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ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 7059–7069

Molecular rearrangement of 1-substituted 9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones—an unexpected pathway to new indole and imidazolinone derivatives

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Received 9 January 2007; revised 18 April 2007; accepted 3 May 2007
Available online 8 May 2007

Abstract—1-Substituted 3a-alkyl/aryl-9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones and 3′-substituted 3-alkyl/aryl-3-ureido-1*H*,3*H*-quinoline-2,4-diones react in boiling acetic acid to give 2-alkyl/aryl-1*H*-indol-3-yl-ureas and/or 1,3-bis[2-(2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-ureas. By the action of hydrochloric acid, the first of them rearrange to give 4-(2-aminophenyl)-1,3-dihydroimidazol-2-ones. The structure of 1,3-bis[2-(2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-ureas was confirmed by their synthesis. All compounds were characteried by their ^{1}H NMR, ^{13}C NMR, IR spectra, atmospheric pressure chemical ioniation mass spectra, and some of them also by ^{15}N NMR spectroscopic data.

1. Introduction

Recently, the reactions of 3-amino-1*H*,3*H*-quinoline-2,4-diones with urea in boiling acetic acid were described.[1,2] Under the same reaction conditions, different rearranged products were obtained depending on the character of the substitution in the starting compounds. Under mild reaction conditions (nitrourea in dioxane), however, 3-amino-1*H*,3*H*-quinoline-2,4-diones react differently producing 3-alkyl/aryl-3-ureido-1*H*,3*H*-quinoline-2,4-diones and/or their cyclic isomers 3a-alkyl/aryl-9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones.[3,4] Both compounds rearrange in boiling acetic acid to give the same products as those isolated from the reaction of 3-amino-1*H*,3*H*-quinoline-2,4-diones with urea and, therefore, they may be considered to be intermediates of the molecular rearrangement of 3-amino-1*H*,3*H*-quinoline-2,4-diones in their reaction with urea in acetic acid.[1–4]

3-Alkyl/aryl-3-ureido-1*H*,3*H*-quinoline-2,4-diones and 3a-alkyl/aryl-9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones arise from addition of 3-amino-1*H*,3*H*-quinoline-2,4-diones to isocyanic acid (produced by degradation of urea or nitrourea) possessing a non-substituted nitrogen atom in position 3′ of the ureido group or that in position 1 of imidazole ring. Our intention, however, was to study the molecular rearrangement even of such compounds that bear an alkyl or aryl group instead of hydrogen in these positions. The preparation procedure of the first set of such starting compounds was described in our recent work.[5] The reaction of 1-unsubstituted 3-amino-1*H*,3*H*-quinoline-2,4-diones **1** with organic isocyanates produced the expected *N*(3′)-substituted 3-alkyl/aryl-3-ureido-1*H*,3*H*-quinoline-2,4-diones (**2**) and/or 1-substituted 9b-hydroxy-3a-alkyl/aryl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones (**3**) (Scheme 1).

We want to show in this work that compounds **2** and **3**, being boiled in acetic acid, also undergo a molecular rearrangement to give products, which possess structures entirely different from products of the rearrangement of compounds analogous to **2** and **3** having R^3=H.

2. Results and discussion

The starting compounds **2** and **3** were prepared from amines **1**[6] according to the literature.[5] Refluxing their solution in acetic acid gave rise to two different types of products (Table 1), which were differentiated by results of their mass spectra.

The first type of reaction products exhibited in mass spectra a molecular peak of *m*/*z* lower by 44 than the molecular

Keywords: Molecular rearrangement; 1,2-Diarylureas; 3-Ureidoindoles; Reaction mechanism.
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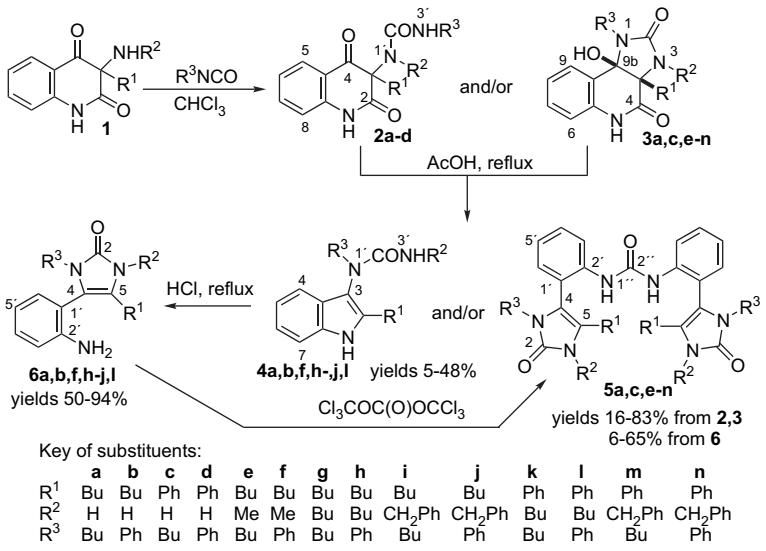
doi:10.1016/j.tet.2007.05.012



