Molecular Rearrangement of 1-Substituted 3-Aminoquinoline-2,4-diones in Their Reaction with Urea and Nitrourea Synthesis and Transformations of Reaction Intermediates

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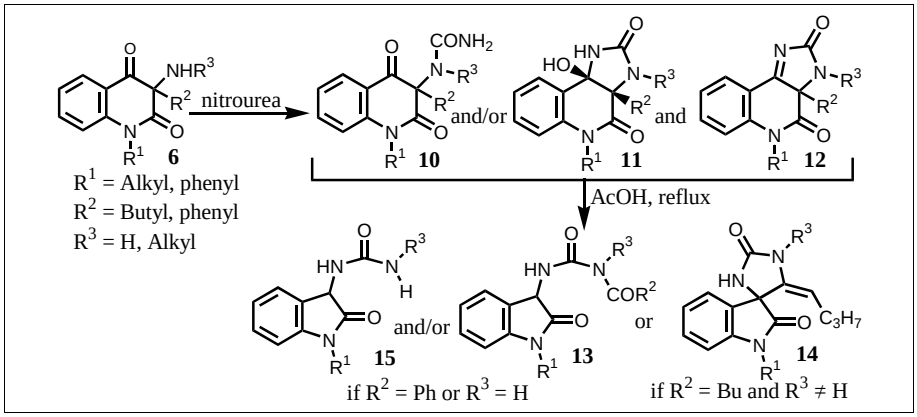

1-Substituted 3-alkyl/aryl-3-amino-1*H*,3*H*-quinoline-2,4-diones (**6**) react with nitrourea to give 3-ureido-1*H*,3*H*-quinoline-2,4-diones (**10**), 9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones (**11**), and 3,3a-dihydro-5*H*-imidazo[4,5-*c*]quinoline-2,4-diones (**12**). Compounds **11** were dehydrated to **12** by the action of phosphorus pentoxide. All three types of compounds rearrange in boiling acetic acid to give three different types of products of molecular rearrangement. A proposed reaction mechanism is discussed.

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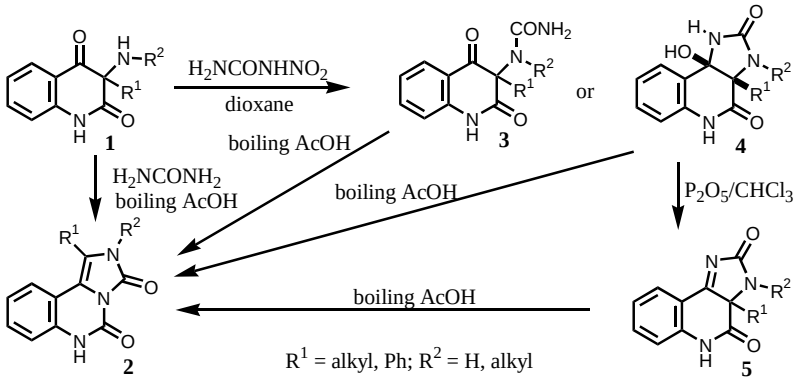
Recently, molecular rearrangement of 1-unsubstituted 3-amino-1*H*,3*H*-quinoline-2,4-diones (**1**) in a reaction with urea in boiling acetic acid, producing 2,6-dihydro-imidazo[1,5-*c*]quinazoline-3,5-diones (**2**) (Scheme 1), has been described [1]. Nitrourea reacts with compounds **1** in acetic acid in the same manner as urea. However, as nitrourea is converted to isocyanic acid much more readily than urea, we attempted to obtain assumed reaction intermediates by adapting reaction conditions. The reaction of compounds **1** with nitrourea in dioxane or aqueous dioxane produced new 3-ureido-1*H*,3*H*-quinoline-2,4-diones (**3**) or 9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinol-ine-2,4-diones (**4**) [2]. Dehydration of compounds **4** yields highly unstable

Scheme 1



3a-alkyl/aryl-3,3a-dihydro-5*H*-imidazo[4,5-*c*]quinoline-2,4-diones (**5**) (Scheme 1). Compounds **3**, **4** and **5** rearrange to imidazoquinazoline derivatives **2** by boiling in acetic acid [2] and, therefore, they are anticipated intermediates of the molecular rearrangement of compounds **1** in their reaction with urea. Compounds analogous to **3** and **4** were also obtained from **1** by a reaction with isocyanates [3].

On the contrary, compounds **6** substituted in position 1 with an alkyl or aryl group react with urea in boiling acetic acid differently to give three different types of compounds [4]. Depending on the character of substitution in starting compounds **6**, either a molecular rearrangement of the quinolone system to indolinone system occurs with formation of 3-(3-acylureido)-2,3-dihydro-1*H*-indol-2-ones (**7**) or 4-alkylidene-1´*H*-spiro[imidazolidine-5,3´-indole]-2,2´-diones (**8**), or expected 3,3*a*-dihydro-5*H*-imidazo[4,5-*c*]quinoline-2,4-diones (**9**) arise (Scheme 2). As opposed to analogous compounds **5**, compounds **9** are relatively stable.

Owing to the fact that compounds **1** produced new heterocyclic systems **3** and **4** with high yields by reacting with nitrourea in dioxane or with isocyanates, we also decided to study an analogous reaction of 1-substituted α-aminoketones **6**. Our first aim was to find whether compounds to be formed would be corresponding 3-ureido derivatives or their cyclic carbinolamide forms, and also to verify what influence is exerted on the course of reaction by substituents in positions 1,3, and at the amino group in position 3. A further objective was to find if the reaction products of compounds **6** with nitrourea would transform to compounds **7** and **8** by boiling in acetic acid and may thus be regarded as intermediates of molecular rearrangement.

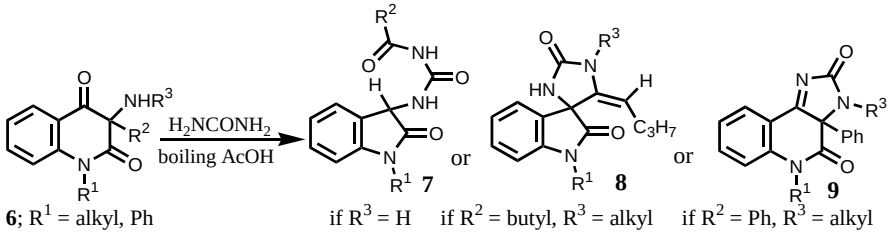
Results and Discussion.

Starting aminoketones **6** were prepared according to the general protocol described in the literature [5]. Reactions of compounds **6** with nitrourea (Scheme 3) were performed analogously to the described reactions [2] of compounds **1**, that is by boiling in dioxane. Results are presented in Table I.

Already first results of nmr spectra measurements indicated the reaction of compounds **6** with nitrourea proceeds similarly to that of compounds **1** [2] and three different types of products arise (Scheme 3). Ureido derivatives **10** are formed only when a primary amino group (**10a**,**b**) is present in position 3 of starting α-aminoketones. The high yield of **10b** is surprising because an acyclic isomer was formed by reacting analogous compounds **1** with nitrourea merely in case a butyl group was present in position 3 of the starting primary amine [2]. Cyclic amidocarbinols **11a**,**b** arose together with ureido derivatives **10a**,**b**, even though compound **11a** appeared only in negligible quantity.

