6H_5); 8.44 (2H, s, 4-2H); 10.70 (2H, s, 2NH)
7a	1.15 (6H, t, *J* = 6.9, $2OCH_2C\underline{H}_3$); 3.40 (6H, s, $2NCH_3$); 3.65 (4H, br. s, $2NCH_2$); 4.07 (4H, q, *J* = 6.9, $2OC\underline{H}_2Me$); 7.45-7.56 (10H, m, $2C_6H_5$); 8.04 (2H, s, 2H-4); 9.34 (2H, s, 2NH)
7b	1.14 (12H, m, $4CH_2C\underline{H}_3$); 3.46 (4H, br. s, $2NCH_2$); 4.05 (8H, m, $4C\underline{H}_2Me$); 7.48-7.57 (10H, m, $2C_6H_5$); 8.05 (2H, s, 2H-4); 8.76 (2H, s, 2NH)
7c	1.15 (6H, t, *J* = 7.2, $2OCH_2C\underline{H}_3$); 2.03 (2H, t, *J* = 6.6, CH_2); 3.21 (4H, m, $2NCH_2$); 3.43 (6H, s, $2NCH_3$); 4.08 (4H, q, *J* = 7.2, $OC\underline{H}_2Me$); 7.44-7.61 (10H, m, $2C_6H_5$); 8.08 (2H, s, 2H-4); 9.43 (2H, s, 2NH)
7d	1.16 (12H, m, $4CH_2C\underline{H}_3$); 1.99 (2H, t, *J* = 6.3, CH_2); 3.17 (4H, m, $2NCH_2$); 4.08 (8H, m, $4C\underline{H}_2Me$); 7.48-7.62 (10H, m, $2C_6H_5$); 8.02 (2H, s, 2H-4); 8.89 (2H, s, 2 NH)
9a	2.85 (3H, d, *J* = 3.6, $NHC\underline{H}_3$); 7.48 (1H, m, H_{Ar}); 7.63-7.69 (6H, m, H_{Ar}); 7.84 (1H, m, H-9); 8.68 (1H, s, H-2); 8.70 (1H, m, H-6); 9.00 (1H, br. s, N<u>H</u>Me); 13.71 (1H, s, 10-NH)
9b	1.16 (3H, t, *J* = 6.3, $NHCH_2C\underline{H}_3$); 3.36 (2H, m, $NHC\underline{H}_2CH_3$); 7.49 (1H, m, H_{Ar}); 7.62-7.76 (6H, m, H_{Ar}); 7.88 (1H, m, H-9); 8.69 (1H, s, H-2); 8.71 (1H, m, H-6); 9.11 (1H, br. s, N<u>H</u>Et); 13.73 (1H, s, 10-NH)

TABLE 4 (continued)

1	2
9c	2.87 (3H, d, *J* = 2.7, NHC<u>H</u>$_3$); 7.66 (7H, m, H_{Ar}); 8.23 (1H, m, H-9); 8.74 (1H, s, H-2); 9.02 (1H, br. s, N<u>H</u>Me); 9.20 (1H, m, H-6)
9d	1.18 (3H, t, *J* = 6.6, NHCH$_2$C<u>H</u>$_3$); 3.34 (2H, m, NHC<u>H</u>$_2$CH$_3$); 7.68-7.83 (7H, m, H_{Ar}); 8.26 (1H, m, H-9); 8.78 (1H, s, H-2); 9.15 (1H, br. s, N<u>H</u>Et); 9.24 (1H, m, H-6)
11a	2.79 (3H, d, *J* = 4.2, NHC<u>H</u>$_3$); 3.51 (2H, br. s, CH$_2$); 3.67 (2H, br. s, CH$_2$); 5.25 (1H, br. s, OH); 7.37-7.82 (8H, m, H_{Ar}); 7.98 (1H, s, H-2); 8.54 (1H, d, *J* = 7.8, H-6); 9.00 (1H, q, *J* = 4.2, N<u>H</u>Me); 12.82 (1H, br. s, NH)
11b	1.85 (2H, t, *J* = 6.3, CH$_2$); 2.80 (3H, d, *J* = 4.2, NHC<u>H</u>$_3$); 3.50-3.61 (4H, m, 2CH$_2$); 4.62 (1H, t, *J* = 4.8, OH); 7.36-7.80 (8H, m, H_{Ar}); 7.98 (1H, s, H-2); 8.54 (1H, d, *J* = 7.8, H-6); 9.00 (1H, q, *J* = 4.2, N<u>H</u>Me); 12.74 (1H, br. s, NH)
11c	2.78 (3H, d, *J* = 4.8, NHC<u>H</u>$_3$); 2.99 (2H, t, *J* = 6.0, C<u>H</u>$_2$Ph); 3.69 (2H, m, CH$_2$NH); 7.23-7.52 (13H, m, H_{Ar}); 7.93 (1H, s, H-2); 8.52 (1H, d, *J* = 7.5, H-6); 8.96 (1H, q, *J* = 4.8, N<u>H</u>Me); 12.64 (1H, t, *J* = 6.6, NH
11d	2.80 (3H, d, *J* = 4.5, NHC<u>H</u>$_3$); 4.69 (2H, d, *J* = 4.5, CH$_2$Het); 6.37 (1H, m, Het); 6.44 (1H, m, Het); 7.36-7.73 (9H, m, H_{Ar}); 8.01 (1H, s, H-2); 8.52 (1H, d, *J* = 7.5, H-6); 8.95 (1H, q, *J* = 4.5, N<u>H</u>Me); 12.85 (1H, br. t, NH)