Scheme 1.

weight of starting compounds **2** or **3**. Comparing results of elemental analyses and ^{13}C NMR spectra of starting compounds **2** or **3** and the corresponding product (Table 2) confirmed that one carbon atom was lost, and the split-off fragment is thus carbon dioxide. According to ^{1}H and ^{15}N NMR spectra, reaction products of the first type contain one –NH– signal at ca. 11.2 ppm and also a urea fragment $–N(R^3)–CO–NH–R^2$ or $–N(R^3)–CO–NH_2$. The highest values of chemical shifts in ^{13}C NMR spectra appear at 156–158 ppm, which rules out the presence of quinolin-2-one or indolin-2-one system. On the basis of these findings and on the fact that all these compounds exhibit sharp, intensive absorption band in the 3416–3480 cm^{-1} region in IR spectra, we adopted a working hypothesis that the compounds in question are ureido derivatives of 3-indolylamine substituted in position 2 by an alkyl or aryl group (**4**) (Scheme 1). Confirmation of the proposed indole structure **4** was obtained by complete interpretation of NMR (Table 2) as well as MS spectra. NH protons resonating at ca. 11.2 ppm gave no cross-peaks with C=O carbon signals at ca. 157 ppm in ^{1}H, ^{13}C HMBC spectra of compounds **4**. On the contrary, appropriate correlation peaks of these C=O carbons were observed with NH protons having δ (^{1}H) 5.3–6.6. Protons in position 7 correlated with N(1) nitrogen and the connection of nitrogens N(1′) and N(3′) via ^{3}J (^{15}N, ^{1}H) was proved using ^{1}H, ^{15}N HMBC spectra of compounds **4b** and **4i**. The ^{1}H, ^{13}C and ^{15}N chemical shifts in compounds **4** are given in Table 2.

Table 1. Reaction of compounds **2** and **3** in boiling acetic acid

Entry	Starting compound				Reaction time (h)	Isolated products (Yield, %)
		R^1	R^2	R^3		
1	**2a**	Bu	H	Bu	1	**4a** (38), **5a** (36)
2	**3a**	Bu	H	Bu	1	**4a** (48), **5a** (34)
3	**2b**	Bu	H	Ph	1	**4b** (7)[a]
4	**3c**	Ph	H	Bu	0.5	**5c** (52)
5	**2d**	Ph	H	Ph	0.5	[b]
6	**3e**	Bu	Me	Bu	1	**5e** (57)
7	**3f**	Bu	Me	Ph	2	**4f** (39), **5f** (21)
8	**3g**	Bu	Bu	Bu	0.5	**5g** (69)
9	**3h**	Bu	Bu	Ph	2	**4h** (48), **5h** (16)
10	**3i**	Bu	CH_2Ph	Bu	1	**4i** (18), **5i** (50)
11	**3j**	Bu	CH_2Ph	Ph	1	**4j** (7), **5j** (41)
12	**3k**	Ph	Bu	Bu	0.5	**5k** (63)
13	**3l**	Ph	Bu	Ph	1	**4l** (5), **5l** (54)
14	**3m**	Ph	CH_2Ph	Bu	0.5	**5m** (73)
15	**3n**	Ph	CH_2Ph	Ph	0.5	**5n** (74)

[a] No other compounds were separated or identified.
[b] No compound was isolated from the very complex reaction mixture.

APCI mass spectra of compounds **4** provide complementary ions in both polarity modes useful for the molecular weight (MW) determination and the identification of alkyl/aryl substitution, such as the neutral losses of butylamine and butene for butyl substitution and similarly for other substituents. All spectra exhibit common peaks of fragment ions at *m/z* 172 formed by the neutral loss of the whole side chain $R^3NHCONHR^2$.