The formation of a mixture of cyclic and acyclic isomers during hydration of 3-(thiocyanatoacetyl)-

Scheme 2



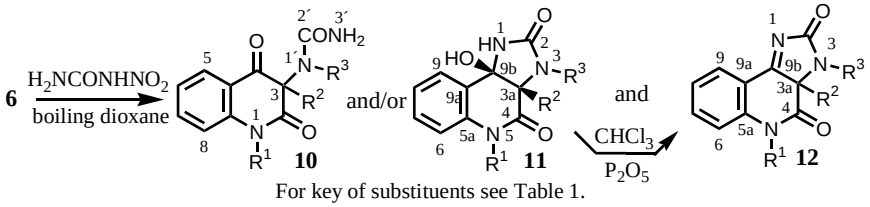
6; R^1 = alkyl, Ph if R^3 = H if R^2 = butyl, R^3 = alkyl if R^2 = Ph, R^3 = alkyl

Table 1

Reaction of N-Substituted α-Aminoketones **6a-g** with Nitrourea.

Entry		Starting compound **6**			Reaction time (hrs)	Isolated compounds (yield %)
		R^1	R^2	R^3		
1	**6a**	Me	Bu	H	2	**10a** (55), **11a** (1.5)
2	**6b**	Me	Ph	H	5	**10b** (58), **11b** (14)
3	**6c**	Me	Bu	Bu	2.5	**6c** (43), **11c** (25), **12c** (3)
4	**6d**	Me	Ph	Bu	8	**11d** (70), **12d** (12)
5	**6e**	Me	Ph	*c*-Hex	14	**6e** (15), **11e** (33), **12e** (17)
6	**6f**	Ph	Bu	Bu	3	**6f** (17), **11f** (24), **12f** (22)
7	**6g**	Ph	Ph	Bu	3	**6g** (48), **11g** (27)
8	**6g**	Ph	Ph	Bu	15	**6g** (6), **11g** (18), **12g** (22)

Scheme 3



For key of substituents see Table 1.

azetidin-2-ones was described by Sápi *et al*. [6]. On the other hand, formation of cyclic isomers of 3-alkyl/aryl-1*H*,3*H*-quinoline-2,4-diones substituted with a carbamoylthio group in position 3 was not observed [7]. Reactions of secondary α-aminoketones **6c**-**g** with nitrourea proceeded independently of the character of substituents R^1, R^2 and R^3, merely with formation of cyclic isomers **11c**-**g**.

Only several examples of the conversion of α-aminoketones to 3-unsubstituted 4-hydroxy-tetrahydroimidazol-2-ones are described in literature. The oldest papers on this problem deal with compounds of 3-aminobornan-2-one series [8,9]. With the exception of our previous paper [2], only two papers have been recently published describing this conversion in 4-amino-3-oxotetrahydrothiophene series [10,11]. Acid catalyzed ring opening of 4-hydroxy-tetrahydroimidazol-2-ones under formation of 2-ureidoketones was described in only one case [8].

The structure of isolated products unambiguously followed from results of ^{13}C nmr spectra. Compounds **10** exhibit in the ^{13}C nmr spectrum a characteristic signal of keto group C-4 in the 191-194 ppm range (Table 2), while this signal is missing in the ^{13}C nmr spectra of compounds **11** and, instead, a signal of sp^3 hybridized carbon atom C-9b appears in the 82-90 ppm range (Tables 3 and 4). Based on 2D experiments, all signals were assigned to their respective atoms (Tables 2 - 4).

The fragmentation behaviour of compounds **10-12** and **15** in APCI mass spectra follows the similar rules as described in our previous works [1-4]. There is no difference between mass spectra of compounds from **10** and **11** series (*e.g*., **10a** and **11a**, **10b** and **11b**), which suggests that compounds **10** are converted to **11** during the ionization process and then the fragmentation behaviour is identical. The presence of hydroxyl group at 9b position causes an extensive fragmentation and low relative abundance of quasimolecular ions unlike compounds **12** without hydroxyl group, where the $[M+H]^+$ ions are the base peaks and the fragmentation in the first-order spectra is negligible. The molecular weights are determined in all cases on the basis of $[M+H]^+$ ions in positive-ion and $[M-H]^-$ ions in negative-ion mode of the first-order APCI mass spectra. The typical neutral losses are the following: 17 (NH_3), 18 (H_2O), 28 (CO), 43 (NHCO), 56 (butene), 58 (butane), 60 (urea), 73 (butylamine), 99 (butylisocyanate), etc.

Table 2

^1H and ^{13}C Chemical Shifts (δ, ppm)
of Compounds **10a,b**, and **15e** in DMSO-d_6

Position	**10a**		**10b**		**15e**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
2	–	172.1	–	170.9	–	175.1
3	–	67.2	–	71.1	5.00	52.7
3a	–	–	–	–	–	128.7
4	–	193.6	–	191.2	7.22	123.3
4a	–	120.3	–	120.0	–	–
5	7.92	127.3	7.85	127.0	7.04	122.0
6	7.26	122.7	7.22	123.0	7.31	128.3
7	7.77	136.1	7.75	136.2	6.99	108.2
7a	–	–	–	–	–	143.8
8	7.42	115.7	7.44	115.9	–	–
8a	–	142.8		142.4	–	–
1´(NH)	7.08	–	7.42	–	6.10	–
2´ [a]	–	157.9	–	158.2	–	156.8
3´(NH)	–	–	–	–	6.56	–
3´(NH_2)	5.72	–	5.84	–	–	–
1´(R^1)	3.44	29.9	3.55	30.2	3.14	26.1
1´(R^2) [b]	1.71	36.7	–	134.7	3.37	48.2
2´(R^2) [b]	1.17	24.7	7.34	126.8	[c]	33.3
3´(R^2) [b]	1.17	22.2	7.41	129.1	[c]	25.3
4´(R^2) [b]	0.79	13.7	7.41	129.2	[c]	24.6

[a] Position 2 in the case of **15e**; [b] At R^3 in the case of **15e**; [c] Cyclohexane methylene protons (10H) occur in region of 1.15-1.92 ppm (δ).

Apart from compounds **10** and/or **11**, also unreacted starting α-aminoketones **6** and dehydration products **12** (Table 1) were isolated from raw products of the reaction of **6** with nitrourea. Prolonged reaction time admittedly brings about a subsequently reduced content of unreacted starting compound **6** in the reaction mixture, but, at the same time, the proportion of dehydration product **12** is increased (see entries 7 and 8 in Table 1). A partial transformation of **11g** to **12g** was already observed during long-term heating of its benzene solution. Thermal instability of compounds **11** is also indicated by double melting point determined in the case of **11d** and **11e**.