* The ^{1}H NMR spectrum of compound **4a** corresponded to that given in [3], the ^{1}H NMR spectrum of compound **6** was recorded in $CDCl_3$.

The structure of compound **11c** was investigated by X-ray structural analysis (Table 5 and Fig. 1). An interesting special feature of its molecular structure is the formation of the fairly stable intramolecular hydrogen bonds N–H···N and N–H···O, closing the six-membered rings N(4)C(14)C(8)C(7)N(2)H(4) and N(3)C(10–12)O(2)H(3).

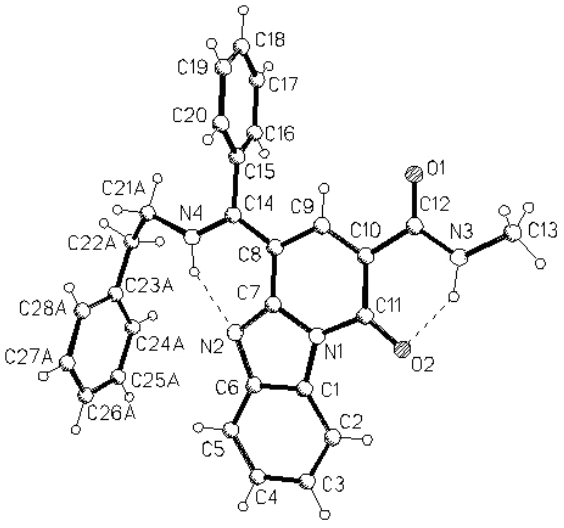


Fig. 1. General form of the molecule of 3-methylcarbamoyl-4-oxo-1-(2-phenylethylamino) phenylmethylidene-1,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine **11c**.

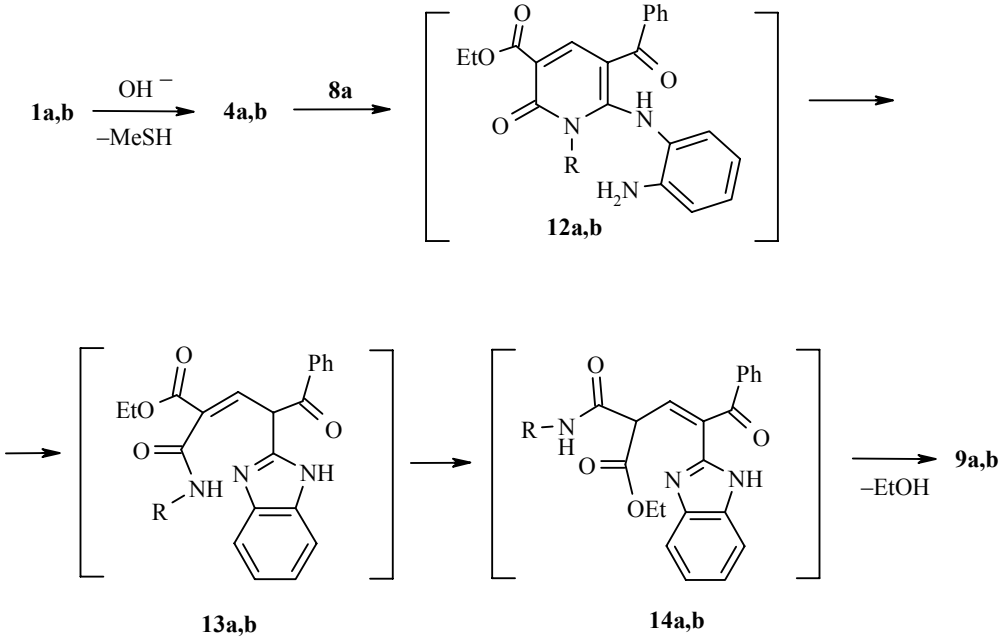
On the basis of the experimental data the following scheme may be proposed for the mechanism of recyclization of dihydropyridin-2-ones **1a,b** into bicyclic derivatives of benzimidazole **9a,b**. It is probable that the first stages of the reaction are the hydrolysis and amination of dihydropyridin-2-ones **1a,b**, respectively, into compounds **4a,b** and intermediates **12a,b**. It should be mentioned that the latter, in all appearances, may also be