More than a thousand 3-aminoindoles and their derivatives are described in the literature but to the best of our knowledge no 2-alkyl/aryl-3-ureidoindole derivative has been described. Structurally closest to compounds **4** are 2-phenyl-3-semicarbazidoindoles and their derivatives, which display antimicrobial and antihistaminic activities.[7,8]

With the intent of transforming 3-ureido derivatives **4** into their respective 3-aminoindoles, we executed their hydrolysis by boiling in concd hydrochloric acid. However, elemental analysis of the reaction products shows that no change in elemental composition of the reacting compounds takes place but the molecular structure changes. Having compared the ^{1}H NMR spectra of compounds **4** (Table 2) and of products of their reaction with hydrochloric acid (Table 3), it is apparent that the signals of the indole –NH– group (at about 11.2 ppm) disappear but a signal for the primary amino group appears instead and resonates at ca. 5 ppm. In IR spectra of the reaction products having the same pattern, two sharp absorption bands appear in the region of 3420-3465 and 3324-3343 cm^{-1}, which are characteristic of a primary amino group in *o*-substituted anilines.[9] Compounds **4f**,**h**–**j**,**l** bear an alkyl or aryl group at both nitrogen atoms of the

Table 2. ^{1}H, ^{13}C, and ^{15}N chemical shifts (δ, ppm) of compounds **4** in DMSO-d_6

Position	4a		4b		4f		4h		4i		4j		4l	
	δ_H	δ_C	δ_H	δ_C or δ_N	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C or δ_N	δ_H	δ_C	δ_H	δ_C
1	11.09	—	11.18	−248.5[a]	11.20	—	11.17	—	11.13	−249.4[b]	11.22	—	11.75	—
2	—	136.7	—	137.2	—	137.8	—	137.3	—	137.4	—	137.7	—	133.5
3	—	113.6	—	114.4	—	113.7	—	113.3	—	112.8	—	113.3	—	114.0
3a	—	124.5	—	125.0	—	124.5	—	124.2	—	124.9	—	124.4	—	125.9
4	7.30	116.6	7.32	116.8	7.26	116.9	7.26	116.5	7.32	116.7	7.31	116.7	7.31	117.5
5	7.03	118.9	7.04	119.4	7.02	119.7	7.02	119.2	7.04	119.1	7.03	119.4	7.08	120.0
6	7.09	120.6	7.11	120.9	7.10	121.2	7.11	120.8	7.10	120.7	7.12	121.0	7.20	122.5
7	7.34	111.1	7.37	111.4	7.38	111.7	7.38	111.3	7.35	111.3	7.37	111.4	7.50	112.0
7a	—	134.1	—	134.3	—	134.6	—	134.2	—	134.4	—	134.4	—	135.0
1′	—	—	—	−281.2	—	—	—	—	—	−299.0	—	—	—	—
2′(C═O)	—	158.4	—	157.4	—	157.5	—	156.2	—	157.7	—	156.7	—	156.2
3′	5.30	—	5.86	−300.6[c]	5.89	—	5.84	—	5.98	−297.9[d]	6.59	—	6.25	—
1 (R^1)	2.64	24.6	2.65	24.9	2.63	25.0	2.62	24.7	2.62	24.8	2.62	24.9	—	131.0
2 (R^1)	1.75	30.8	1.65	30.1	1.61	30.2	1.63	29.8	1.73	30.3	1.62	30.0	7.84	126.2
	1.66		1.56		1.51		1.54		1.64		1.54			
3 (R^1)	1.41	22.1	1.28	22.1	1.26	22.2	1.25	22.0	1.39	22.3	1.25	22.1	7.50	128.8
4 (R^1)	0.97	13.7	0.87	—	0.83	13.9	0.87	13.6	0.93	13.8	0.83	13.7	7.39	128.0
1 (R^2)	5.30	—	5.86	—	2.62	27.6	3.06	39.5	4.13	43.5	4.24	44.6	3.08	39.7
									4.20				2.96	
2 (R^2)	—	—		—	—	—	1.34	31.9	—	137.4	—	141.0	1.22	31.9
3 (R^2)	—	—		—	—	—	1.22	19.3	7.20	126.3	7.29	127.1	1.08	19.3
4 (R^2)	—	—		—	—	—	0.87	13.6	7.27	127.9	7.26	128.0	0.77	13.8
5 (R^2)	—	—		—	—	—	—	—	7.20	126.3	7.20	126.5	—	—
1 (R^3)	3.55	47.7	—	144.4	—	144.6	—	144.3	3.60	48.2	—	144.4	—	144.7
2 (R^3)	1.41	30.8	7.27	124.6	7.23	124.5	7.23	124.9	1.42	31.0	7.29	124.4	7.25	123.8
3 (R^3)	1.28	19.5	7.24	128.1	7.23	128.4	7.23	128.0	1.29	19.7	7.26	128.1	7.21	128.1
4 (R^3)	0.86	13.7	7.04	123.6	7.04	123.7	7.04	123.1	0.87	13.8	7.04	123.5	7.00	123.3

[a] ^{1}J (^{15}N, ^{1}H) (Hz): 97.7.
[b] ^{1}J (^{15}N, ^{1}H) (Hz): 97.7.
[c] ^{1}J (^{15}N, ^{1}H) (Hz): 92.0.
[d] ^{1}J (^{15}N, ^{1}H) (Hz): 92.2.