Compounds **12d,e,g** were already isolated earlier [4] as products of the reaction of corresponding amines **6d,e,g** with urea in acetic acid. Structure of new compounds **12c,f** was established from analogy of their nmr spectra to nmr spectra of previously described compounds **12d,e,g**

Table 3

^{1}H and ^{13}C Chemical Shifts (δ, ppm) of Compounds **11a**-**e** in DMSO-d_6

Position	**11a**		**11b**		**11c**		**11d**		**11e**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1	7.29 [a]	–	7.56 [a]	–	7.29	–	7.57	–	7.27	–
2	–	160.2	–	160.4	–	158.9	–	160.6	–	159.2
3	7.16 [a]	–	7.72 [a]	–	–	–	–	–	–	–
3a	–	66.9	–	70.5	–	69.1	–	75.4	–	76.4
4	–	171.3	–	170.6	–	170.7	–	170.0	–	169.8
5a	–	136.9	–	137.1	–	136.5	–	136.9	–	136.9
6	7.19	114.6	7.34	115.1	7.15	114.5	7.30	115.0	7.28	114.8
7	7.42	129.7	7.51	130.0	7.41	129.6	7.45	130.0	7.44	129.9
8	7.15	122.7	7.19	123.3	7.18	123.0	7.13	123.1	7.11	123.0
9	7.72	126.7	7.70	127.2	7.78	126.1	7.61	127.4	7.60	127.3
9a	–	125.1	–	124.5	–	125.7	–	124.0	–	124.1
9b	–	83.6	–	84.5	–	82.6	–	89.5	–	83.9
1´ (R^1)	3.37	29.9	3.46	30.0	3.40	29.4	3.51	29.8	3.51	29.9
1´ (R^2)	1.74	31.9	–	135.6	1.92	31.3	–	133.5	–	134.0
2´ (R^2)	1.01	25.0	7.21	126.5	1.00	24.5	7.24	128.0	7.24	127.9
	0.97				0.76					
3´ (R^2)	1.14	22.6	7.28	127.9	1.17	22.6	7.34	128.4	7.33	128.7
4´ (R^2)	0.75	13.7	7.28	127.8	0.72	13.9	7.34	128.3	7.33	128.2
1´ (R^3)	–	–	–	–	3.53	40.4	3.28	44.1	2.94	55.2
					3.35		3.02			
2´ (R^3)	–	–	–	–	1.61	32.7	2.03	31.0	[b]	[b]
					1.50		1.65			
3´ (R^3)	–	–	–	–	1.33	19.9	1.23	20.3	[b]	[b]
4´ (R^3)	–	–	–	–	0.95	13.9	0.89	13.9	[b]	[b]
OH	6.56	–	6.37	–	6.57	–	6.55	–	6.45	–

[a] The assignment may be opposite; [b] N-Cyclohexyl group is not „symmetrical“ on the NMR time scale, all hydrogen and carbon atoms are non-equivalent and considerably broadened (δ_H = 2.32 – 1.01, δ_C = 32.0, 28.9, 26.7, 26.4, 25.7).

(Table 4). Results of attempts at preparing compounds **12** by dehydrating compounds **10** and **11** with phosphorus pentoxide in chloroform are presented in Table 5. Consistently with dehydration results of compounds **3** and **4**, when we did not succeed in obtaining anticipated products **5a,b** [2], we were also unsuccessful in obtaining dehydrated products **12a,b** from analogous compounds **10a**,**b** and **11b**. Complex mixtures of compounds arose and these could not be chromatographically separated.

Dehydration of compounds substituted at the nitrogen atom in position 3 (**11c-g**) proceeded without problems and corresponding compounds **12c-g** were obtained in high yields (Table 5). Stability of 1-substituted imidazoquinolinediones **12** is substantially higher than that of analogous compounds **5**. Comparing results of Entries 5 and 6 (Table 5) is worth attention; prolonged reaction time when dehydrating **11c** effects a subsequent molecular rearrangement of primarily formed product **12c** to spiro-compound **14c**. When dehydrating other compounds **11** no formation of rearranged products was observed.

As assumed, products of molecular rearrangement arise by boiling compounds **10**, **11** and **12** in acetic acid (Scheme 4, Table 6). In accord with results of molecular rearrangement of compounds **6** when reacted with urea in acetic acid [4], analogous compounds **11** and **12** also yield derivatives of indol-2-one by boiling in acetic acid (Scheme 4). Secondary α-aminoketones **6**, bearing a phenyl group in position 3, produced imidazoquinolinediones **9** by a reaction with urea in acetic acid, and indole derivatives **7** were isolated in merely insignificant quantity as products of molecular rearrangement [4]. From Table 6 it is obvious that also in the reaction of compounds **11d,e,g** and **12d,e,g** (Table 6, Entries 6-9 and 12-13) in boiling acetic acid the yield of rearranged products **13** and/or **15** was relatively low while a considerable quantity of **12**, largely stable under given reaction conditions, was recovered. In the reactions of **11e** and **12e** (Table 6, Entries 8-9), the primary product of the rearrangement is certainly compound **13e**. However, under given reaction conditions, it is hydrolyzed to **15e** and benzoic acid. At the same time, hydrolysis of ureido group under formation of N-cyclohexyl benzamide takes place.

Compounds **12d,g**, **13a,b,d** and **14c,f** were tested for their enzyme inhibition activity against cyclin-dependent kinase (CDK) and their toxicity against cell lines K-562 (chronic myeloid leukemia) and MCF7 (breast carcinoma). No compound exhibits any significant activity against CDK and only one compound (**14f**)

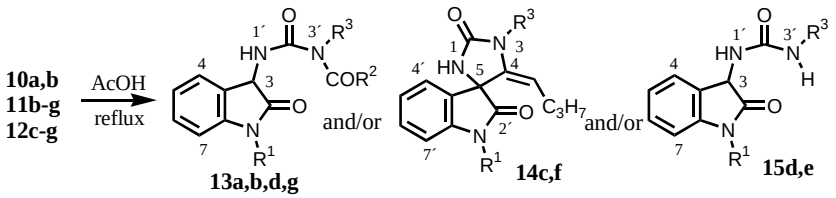
Table 4

^{1}H and ^{13}C Chemical shifts (δ, ppm) of Compounds **11f-g** and **12c,f** in DMSO-d_6

Position	**11f**		**11g**		**12c**		**12f**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1	7.45	–	7.75	–	–	–	–	–
2	–	159.0	–	160.6	–	166.1	–	166.3
3a	–	69.5	–	75.8	–	75.0	–	75.3
4	–	171.0	–	170.2	–	168.2	–	168.4
5a	–	137.5	–	137.8	–	141.5	–	142.6
6	6.17	115.5	6.37	116.2	7.48	116.6	6.45	117.2
7	7.22	129.3	7.26	129.7	7.79	135.5	7.60	135.1
8	7.15	123.2	7.12	123.3	7.37	124.0	7.34	124.0
9	7.83	126.6	7.70	127.8	7.91	126.1	7.98	126.3
9a	–	125.3	–	123.9	–	116.3	–	116.0
9b	–	83.1	–	84.3	–	184.6	–	184.4
1´ (R^1)	–	137.9	–	137.9	3.37	29.8	–	137.0
2´ (R^1)	7.20	129.0	7.40	129.0	–	–	[a]	[a]
3´ (R^1)	7.63	130.3	7.68	130.3	–	–	[a]	[a]
4´ (R^1)	7.55	128.7	7.59	128.8	–	–	[a]	[a]
1´ (R^2)	2.03	31.4	–	133.3	2.22	35.3	2.39	35.2
	2.01				1.81		2.16	
2´ (R^2)	1.20	24.7	7.51	128.2	0.84	24.3	0.87	24.4
					0.70		0.80	
3´ (R^2)	1.26	22.7	7.45	128.4	1.14	21.2	1.22	21.3
4´ (R^2)	0.80	13.7	7.38	128.5	0.74	13.7	0.80	13.7
1´ (R^3)	3.47	40.6	3.26	44.1	3.51	41.4	3.51	41.4
	3.35		3.01		3.37		3.34	
2´ (R^3)	1.63	32.6	2.00	30.9	1.81	30.6	1.79	30.6
	1.52		1.65					
3´ (R^3)	1.34	19.9	1.27	20.2	1.40	20.0	1.38	19.9
	1.30		1.21					
4´ (R^3)	0.86	13.9	0.86	13.8	0.98	13.7	0.95	13.7
OH	6.71	–	6.71	–	–	–	–	–

[a] N-Phenyl group is not „symmetrical“ on the NMR time scale, all hydrogen and carbon atoms are non-equivalent and considerably broadened.