Table 5. Main Bond Lengths in Compound **11c**

Bond	*l*, Å	Bond	*l*, Å
C(1)–N(2)	1.328(2)	C(7)–C(8)	1.391(2)
C(1)–C(2)	1.400(3)	C(8)–N(5)	1.353(2)
C(2)–C(3)	1.363(3)	C(8)–N(4)	1.386(2)
C(3)–N(1)	1.376(2)	C(9)–N(5)	1.321(2)
N(1)–N(2)	1.377(2)	C(9)–C(10)	1.419(3)
N(3)–N(4)	1.3597(19)	C(10)–C(11)	1.357(3)
C(6)–N(3)	1.338(2)	C(11)–N(4)	1.368(2)
C(6)–C(7)	1.399(2)		

obtained directly on amination of dihydropyridin-2-ones **1a,b** with *o*-phenylenediamine **8a** [1]. The intermediate products **12a,b** are possibly subject to intramolecular nucleophilic attack by the free amino group of the *o*-phenylenediamine fragment at the endocyclic N atom, being converted in this way into benzimidazole derivatives **13a,b**. The latter, to all appearances, are transformed into the bicyclic heterocompounds **9a,b** through the conformation of **14a,b** most advantageous for intramolecular cyclization. Evidently, the recyclizations of dihydropyridin-2-ones **1a,b** into 5-oxo-1,2,3,5-tetrahydroimidazo[1,2-*a*]pyridines **3a,b**, 6-oxo-1,2,3,5-tetrahydro-2H-pyrido[1,2-*a*]pyrimidines **3c,d** and 4-oxo-4*H*-benzo[4,5][1,3]thiazolo[3,2-*a*]pyridines **9c,d** are brought about in a similar manner.

It is known that substituted benzo[4,5]imidazo[1,2-*a*]pyridines and benzo[4,5][1,3]thiazolo[3,2-*a*]pyridines display fungicidal [7, 8], antimicrobial [9], antitumor [8, 10], antiviral [11], and antibacterial [8] properties. As a result of the investigations carried out by us new possibilities have been found for the synthesis and functionalization of 1,6-annelated derivatives of 3-alkylcarbamoyl-5-benzoylpyridin-2-ones **3a-d**, **9a-d** which are promising biologically active compounds.



12 –14 a R = Me, **b** R = Et

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian-300 instrument (300 and 75 MHz respectively), internal standard was TMS. The IR spectra were recorded on a UR-20 instrument in KBr disks.

X-Ray structural investigation of a monocrystal of 11c, grown in ethanol, with linear dimensions 0.48×0.28×0.12 mm was carried out at room temperature on a Bruker Smart Apex II diffractometer (λMo$K\alpha$ radiation, graphite monochromator, $\theta_{max} = 26.56^{o}$, segment of sphere $-11 \le h \le 16$, $-13 \le k \le 15$, $-17 \le l \le 17$). In all 14214 reflections were collected, of which 4436 were symmetrically independent (*R*-factor averaging 0.034). Crystals of compound **11c**: $C_{28}H_{24}N_4O_2$, M = 448.51, monoclinic, space group $P2_1/n$ (No. 14), a = 13.2132 (10), b = 12.6692(9), c = 14.7662(13) Å, β = 111.446(3)°, V = 2300.7(3) Å^3, Z = 4, d_{calc} = 1.295, μ = 0.084 mm^{-1}, $F(000)$ = 944. The structure was solved by the direct method and refined by least squares in a full matrix anisotropic approximation using the SHELXS97 and SHELXL97 programs [12, 13]. The atoms of the phenyl rings C(23-29), and also atoms C(21) and C(22) and the protons associated with them, were randomized in the two positions A and B with populations 55 and 45% respectively. All the hydrogen atoms linked with carbon atoms were positioned geometrically, and the H(N) atoms participating in the formation of hydrogen bonds were shown objectively and refined isotropically. In the refinement 2666 reflections with $I > 2\sigma(I)$ were used (364 parameters being refined, number of reflections per parameter 7.32, the weighting scheme used was $\omega = 1/[\sigma^2(F_0^2) + (0.1P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$). An absorption correction was introduced according to the SADABS program (ratio of minimum to maximum correction T_{min}/T_{max} = 0.85). The final values of the divergence factors were $R1(F^2)$ 0.0955, $R_w(F^2)$ 0.1679, *GOOF* 0.995 for all reflections and $R1(F^2)$ 0.0492, $R_w(F^2)$ 0.1331, GooF 0.993 for reflections with $I > 2\sigma(I)$. The residual electron density from the Fourier difference series after the last ring of refining was 0.25 and -0.18 e/Å^3. A complete set of the X-ray structural data for compound **11c** has been deposited in the Cambridge structural data bank (CCDC 6839232).