Table 3. ^{1}H, ^{13}C, and ^{15}N chemical shifts (δ, ppm) of compounds **6** in DMSO-d_6

Position	6f		6h		6i		6j		6l	
	δ_H	δ_C or δ_N	δ_H	δ_C or δ_N	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1	—	−258.5	—	−246.4	—	—	—	—	—	
2	—	152.6	—	152.4	—	153.4	—	152.9	—	152.3
3	—	[a]	—	−235.8	—	—	—	—	—	—
4	—	115.3	—	115.5	—	116.2	—	116.1	—	117.4
5	—	121.7	—	121.3	—	119.6	—	121.5	—	122.1
1′	—	113.0	—	113.2	—	112.8	—	113.0	—	112.6
2′	—	147.8	—	147.7	—	147.9	—	147.7	—	148.2
3′	6.60	114.4	6.62	114.5	6.78	114.6	6.62	114.5	6.48	114.3
4′	6.99	129.3	6.99	129.4	7.12	129.8	7.00	129.4	6.92	129.7
5′	6.45	115.5	6.45	115.7	6.62	115.9	6.46	115.7	6.36	115.4
6′	6.82	132.1	6.83	132.1	6.98	132.1	6.87	132.1	6.92	132.8
NH_2	5.01	−319.6	4.97	−319.7	4.92	—	4.99	—	5.03	—
1(R^1)	2.40	22.9	2.54	22.9	2.21	22.9	2.32	23.0	—	129.5
	2.33		2.36		2.13		2.21			
2(R^1)	1.48	30.4	1.53	30.8	1.13	30.8	1.20	30.5	7.43	129.5
	1.43		1.48							
3(R^1)	1.26	21.6	1.24	21.7	1.04	21.5	1.09	21.5	7.38	128.4
4(R^1)	0.79	13.6	0.78	13.7	0.75	13.4	0.63	13.4	7.33	132.8
1(R^2)	3.26	27.5	3.66	40.8	4.86	43.8	4.92	44.1	3.71	41.0
					4.94		5.01		3.63	
2(R^2)	—	—	1.69	31.4	—	138.7	—	138.3	1.47	30.8
3(R^2)	—	—	1.39	19.7	7.29	126.6	7.38	126.8	1.22	19.3
4(R^2)	—	—	0.99	13.7	7.39	128.5	7.43	128.0	0.79	13.5
5(R^2)	—	—	—		7.30	127.1	7.34	127.2		
1(R^3)	—	136.0	—	136.0	3.55	40.5	—	136.0	—	135.7
					3.32					
2(R^3)	7.17	126.4	7.17	126.3	1.34	30.8	7.25	126.4	7.26	126.8
3(R^3)	7.27	128.2	7.27	128.2	1.13	19.2	7.28	128.2	7.28	128.3
4(R^3)	7.17	126.1	7.17	126.0	0.61	13.4	7.20	126.2	7.20	126.6

[a] Not observed.

ureido group. If these compounds transform in all cases into a product containing a primary amino group, then this group must originate by the opening of the indole ring. For this reason, for products arising from compounds **4** in hydrochloric acid, we proposed and presently confirmed structure **6** for which the presence of the amino group, being placed on a 1,2-disubstituted benzene ring, was proved in the ^{1}H NMR spectra. The ^{1}H, ^{13}C and ^{15}N chemical shifts in compounds **6f**,**h**–**j**,**l** are given in Table 3.

The NMR spectroscopic data of the reaction products of compounds **4a**,**b** with concd hydrochloric acid are missing in Table 3. As well as compounds **4f**,**h**–**j**,**l**, also compounds **4a**,**b** yield compounds **6a**,**b** that have been characterised by IR and MS spectra. However, their NMR spectra in DMSO-d_6 were identical with those of compounds **4a**,**b**. As we confirmed by TLC, compounds **6a**,**b** are very unstable in polar medium (DMSO, DMF, methanol) and quickly change back to **4a**,**b**. In methanol solution, at least five other compounds arise. The conversion of **6a**,**b** to **4a**,**b** proceeds even during long-time boiling of their chloroform or ethyl acetate solutions. In non-polar solvents, compounds **6a**,**b** are only slightly soluble.