Scheme 4



For key of substituents see Table 1.

exhibits high toxicity against K-562 and MCF7 (GI_{50} = 22 and 25 μmoles, respectively). Analogous compound **14c**, substituted with methyl group at N-1, exhibits essentially lower toxicity against K-562 and MCF7 (GI_{50} > 100 and > 167 μmoles, respectively).

In our earlier work [4] we sought to describe the mechanism of molecular rearrangements of compounds **6** during their reaction with urea by means of two different paths, depending on whether starting α-aminoketone **6** bore a primary or secondary amino group. From results presented in Table 6 it unambiguously follows that the anticipated intermediates of molecular rearrangement are compounds **11** and/or **12** because couples of identically substituted **11** or **12** yield the same reaction product. Compounds of type **12** derived from primary amino derivatives **6** could not be obtained by dehydrating compounds **11a,b** (Table 5). Thence it may be considered that rearrangement in acetic acid occurs with these compounds already in the stage of amidocarbinol **11**. The significant role of compound **11** in rearrangement mechanism is also indicated by the fact that greater yields of rearranged product were obtained when **11** was the starting compound (compare Entries 4, 5 and 10, 11 in Table 6). A proposed reaction mechanism is presented in Scheme 5.

Table 5

Dehydration of **10** and **11** with Phosphorus Pentoxide

Entry	Starting compound	Reaction time (min)	Yield of **12** (%)
1	**10a**	60	[a]
2	**10a**	300	[a]
3	**10b**	45	[a]
4	**11b**	45	[a]
5	**11c**	20	58
6	**11c**	30	17 [b]
7	**11d**	30	69
8	**11d**	20	76
9	**11e**	20	85
10	**11f**	15	72
11	**11g**	30	68
12	**11g**	30	75

[a] Inseparable mixture of several compounds arises; [b] Compound **14c** (15%) was also obtained.

Table 6

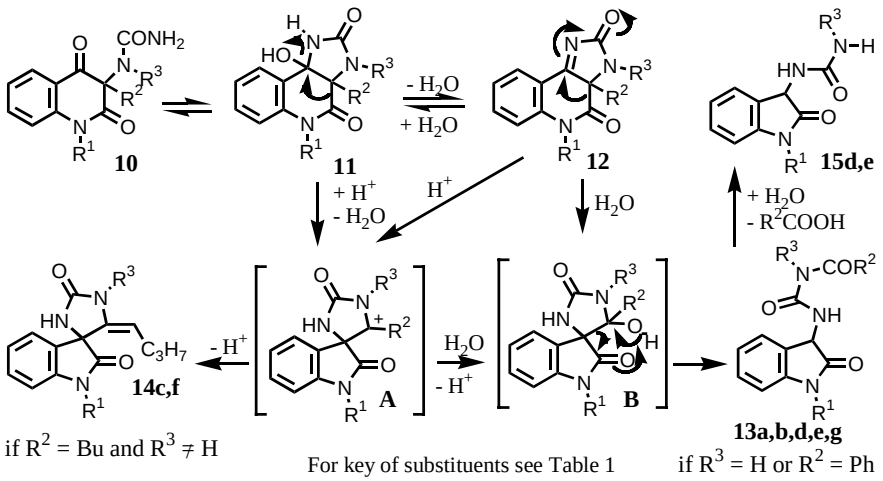
Rearrangement of Compounds **10**, **11**, and **12** in Boiling Acetic Acid

Entry	Starting compound	Reaction time (hrs)	Isolated compounds (yield %)
1	**10a**	3.5	**13a** (41)
2	**10b**	2	**13b** (69)
3	**11b**	1.5	**13b** (61)
4	**11c**	1	**14c** (64)
5	**12c**	1	**14c** (43)
6	**11d**	2	**12d** (25), **15d** (9)
7	**12d**	5	**12d** (69), **13d** (7), **15d** (6)
8	**11e**	1.5	**15e** (39), [a]
9	**12e**	2	**12e** (11), **15e** (37), [b]
10	**11f**	1	**14f** (82)
11	**12f**	2.5	**14f** (75)
12	**11g**	1.5	**11g** (10), **12g** (19), **13g** (31)
13	**12g**	1.5	**12g** (25), **13g** (28)

[a] Benzoic acid (40%) and *N*-cyclohexylbenzamide (6%) were also isolated; [b] Benzoic acid (51%) and *N*-cyclohexylbenzamide (4%) were also isolated.

Compound **10** is in equilibrium with compound **11**. We have already described similar equilibrium between acyclic ureido derivatives and cyclic amidocarbinols [2,3]. Dehydration of **11** gives imidazoquinolinedione **12** but, this change can be reversible. The key intermediate is carbocation **A**, which arises by nucleophilic 1,2-shift of secondary amide group in **11** or **12**. Intermediate **A** can be stabilized in two ways. The first is elimination of proton from the butyl group (R^3) with formation of products **14c**,**f** that can take place only in those cases when substituent R^2 is an alkyl and R^3 is not hydrogen.

Scheme 5



The second way of transforming intermediate **A** (in case R^2 is phenyl or R^3 is hydrogen) is formation of C=N or C=N$^+$ double bond. After addition of water, unstable carbinolamide **B** arises, in which a splitting of the labile C-C bond between carbinolamide and lactame groupings proceeds to give acylureido derivatives **13a**,**b**,**d**,**e**,**g**. Ureido derivatives **15d**,**e** are formed through hydrolysis of benzoylureido derivatives **13d**,**e**, originated benzoic acid was isolated (Table 6, Entries 8 and 9). In our previous work [4], reactions of 3-phenyl-substituted aminoketones **6** with urea produced compounds **13** and **15** in merely trace quantities as side-products, the principal products being compounds **12**. When we now proceeded from compounds **11d**,**e**,**g** and **12d**,**e**,**g,** corresponding products **13** and **15** were obtained in greater quantities but reaction yield was nevertheless low (Table 6, Entries 6-9 and 12-13). That indicates the presence of phenyl group in position 3a is a stabilizing factor for compounds **11** and **12** derived from secondary amines.