6-Alkylcarbamoyl-8-benzoyl-5-oxo-1,2,3,5-tetrahydroimidazo[1,2-*a*]pyridines 3a,b, 7-Alkylcarbamoyl-9-benzoyl-6-oxo-1,2,3,5-tetrahydro-2H-pyrido[1,2-*a*]pyrimidines 3c,d, 3-Alkylcarbamoyl-1-benzoyl-4-oxo-4,10-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridines 9a,b, 3-Alkylcarbamoyl-1-benzoyl-4-oxo-4H-benzo[4,5][1,3]thiazolo[3,2-*a*]pyridines 9c,d. A solution of 1,2-dihydropyridin-2-one **1a,b** (1 mmol) and amine **2a,b** (1.5 mmol) or amine **8a,b** (1.0 mmol) in 2-propanol (4 ml) was boiled for 2-6 h, cooled, and the precipitate of compounds **3a-d**, **9a-d** filtered off. Dipyridyl oxides **4a,b** were isolated on evaporating the filtrate.

1-Alkyl-6-(1-alkyl-5-benzoyl-3-ethoxycarbonyl-2-oxo-1,2-dihydropyrid-6-yl)oxy-5-benzoyl-3-ethoxycarbonyl-2-oxo-1,2-dihydropyridines 4a,b were obtained by the method of [3].

N,N'-Di(1-alkyl-5-benzoyl-3-ethoxycarbonyl-2-oxo-1,2-dihydropyrid-6-yl)-1,2-diaminoethane (1,3-diaminopropane) 7a-d. A solution of amine **2a,b** (0.5 mmol) in 2-propanol (3 ml) was added dropwise with stirring to a solution of 1,2-dihydropyridin-2-one **1a,b** (dipyridyl oxide **4a,b**) (1 mmol) in 2-propanol (3 ml). The reaction mass was maintained at 20°C for 3 h and the solid compound **7a-d** filtered off.

Recyclization of N,N'-Di(1-alkyl-5-benzoyl-3-ethoxycarbonyl-2-oxo-1,2-dihydropyrid-6-yl)-1,2-diaminoethane (7a) into 8-Benzoyl-6-methylcarbamoyl-5-oxo-1,2,3,5-tetrahydroimidazo[1,2-*a*]pyridine (3a). A solution of compound **7a** (0.626 g, 1 mmol) and diaminoethane **2a** (0.18 g, 3 mmol) in 2-propanol (4 ml) was boiled for 5 h, cooled, and solid compound **3a** was filtered off. Yield was 0.559 g, 81%).

Di[2'-(5-benzoyl-3-ethoxycarbonyl-1-methyl-2-oxo-1,2-dihydropyrid-6-yl)aminoethyl] Disulfide (6). A solution of 1,2-dihydropyridin-2-one **1a** (0.331 g, 1 mmol), 1-amino-2-mercaptoethane hydrochloride (0.170 g, 1.5 mmol), and triethylamine (0.152 g, 1.5 mmol) in 2-propanol (4 ml) was boiled for 3 h, cooled, and solid compound **6** was filtered off.

Amination of 4-Oxo-4,10-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine (9a) with Alkylamines 10. A mixture of compound **9a** (0.345 g, 1 mmol) and alkylamine **10** (3 mmol) was maintained at 120-140°C for 10-20 min, cooled, boiled with 2-propanol (3 ml), cooled, and solid compound **11** was filtered off.

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