The typical feature of first-order APCI mass spectra of compounds **6** is the absence or low relative abundance of fragment ions, which simplifies the MW determination based on the presence of $[M+H]^{+}$ ions in the positive-ion mode and $[M-H]^{-}$ ions in the negative-ion mode. The characteristic neutral losses corresponding to the individual alkyl substituents are observed in tandem mass spectra, such as losses of alkenes, alkyl radicals, alkyl/aryl isocyanates and some other less structurally important species, e.g., NH_3, CO, NHCO, $NH_2CO^{\bullet}$. The common fragment ions observed in MS/MS spectra of all compounds **6** (except for **6l**) are the rearrangement loss of $R^3NHCONHR^2$ providing the fragment ion at *m*/*z* 172 (or 170 in the negative-ion mode) followed by the neutral loss of propene giving the peak at *m*/*z* 130. These ions are identical as for compounds **4**.

Almost 6000 compounds based on imidazolin-2-one are described in the literature, a number of them displaying interesting biological activity.[10] None of the described compounds, however, bears a 2-aminophenyl substituent in position 4. To the best of our knowledge, the undoubtedly interesting transformation of the indole system to imidazolin-2-one system has not been described either. Compounds closest in structure to imidazolin-2-ones **6** are 2,6-dihydroimidazo[1,5-*c*]quinazoline-3,5-diones described in our earlier paper.[1] This indicates that the mechanism of the transformation of compounds **2** and **3** in acetic acid is probably very similar to that of their analogues having R^3=H and proceeds through an isocyanate intermediate.[1,3]

Along with compounds **4**, a second type of product was also produced by the reaction of compounds **2** and **3** in boiling acetic acid (Scheme 1). These compounds displayed in MS an even value of molecular weights, which may by expressed by relation $MW=2MW_4+26$, or $MW=2MW_3-62$. This could indicate that in formation of these compounds, carbon dioxide splits away from a molecule of starting compound **2** or **3**, and a molecule of water from the other. During fragmentation of protonated molecules of the second type products, two primary product ions arise, which differ by *m*/*z* 26. Such fragmentation is characteristic of 1,3-diphenylurea derivatives where the corresponding aniline and isocyanate are formed.[9] For that reason, we adopted the basic hypothesis that the fragment –NH–CO–NH– is present in products of the second type. Nevertheless, formation of –NH–CO–NH– bridge may be explained only through transformation of the primary amino group present in compounds **6** and for that reason we suggested structure **5** (Scheme 1) as a working hypothesis for the second type of product from the reaction of compounds **2** and **3** in acetic acid. The correctness of this hypothesis was proved by an independent synthesis of compounds **5** from compounds **6** and triphosgene (see below).

In NMR spectra of compounds **5** (Table 4), the signals of two components exist differing only slightly both in proton and carbon chemical shifts and having relative integral ratio rather close to 1:1 (except for compound **5f** where the ratio was ca. 1.44:1). The highest values of ^{13}C chemical shifts appear below 154 ppm. This observation rules out the possible presence of an indolone system (C-2 at around 174 ppm), a quinolinedione system (C-4 at around 200 ppm, C-2 at around 170 ppm) and also a 2-quinolone system (C-2 at around 162 ppm). The presence of two pairs of ^{13}C resonances at ca. 151.3–153.7 always having a 2:1 ratio was another important feature of ^{13}C NMR spectra of compounds **5** leading to a proposal of their correct structure being based on the existence of two pairs of the same fragments bound to a 'spacer' having only one carbon. The ^{13}C resonances at about 152 ppm are typical of substituted ureas containing –NH–CO–NH– fragment.

Three basic conformations of compounds **5** can arise in the course of transformation of compounds **6**: extended *Z*,*Z* *Z*,*E*, or folded *E*,*E* (Fig. 1). The extended *Z*,*Z*-conformation is typical for 1,3-diarylureas, whereas folded *E*,*E*-conformation is typical for 1,3-dialkyl-1,3-diarylureas.[11–13] The presence of two sets of signals, caused by co-occurrence of *E*,*E*-*syn* and *E*,*E*-*anti* conformers in unequal ratio, was recently established in the ^{1}H NMR spectrum of 1,3-dimethyl-1,3-di(1-naphthyl)-urea.[13] By analogy, the appearance of two sets of signals in the NMR spectra of compounds **5** bears evidence of co-occurrence of two conformers in an unequal ratio. Nevertheless, we do not have any evidences for their geometry in the meanwhile. As we found with compound **5a**, during gradual elevating of temperature the corresponding couples of signals in ^{1}H NMR come near, but even at 97 °C they were not coincident. It shows that the energy barrier for interconversion of two conformers of **5** is high, which is in accord with restricted rotation around all the single bonds in a molecule, caused by substituents in positions 1, 3 and 5 of imidazolinone nucleus (Fig. 1).