For generalization of molecular rearrangement of 3-ureidoquinolinediones and 9b-hydroxy-3,3a,5,9b-tetrahydro-

1*H*-imidazo[4,5-*c*]quinoline-2,4-diones it will be necessary to study also rearrangements of compounds **10** and **11** analogues bearing an alkyl or aryl group in position 3´. At the present time, we are starting work on this problem.

The conversion of compounds **10** and **11** to spiro compounds **14** or 3-ureidoindoles **13** and **15**, respectively, is not merely interesting from a theoretical point of view but, owing to the simple reaction protocol and relatively good yields, presents an easy pathway to preparing unsymmetrical 1,3-disubstituted ureas based on indol-2-one structure.

EXPERIMENTAL

The melting points were determined on a Kofler block or Gallencamp apparatus. IR (KBr) spectra were recorded on a Mattson 3000 spectrophotometer. NMR spectra were recorded on a Bruker Avance spectrometer (500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C, 50.68 MHz for ^{15}N) in DMSO-d_6 or $CDCl_3$. ^{1}H and ^{13}C chemical shifts are given on the δ scale (ppm) and are referenced to internal TMS. All 2D experiments (gradient-selected (gs)-COSY, NOESY, gs-HMQC, gs-HMBC) were performed using manufacturer's software. Proton spectra were assigned using gs-COSY. Protonated carbons were assigned by gs-HMQC. Quaternary carbons were assigned by gs-HMBC. The positive-ion and negative-ion APCI mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) within the mass range m/z = 50 - 1000. Samples were dissolved in acetonitrile and analyzed by direct infusion at the flow rate of 50 μL/min. The ion source temperature was 350°C, the APCI probe temperature was 350°C, the flow rate and the pressure of nitrogen were 4 L/min and 45 psi, respectively. For ms/ms measurements, the isolation width of precursor ions was 4 m/z and the collision amplitude was 0.8 V. The tuning parameter target mass was set at 400 m/z. Column chromatography was carried out on Silica gel (Merck, grade 60, 70-230 mesh) using benzene and then successive mixtures of benzene-ethyl acetate (in rations from 99:1 to 8:2, solvent system S1) or using chloroform and then successive mixtures of chloroform-ethanol (in rations from 99:1 to 8:2, solvent system S2). Reactions as well as the course of separation and also the purity of compounds were monitored by tlc (elution systems benzene-ethyl acetate, 4:1 (S3), chloroform-ethanol, 9:1 (S4) and/or 19:1 (S5), and chloroform-isopropyl alcohol, 9:1 (S6) on Alugram® SIL G/UV_{254} foils (Macherey-Nagel). Elemental analyses (C, H, N) were performed with an EA 1108 Elemental Analyzer (Fisons Instrument).

3-Amino-1*H*,3*H*-quinoline-2,4-diones (**6a-g**) were prepared according to the general procedure described in literature [5].

General Procedure for the Reaction of 1-Substituted 3-Amino-1*H*,3*H*-quinoline-2,4-diones (**6a-g**) with Nitrourea.

Nitrourea (1.05 g, 10 mmoles) was added to a stirred solution of **6** (5 mmoles) in dioxane (10 ml). The solution was stirred at 80°C for the time given in Table 1. The solution was cooled and evaporated to dryness. Water (50 ml) was added; the insoluble portion was collected by filtration with suction and repeatedly crystallized from appropriate solvent (in the case of the crude reaction products of **6a** and **6b**). The crude products of the reactions of **6c**, **6d**, and **6e** were repeatedly crystallized from appropriate solvents; the mother liquors after crystallization were collected with the benzene extract of the aqueous fraction and column chromatographed on silica gel using solvent system S1 or S2. In cases when evaporated reaction mixture was oily (crude products of the reaction of **6f** and **6g**), it was mixed with water (50 ml) and three times extracted with benzene. The benzene extract was evaporated to dryness and column chromatographed on silica gel using solvent system S1 or S2.

3-Butyl-1-methyl-3-ureido-1*H*,3*H*-quinoline-2,4-dione (**10a**).

This compound was obtained in 55% yield by repeated fractional crystallization (ethyl acetate) of its mixture with **11a**. Colorless crystals, mp 110-119°C (ethyl acetate); ir: ν 3452, 3356, 3260, 2956, 2932, 2871, 1660, 1601, 1538, 1474, 1365, 1302, 1226, 1195, 1116, 863, 758, 665, 620, 550, 534 cm^{-1}. Positive-ion APCI-ms: *m/z* 290 $[M+H]^+$, 272 $[M+H-H_2O]^+$, 255 $[M+H-H_2O-NH_3]^+$, 247 $[M+H-NHCO]^+$, 229 $[M+H-NHCO-H_2O]^+$ (100%), 216 $[M+H-H_2O\text{-butene}]^+$, 201 $[M+H-NHCO-H_2O-CO]^+$. Positive-ion APCI-ms/ms of *m/z* 272: *m/z* 255 $[M+H-H_2O-NH_3]^+$ (100%), 242 $[M+H-H_2CO]^+$, 229 $[M+H-NHCO-H_2O]^+$, 216 $[M+H-H_2O\text{-butene}]^+$. Negative-ion APCI-ms: *m/z* 288 $[M-H]^-$, 270 $[M-H-H_2O]^-$, 245 $[M-H-NHCO]^-$, 230 $[M-H-NHCONH]^-$(100%), 214 $[M-H-H_2O\text{-butene}]^-$, 187 $[M-H-NHCO\text{-butane}]^-$. Negative-ion APCI-ms/ms of *m/z* 270: *m/z* 227 $[M-H_2O-NHCO]^-$, 213 $[M-H-H_2O\text{-butyl}]^-$, 187 $[M-H-NHCO\text{-butane}]^-$ (100%).

Anal. Calcd. for $C_{15}H_{19}N_3O_3$: C, 62.27; H, 6.62; N, 14.52. Found: C, 62.35; H, 6.72; N, 14.37.

1-Methyl-3-phenyl-3-ureido-1*H*,3*H*-quinoline-2,4-dione (**10b**).

This compound was obtained in 58% yield by repeated crystallization (isopropyl alcohol) of its mixture with **11b**. Colorless crystals, mp 246-252°C; ir: ν 3431, 3411, 3313, 3260, 1682, 1661, 1599, 1495, 1476, 1364, 1301, 1194, 1181, 1131, 1037, 781, 764, 693, 631, 574, 545, 527 cm^{-1}. Positive-ion APCI-ms: *m/z* 310 $[M+H]^+$, 292 $[M+H-H_2O]^+$, 267 $[M+H-NHCO]^+$, 249 $[M+H-H_2O-NHCO]^+$ (100%), 221 $[M+H-H_2O-NHCO-CO]^+$, 189 $[M+H-H_2O-NHCO-NH_2CONH_2]^+$, 161 $[C_6H_4NHCOCH_2CO]^+$, 146 $[C_6H_4(CO)NCO]^+$. Positive-ion APCI-ms/ms of *m/z* 292: *m/z* 264 $[M+H-H_2O-CO]^+$, 249 $[M+H-H_2O-NHCO]^+$, 221 $[M+H-H_2O-NHCO-CO]^+$, 189 $[M+H-H_2O-NHCO-NH_2CONH_2]^+$, 161 $[C_6H_4NHCOCH_2CO]^+$, 146 $[C_6H_4(CO)NCO]^+$ (100%). Negative-ion APCI-ms: *m/z* 308 $[M-H]^-$, 290 $[M-H-H_2O]^-$, 264 $[M-H-NH_2CO]^-$, 250 $[M-H-NHCONH_2]^-$ (100%), 208 $[M-H-NHCONH-CH_2CO]^-$, 187 $[M-H-H_2O-NHCO-NH_2CONH_2]^-$. Negative-ion APCI-ms/ms of *m/z* 290: *m/z* 275 $[M-H-H_2O-CH_3]^-$, 247 $[M-H-H_2O-NHCO]^-$, 187 $[M-H-H_2O-NHCO-NH_2CONH_2]^-$ (100%).