According to the large number of atoms in the molecules of **5**, complete assignment of all doubled signals is very troublesome and, in some cases, almost impossible. Still better, we succeeded in assignment of ^{1}H and ^{13}C NMR signals of compounds **5a**,**c**,**f** (Table 4). For compounds **5e**,**g**,**h**–**n**, in which the overlap of doubled signals is very strong, characterisation of only selected signals is presented in Table 5.

Table 4. ^{1}H, ^{13}C, and ^{15}N chemical shifts (δ, ppm) of compounds **5a**,**c**,**f** in DMSO-d_6

Position	5a		5c		5f	
	δ_H	δ_C or δ_N	δ_H	δ_C or δ_N	δ_H	δ_C
1	10.25[a]	−248.6[b]	10.90, 10.86	[c]		−256.3
2	—	153.70, 153.66	—	153.43, 153.39	—	152.40, 151.94
3	—	−247.2	—	[c]	—	[d]
4	—	114.77, 114.47	—	116.70, 116.68	—	114.22, 113.87
5	—	119.35, 119.29	—	118.41, 118.39	—	119.27, 119.24
1′	—	120.11, 119.96	—	120.56, 120.54	—	122.60, 122.58
2′	—	138.65, 138.55	—	139.01, 138.96	—	138.26, 138.18
3′	7.96	122.53, 122.47	7.95, 7.93	123.07, 122.99	7.78, 7.64	121.95, 121.65
4′	7.38	128.81, 128.73	7.44	129.71, 129.65	7.24	128.47, 128.42
5′	7.12	122.61, 122.55	7.11	123.29, 123.27	[e]	[e]
6′	7.19	131.96, 131.81	7.19	132.29, 132.19	7.05, 6.97	131.49, 131.45
NHCONH	8.29[a]	−275.3[f]	8.34, 8.32	[c]	8.31, 8.14	−274.8
NH*CO*NH	—	153.20, 153.18	—	153.00, 152.97	—	152.51, 152.19
1(R^1)	2.16, 2.11	24.06, 24.3	—	129.81, 129.77	2.43, 2.28	23.23, 22.95
2(R^1)	1.75, 1.66	30.15, 30.04	7.15	124.88, 124.86	1.57, 1.48	30.19, 30.07
3(R^1)	1.21	21.82, 21.80	7.22	128.40, 128.38	1.28, 1.24	22.00, 21.80
4(R^1)	0.76	13.57	7.15	126.46, 126.42	0.77, 0.74	13.53, 13.27
1(R^2)	10.25[a]	−248.5	10.90, 10.86	[c]	3.29, 3.25	27.77, 27.65
1(R^3)	3.37, 3.21	40.29, 40.17	3.44, 3.37 3.17, 3.09	40.19, 40.11	—	135.54, 135.50
2(R^3)	1.35, 1.29	30.87, 30.81	1.35, 1.29	30.71, 30.69	[e]	126.10, 126.00
3(R^3)	1.09	19.33, 19.31	1.10	19.29, 19.25	7.24	128.29, 128.25
4(R^3)	0.70	13.38	0.70	13.45	[e]	[e]

[a] Broadened signal.
[b] ^{1}J (^{15}N, ^{1}H) (Hz): 96.1.
[c] Not measured.
[d] Not observed.
[e] Strong overlap of signals, the assignment would be uncertain.
[f] ^{1}J (^{15}N, ^{1}H) (Hz): 89.2.

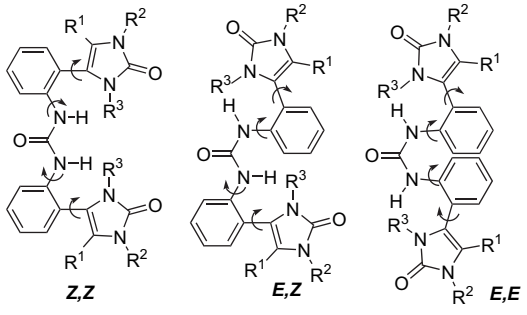


Figure 1. Three possible ground-state conformers of compounds **5**.

APCI mass spectra allow an easy and unambiguous identification of MWs for compounds **5** due to the presence of (de)-protonated molecules as the base peaks or at least intensive peaks in both positive-ion and negative-ion spectra. The cleavage of N–C bond in the –NH–CO–NH– group gives two series of ions labelled as $[F]^+$ and $[F+26]^+$. The corresponding analogues in negative-ion spectra are $[F-2H]^-$ and $[F+26-2H]^-$ observed for most compounds **6** both in first-order and tandem mass spectra. Other product ions are found in MS/MS spectra depending on the alkyl/aryl substitution, such as neutral losses of alkenes, amines, isocyanates, etc.

All our attempts at hydrolysing compounds **5** to the corresponding imidazolinones **6** failed. A short boil in concd hydrochloric acid does not change compounds **5**, and prolonged boiling produces complicated mixtures that we failed to separate by column chromatography. For that reason, we decided to confirm the structure of compounds **5** by their synthesis, and that through a reaction of imidazolinones **6**

Table 5. ^{1}H chemical shifts of NH protons and ^{13}C chemical shifts (δ, ppm) of CO groups of compounds **5** in DMSO-d_6

Compound	δ_H (NHCONH)	δ_C (NHCONH)	δ_H (R^2NCONR^3)	δ_C (R^2NCONR^3)
5a	8.29[a]	153.20, 153.18	10.25[a,b]	153.70, 153.66
5c	8.34, 8.32	153.00, 152.97	10.90, 10.86[b]	153.43, 153.39
5e	8.25, 8.23	153.03, 152.78	—	153.44, 153.25
5f	8.31, 8.14	152.51, 152.19	—	152.40, 151.94
5g	8.16[a]	153.02, 152.88	—	152.86, 152.80
5h	8.25, 8.07	152.10, 151.93	—	152.21, 152.14
5i	8.22, 8.21	152.98, 152.93	—	153.15, 153.07
5j	8.35, 8.14	152.15, 151.94	—	152.79, 152.70
5k	8.07[a]	152.40, 152.32	—	152.83, 152.80
5l	7.93[a]	151.51, 151.45	—	152.15, 151.94
5m	8.26, 8.18	152.47, 152.43	—	153.11, 153.09
5n	8.03, 8.01	151.36, 151.33	—	152.55, 152.50

[a] Broadened signal.
[b] R^2=H.

with triphosgene (bis(trichloromethyl)carbonate). Applying the usual procedure taken from the literature,[14,15] which runs in a solution of dichloromethane at lowered temperature, the reaction did not proceed even in prolonged reaction time and merely starting compounds **6** were isolated from the reaction mixture. Performing the reaction in boiling dichloromethane brought about formation of a complex mixture of compounds. Only when the reaction of **6** with triphosgene was performed in boiling benzene in the presence of catalytic 4-dimethylaminopyridine, the desired end was achieved and compounds **5f**,**h–j**,**l** were obtained in good yields. The result indicates that the reactivity of compounds **6** is greatly reduced. We assume it is quite probable that the corresponding isocyanate will admittedly arise, but its reactivity with a second molecule of **6** is limited due to strong steric hindrance by the substituents at the imidazolinone nuclei of both reaction components. A very low yield was provided by the transformation of **6a** into **5a**, and we did not succeed in obtaining compound **5b** at all. In the both cases, the corresponding isomeric compounds **4** were obtained in high yields. This result show that N-3 unsubstituted compounds **6a** and **6b** are highly unstable and their transformations into compounds **4a** and **4b** under the given reaction conditions proceeds more rapidly than their reaction with triphosgene.

The formation of indole and imidazolinone derivatives through molecular rearrangement of quinolinedione derivatives **2** and **3** is unexpected, but may be explained through a reaction mechanism whose proposal is given in Scheme 2. With compounds **2**, we assume cyclisation must take place, with formation of carbinolamide isomer **3**. In order to explain the formation of compound **5**, intermediate **B** bearing the isocyanate group must arise from compound **3**. The isocyanate group can be formed only by transformation of the lactam group in starting compound **3**, and that either through intermediate carbocation **A** or through direct dehydration of compound **3** in accord with the mechanism proposed earlier.[1] In the case of 1′-unsubstituted analogues of **3**, intramolecular addition of the NH group in position 3 to isocyanate group of intermediate **B** (R^3=H) take place, which leads to formation of imidazoquinazolines.[1] In case $R^3 \neq H$, however, similar intramolecular addition cannot occur. Hydrolysis of the isocyanate group gives rise to imidazolinone **6**, which is unstable under the given reaction conditions and transforms through intermediate **C** into indole derivative **4**. The second reaction product **5** is formed by addition of aniline **6** to non-reacted isocyanate intermediate **B**.