Anal. Calcd. for $C_{17}H_{15}N_3O_3$: C, 66.01; H, 4.89; N, 13.58. Found: C, 65.85; H, 4.97; N, 13.42.

3a-Butyl-9b-hydroxy-5-methyl-3,3a,5,9b-tetrahydro-1*H*-imidazo-[4,5-*c*]quinoline-2,4-dione (**11a**).

This compound was obtained in 1.5% yield by repeated fractional crystallization (ethyl acetate) of its mixture with **10a**. Colorless crystals, mp 186-196°C; ir: ν 3312, 3251, 2956, 2930, 2872, 1717, 1636, 1604, 1478, 1392, 1297, 1234, 1119, 1077, 985, 947, 758, 733, 701, 634, 604, 541, 515 cm^{-1}. All ms and ms/ms spectra are identical as for **10a**.

Anal. Calcd. for $C_{15}H_{19}N_3O_3$: C, 62.27; H, 6.62; N, 14.52. Found: C, 62.35; H, 6.72; N, 14.37.

9b-Hydroxy-5-methyl-3a-phenyl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (**11b**).

This compound was obtained in 14% yield by repeated crystallization (isopropyl alcohol) of its mixture with **10b**. Colorless crystals, mp 228-236°C; ir: ν 3430, 3400, 3196, 3101, 2843, 1725, 1656, 1601, 1472, 1421, 1377, 1301, 1272, 1173, 1150, 1132, 1081, 1049, 1032, 855, 782, 763, 722, 698, 655, 551 cm^{-1}. All ms and ms/ms spectra are identical as for **10b**.

Anal. Calcd. for $C_{17}H_{15}N_3O_3$: C, 66.01; H, 4.89; N, 13.58. Found: C, 65.85; H, 4.97; N, 13.42.

3,3a-Dibutyl-9b-hydroxy-5-methyl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (**11c**).

This compound was obtained in 25% yield as colorless crystals, mp 117-122°C (benzene–hexane); ir: ν 3310, 2958, 2934, 2971, 1689, 1676, 1606, 1475, 1419, 1368, 1303, 1114, 1070, 1048, 995, 755, 653, 608, 543, 514 cm^{-1}. APCI-ms: *m/z* 346 $[M+H]^+$, 328 $[M+H-H_2O]^+$ (100%), 303 $[M+H-NHCO]^+$, 272 $[M+H-H_2O\text{-butene}]^+$, 255 $[M+H-H_2O\text{-butylamine}]^+$, 229 $[M+H-H_2O\text{-butene-NHCO}]^+$, 216 $[M+H-H_2O\text{-2*butene}]^+$. Positive-ion APCI-ms/ms of *m/z* 346: *m/z* 303 $[M+H-NHCO]^+$ (100%). Negative-ion APCI-ms: *m/z* 344 $[M-H]^-$, 326 $[M-H-H_2O]^-$ (100%), 298 $[M-H-H_2O\text{-CO}]^{\cdot-}$, 270 $[M-H-H_2O\text{-butene}]^-$, 227 $[M-H-H_2O\text{-butene-NHCO}]^-$, 212 $[M-H-H_2O\text{-butene-NHCO-}CH_3]^{\cdot-}$, 187. Negative-ion APCI-ms/ms of *m/z* 344: *m/z* 326 $[M-H-H_2O]^-$, 300 $[M-H-NH_2CO]^-$ (100%), 244 $[M-H-NH_2CO\text{-butene}]^{\cdot-}$, 227 $[M-H-H_2O\text{-butene-NHCO}]^-$, 212 $[M-H-H_2O\text{-butene-NHCO-}CH_3]^{\cdot-}$.

Anal. Calcd. for $C_{19}H_{27}N_3O_3$: C, 66.06; H, 7.88; N, 12.16. Found: C, 66.21; H, 7.61; N, 12.03.

3-Butyl-9b-hydroxy-5-methyl-3a-phenyl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (**11d**).

This compound was obtained in 70% yield as colorless crystals, mp 140-158°C and then 208-211°C (methanol); ir: ν 3288, 3071, 3034, 2954, 2861, 1699, 1665, 1604, 1476, 1411, 1370, 1299, 1219, 1151, 1136, 1113, 1085, 1052, 1010, 866, 828, 757, 965, 633, 517 cm^{-1}. Positive-ion APCI-ms: *m/z* 366 $[M+H]^+$, 348 $[M+H-H_2O]^+$ (100%), 323 $[M+H-NHCO]^+$, 292 $[M+H-H_2O\text{-butene}]^+$, 250 $[M+H-NHCO\text{-butylamine}]^+$, 222 $[M+H-NHCO\text{-butylamine-CO}]^+$. Positive-ion APCI-ms/ms of *m/z* 366: *m/z* 323 $[M+H-NHCO]^+$ (100%). Negative-ion APCI-ms: *m/z* 364 $[M-H]^-$, 320 $[M-H-NHCO]^{\cdot-}$, 270 $[M-H-H_2O\text{-}C_6H_4]^-$ (100%). Negative-ion APCI-ms/ms of *m/z* 364: *m/z* 320 $[M-H-NHCO]^{\cdot-}$ (100%).

Anal. Calcd. for $C_{21}H_{23}N_3O_3$: C, 69.02; H, 6.34; N, 11.50. Found: C, 68.85; H, 6.52; N, 11.37.

3-Cyclohexyl-9b-hydroxy-5-methyl-3a-phenyl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (**11e**).

This compound was obtained in 33% yield as colorless crystals, mp 255-260°C and then 285-290°C (methanol); ir: ν 3548, 3223, 3079, 2932, 2918, 2849, 1697, 1674, 1604, 1501, 1468, 1410, 1362, 1311, 1267, 1225, 1150, 1074, 1052, 1012, 786, 758, 697, 654, 634, 537 cm^{-1}. Positive-ion APCI-ms: *m/z* 392 $[M+H]^+$, 374 $[M+H-H_2O]^+$ (100%), 349 $[M+H-NHCO]^+$, 292 $[M+H-H_2O\text{-cyclohexene}]^-$, 267 $[M+H-NHCO\text{-cyclohexene}]^+$, 250 $[M+H-NHCO\text{-cyclohexene-}NH_3]^+$, 221 $[M+H-NHCO\text{-cyclohexene-}NH_3\text{-CO}]^+$, 146 $[C_6H_4(CO)NCO]^+$. Positive-ion APCI-ms/ms of *m/z* 392: *m/z* 349 $[M+H-NHCO]^+$ (100%), 267 $[M+H-NHCO\text{-cyclohexene}]^+$, 250 $[M+H-NHCO\text{-cyclohexene-}NH_3]^+$, 222 $[M+H-NHCO\text{-cyclohexene-}NH_3\text{-CO}]^+$. Negative-ion APCI-ms: *m/z* 390 $[M-H]^-$, 346 $[M-H-NH_2CO]^-$, 296 $[M-H-H_2O\text{-}C_6H_4]^-$ (100%), 214 $[M-H-H_2O\text{-}C_6H_4\text{-cyclohexene}]^-$. Negative-ion APCI-ms/ms of *m/z* 390: *m/z* 346 $[M-H-NH_2CO]^-$ (100%).

Anal. Calcd. for $C_{23}H_{25}N_3O_3$: C, 70.57; H, 6.44; N, 10.73. Found: C, 70.48; H, 6.61; N, 10.59.

3,3a-Dibutyl-9b-hydroxy-5-phenyl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (**11f**).

This compound was obtained in 24% yield as colorless crystals, mp 124-132°C (benzene–hexane); ir: ν 3365, 3238, 2959, 2870, 1710, 1692, 1604, 1593, 1498, 1466, 1418, 1365, 1343, 1309, 1257, 1124, 1071, 1049, 1002, 955, 755, 701, 629, 569, 515 cm^{-1}. Positive-ion APCI-ms: *m/z* 408 $[M+H]^+$, 390 $[M+H-H_2O]^+$ (100%), 365 $[M+H-NHCO]^+$, 334 $[M+H-H_2O\text{-butene}]^+$, 308 $[M+H-NHCO\text{-butyl}]^{+\cdot}$. Positive-ion APCI-ms/ms of *m/z* 408: *m/z* 365 $[M+H-NHCO]^+$ (100%). Negative-ion APCI-ms: *m/z* 406 $[M-H]^-$ (100%), 388 $[M-H-H_2O]^-$, 360 $[M-H-H_2O\text{-CO}]^-$, 332 $[M-H-H_2O\text{-butene}]^-$, 289 $[M-H-H_2O\text{-butene-NHCO}]^-$. Negative-ion APCI-ms/ms of *m/z* 406: *m/z* 363 $[M-H-NHCO]^-$ (100%), 319 $[M-H-NHCO-NH_2CO]^{\cdot-}$.

Anal. Calcd. for $C_{24}H_{29}N_3O_3$: C, 70.74; H, 7.17; N, 10.31. Found: C, 70.53; H, 7.32; N, 10.16.

3-Butyl-3a,5-diphenyl-9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (**11g**).

This compound was obtained in respective yields of 27% (Table 1, Entry 7) and 18% (Table 1, Entry 8) as colorless crystals, mp 157-161°C (benzene–cyclohexane); ir: ν 3420, 3248, 2954, 2928, 2869, 1704, 1686, 1605, 1593, 1498, 1464, 1410, 1374, 1347, 1263, 1229, 1137, 1067, 1071, 979, 943, 872, 808, 756, 701, 636, 608, 520 cm^{-1}. Positive-ion APCI-ms: *m/z* 428 $[M+H]^+$, 410 $[M+H-H_2O]^+$ (100%), 385 $[M+H-NHCO]^+$. Positive-ion APCI-ms/ms of *m/z* 428: *m/z* $[M+H-NHCO]^+$ (100%). Negative-ion APCI-ms: *m/z* 426 $[M-H]^-$, 383 $[M-H-NHCO]^-$, 332 $[M-H-H_2O\text{-}C_6H_4]^-$ (100%). Negative-ion APCI-ms/ms of *m/z* 426: *m/z* 383 $[M-H-NHCO]^-$ (100%).

Anal. Calcd. for $C_{26}H_{25}N_3O_3$: C, 73.05; H, 5.89; N, 9.83. Found: C, 72.89; H, 6.03; N, 9.77.

3,3a-Dibutyl-5-methyl-3,3a-dihydro-5*H*-imidazo[4,5-*c*]quinoline-2,4-dione (**12c**).

This compound was obtained in 3% yield as colorless crystals, mp 100-102°C (benzene–hexane); ir: ν 2950, 2930, 2876, 2858, 1734, 1690, 1610, 1471, 1347, 1292, 1258, 1164, 1127, 1096, 1047, 1002, 982, 961, 773, 684, 574, 535, 505 cm^{-1}. Positive-ion APCI-ms: *m/z* 328 $[M+H]^+$ (100%), 272 $[M+H-butene]^+$, 255 $[M+H-butylamine]^+$, 229 $[M+H-butylisocyanate]^+$. Positive-ion APCI-ms/ms of *m/z* 328: *m/z* 272 $[M+H-butene]^+$, 255 $[M+H-butylamine]^+$, 229 $[M+H-butylisocyanate]^+$ (100%). Negative-ion APCI-ms: *m/z* 326 $[M-H]^-$, 298 $[M-H-CO]^-$, 270 $[M-H-butene]^-$ (100%), 227 $[M-H-butene-NHCO]^-$, 213 $[M-H-butene-butane]^-$, 187. Negative-ion APCI-ms/ms of *m/z* 326: *m/z* 298 $[M-H-CO]^-$, 227 $[M-H-butene-NHCO]^-$ (100%), 213 $[M-H-butene-butane]^-$, 187.

Anal. Calcd. for $C_{19}H_{25}N_3O_2$: C, 69.70; H, 7.70; N, 12.83. Found: C, 69.57; H, 7.87; N, 12.59.

3-Butyl-5-methyl-3a-phenyl-3,3a-dihydro-5*H*-imidazo[4,5-*c*]-quinoline-2,4-dione (**12d**).

This compound was obtained in 12% yield as yellowish crystals, mp 198-199°C (benzene–hexane); lit [4], mp 198-200°C (benzene–hexane). The ir spectrum of **12d** was identical with that of authentic sample [4].

3-Cyclohexyl-5-methyl-3a-phenyl-3,3a-dihydro-5*H*-imidazo-[4,5-*c*]quinoline-2,4-dione (**12e**).

This compound was obtained in 17% yield as colorless crystals, mp 290-292°C (methanol); lit [4], mp 291-294°C (ethanol). The ir spectrum of **12e** was identical with that of authentic sample [4].

3,3a-Dibutyl-5-phenyl-3,3a-dihydro-5*H*-imidazo[4,5-*c*]quinoline-2,4-dione (**12f**).

This compound was obtained in 22% yield as yellowish crystals, mp 151-154°C (hexane); ir: ν 3053, 2956, 2928, 2871, 1737, 1704, 1617, 1605, 1492, 1465, 1345, 1292, 1279, 1249, 1162, 1113, 1093, 1006, 765, 757, 701, 651, 601, 577, 514 cm^{-1}. Positive-ion APCI-ms: *m/z* 390 $[M+H]^+$ (100%), 334 $[M+H\text{-butene}]^+$, 291 $[M+H\text{-butylisocyanate}]^+$. Positive-ion APCI-ms/ms of *m/z* 390: *m/z* 373 $[M+H\text{-}NH_3]^+$, 347 $[M+H\text{-NHCO}]^+$, 334 $[M+H\text{-butene}]^+$, 317 $[M+H\text{-butene-}NH_3]^+$, 291 $[M+H\text{-butylisocyanate}]^+$ (100%). Negative-ion APCI-ms: *m/z* 388 $[M\text{-}H]^-$, 360 $[M\text{-H-CO}]^-$, 332 $[M\text{-H-butene}]^-$ (100%), 289 $[M\text{-H-butene-NHCO}]^-$. Negative-ion APCI-ms/ms of *m/z* 388: *m/z* 360 $[M\text{-H-CO}]^-$ (100%), 289 $[M\text{-H-butene-NHCO}]^-$.

Anal. Calcd. for $C_{24}H_{27}N_3O_2$: C, 74.01; H, 6.99; N, 10.79. Found: C, 74.16; H, 7.08; N, 10.57.

3-Butyl-3a,5-diphenyl-3,3a-dihydro-5*H*-imidazo[4,5-*c*]quinoline-2,4-dione (**12g**).

This compound was obtained as yellowish crystals, mp 177-179°C (benzene–hexane); lit [4], mp 83-86°C (benzene – hexane). Now we found that published [4] mp belong to an adduct of **12g** with benzene and mp of sample dried at 105°C for 2 h is 177-179°C; ir: ν 2964, 2953, 2923, 2870, 1735, 1701, 1614, 1602, 1594, 1492, 1464, 1448, 1352, 1309, 1278, 1247, 1135, 1070, 776, 765, 751, 697, 652, 603, 511 cm^{-1}.

General Procedure for the Reaction of **10** and **11** with Phosphorus Pentoxide.

Phosphorus pentoxide (0.1064 g, 0.75 mmol) was added in one portion to the vigorously stirred and cooled (0°C) solution of compound 11 or 12 (0.5 mmol) in chloroform (15 ml). The mixture was stirred at rt under absorption tube filled with anhydrous calcium chloride for the time given in Table 4. After this time, the reaction mixture was poured into the column of silica gel (10 g). The column was washed with chloroform, eluent was evaporated to dryness *in vacuo* and crystallized from appropriate solvent. Yields are given in Table 5, isolated compounds **12** were identical with those characterized in the foregoing general procedure chapter.

General Procedure for Rearrangement of **10**, **11** and **12** in Acetic Acid.

A solution of starting compound **10**, **11**, or **12** (0.5 mmol) in acetic acid (5 ml) was refluxed for the time given in Table 6. After cooling, the solution was evaporated to dryness and the residue was crystallized from appropriate solvent. In some cases, the mother liquors were chromatographed on silica gel using solvent system S1 or S2. Results are listed in Table 6.

1-Methyl-3-(3-pentanoylureido)-2-oxo-2,3-dihydro-1*H*-indole (**13a**).

This compound was obtained from **10a** in 41% yield as colorless crystals, mp 193-197°C (methanol); lit [4], mp 190-196°C (ethanol). The ir spectrum of **13a** was identical with that of authentic sample [4].

3-(3-Benzoylureido)-1-methyl-2-oxo-2,3-dihydro-1*H*-indole (**13b**).

This compound was obtained in respective yields of 69% (from **10b**) and 61% (from **11b**) as colorless crystals, mp 211-213°C (methanol); lit [4], mp 213-214°C (ethanol). The ir spectrum of **13b** was identical with that of authentic sample [4].

3-(3-Benzoyl-3-butylureido)-1-methyl-2-oxo-2,3-dihydro-1*H*-indole (**13d**).

This compound was obtained in 7% yield from **12d** as colorless crystals, mp 155-158°C (ethanol); lit [4], mp 156-158°C (benzene-hexane). The ir spectrum of **13d** was identical with that of authentic sample [4].

3-(3-Benzoyl-3-butylureido)-1-phenyl-2-oxo-2,3-dihydro-1*H*-indole (**13g**).

This compound was obtained in respective yields of 31% (from **11g**) and 28% (from **12g**) as colorless crystals, mp 193-198°C (methanol); lit [4], mp 183-188°C (benzene-hexane). The ir spectrum of **13g** was identical with that of authentic sample [4].

(*E*)-3-Butyl-4-butylidene-1´-methyl-1´*H*-spiro[imidazolidine-5,3´-indole]-2,2´-dione (**14c**).

This compound was obtained in respective yields of 64% (from **11c**) and 43% (from **12c**) as colorless crystals, mp 197-201°C (ethanol); lit [4], mp 196-200°C (ethanol). The ir spectrum of **14c** was identical with that of authentic sample [4].

(*E*)-3-Butyl-4-butylidene-1´-phenyl-1´*H*-spiro[imidazolidine-5,3´-indole]-2,2´-dione (**14f**).

This compound was obtained in respective yields of 82% (from **11f**) and 75% (from **12f**) as colorless crystals, mp 125-129°C (benzene-hexane); lit [4], mp 124-128°C (benzene-hexane). The ir spectrum of **14f** was identical with that of authentic sample [4].

3-(3-Butylureido)-1-methyl-2-oxo-2,3-dihydro-1*H*-indole (**15d**).

This compound was obtained in respective yields of 9% (from **11d**) and 6% (from **12d**) as colorless crystals, mp 190-193°C (ethanol); lit [4], mp 192-195°C (benzene). The ir spectrum of **15d** was identical with that of authentic sample [4].

3-(3-Cyclohexylureido)-1-methyl-2-oxo-2,3-dihydro-1*H*-indole (**15e**).

This compound was obtained in respective yields of 39% (from **11e**) and 37% (from **12e**) as colorless crystals, mp 218-223°C (methanol); ir: ν 3348, 3286, 3099, 3059, 3001, 2920, 2850, 1711, 1628, 1566, 1518, 1495, 1468, 1420, 1375, 1349, 1314, 1248, 1226, 1155, 1126, 1090, 1017, 891, 748, 685, 575,

540, 483 cm^{-1}. Positive-ion APCI-ms: *m/z* 288 $[M+H]^+$, 188 $[M+H\text{-cyclohexyl-}NH_3]^{+\cdot}$, 161 $[M+H\text{-cyclohexane-NHCO}]^+$, 146 $[C_6H_4(CO)NCO]^+$ (100%). Positive-ion APCI-ms/ms of *m/z* 288: *m/z* 188 $[M+H\text{-cyclohexyl-}NH_3]^{+\cdot}$, 161 $[M+H\text{-cyclohexane-NHCO}]^+$ (100%), 146 $[C_6H_4(CO)NCO]^+$, 100 $[cyclohexylNH_3]^+$. Negative-ion APCI-ms: *m/z* 286 $[M-H]^-$ (100%), 187 $[M\text{-H-cyclohexylNH}]^{-\cdot}$, 160 $[M\text{-H-cyclohexyl-NHCO}]^{-\cdot}$. Negative-ion APCI-ms/ms of *m/z* 286: *m/z* 187 $[M\text{-H-cyclohexylNH}]^{-\cdot}$ (100%), 160 $[M\text{-H-cyclohexyl-NHCO}]^{-\cdot}$.

Anal. Calcd. for $C_{16}H_{21}N_3O_2$: C, 66.88; H, 7.37; N, 14.62. Found: C, 66.67; H, 7.52; N, 14.49.

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