We concede that intermediate isocyanate **B** may react with acetic acid to produce mixed anhydride –NH–C(O)–O–C(O)–CH_3. Nevertheless, this anhydride would have to react in further steps in the same manner as isocyanate **B**. This proposal of the reaction mechanism is supported by the fact that when R^1=Ph, very little amount of compounds **4** is produced due to lowered tendency to intramolecular addition of amino group in **6** (Scheme 2)

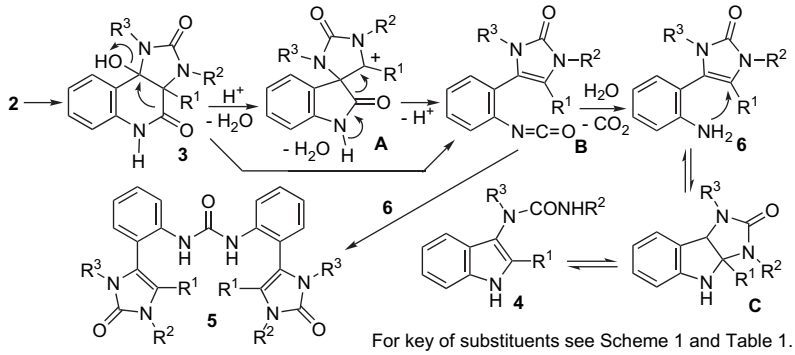
The proposed reaction mechanism finds analogy in the literature. It is well-known that derivatives of tryptophan produce, through intramolecular nucleophilic addition in a strongly acidic environment, cyclic tautomers—hexahydropyrrolo[2,3-*b*]indole alkaloids and their derivatives, which in a weakly acidic environment transform back into derivatives of tryptophan.[16–20] Intermediate **C** is actually an aza-analogue of hexahydropyrrolo[2,3-*b*]indole alkaloids, its formation through intramolecular nucleophilic addition of amino group in compounds **6** is easy to explain and its subsequent transformation into acyclic tautomers **4** is analogous to transformation of hexahydropyrrolo[2,3-*b*]indoles in a weakly acidic environment.

In conclusion, we would like to mention that the described transformations of the addition products of α-aminoketones **1** with isocyanates in boiling acetic acid into indole and imidazolinone derivatives are very interesting from the viewpoint of theory and also, owing to simple reaction protocol, open a path to prepare new compounds of types **4**–**6**. Due to the significant biological activity of a number of indole derivatives and also 1,3-diarylureas,[21] compounds **4** and **5** may be interesting structures for study in this direction.

3. Experimental

3.1. General

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 500 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. ^{15}N chemical shifts were referred to external neat nitromethane in co-axial capillary (δ=0.0). All 2D experiments (gradient-selected (gs)-COSY, NOESY, gs-HMQC, gs-HMBC) were



Scheme 2.

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 APCI mass spectra were measured on an ion trap analyser Esquire 3000 (Bruker Daltonics, Bremen, Germany) within the mass range m/z=50–500. Samples were dissolved in acetonitrile and analysed 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, and 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 in the range 0.7–0.8 V. Column chromatography was carried out on Silica gel (Merck, grade 60, 70–230 mesh) using chloroform and then successive mixtures of chloroform–ethanol (in rations from 99:1 to 8:2, solvent system S1) or benzene and then successive mixtures of benzene–ethyl acetate (in rations from 99:1 to 8:2, solvent system S2). Reactions as well as the course of separation and also the purity of substances were monitored by TLC (elution systems benzene–ethyl acetate, 4:1 (S3), chloroform–ethanol, 9:1 (S4) and/or 19:1 (S5), and chloroform–ethyl acetate, 7:3 (S6)) on Alugram® SIL G/UV_{254} foils (Macherey–Nagel). Elemental analyses (C, H, N) were performed with an EA 1108 Elemental Analyser (Fisons Instrument).

3′-Substituted 3-ureido-1*H*,3*H*-quinoline-2,4-diones **2** and 1-substituted 3a-alkyl/aryl-9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones **3** were prepared according to the protocol described in Ref. 5.

3.2. General procedure for the reaction of 3′-substituted 3-ureido-1*H*,3*H*-quinoline-2,4-diones (2) and 1-substituted 3a-alkyl/aryl-9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones (3) in acetic acid

The solution of **2** or **3** (0.5 mmol) in acetic acid (5 mL) was refluxed for 0.5–2 h (Table 1). The course of the reaction was monitored by TLC. The reaction mixture was evaporated in vacuo to dryness and the residue was crystallised from appropriate solvent or column chromatographed. In some cases, mother liquors after crystallisation of the products were column chromatographed.

3.2.1. 1-Butyl-1-(2-butyl-1*H*-indol-3-yl)-urea (4a). Compound was obtained from **2a** (yield 38%) and **3a** (yield 48%) besides **5a**. Colourless crystals; mp 135–142 °C (hexane); IR: 3480, 3318, 3254, 3198, 2956, 2931, 2870, 1655, 1583, 1456, 1425, 1379, 1362, 1344, 1232, 1122, 1108, 768, 743, 625, 571, 522, 505 cm^{-1}. Positive-ion APCI-MS: m/z 288 $[M+H]^+$ (100%), 271 $[M+H-NH_3]^+$, 243 $[M+H-NH_3-CO]^+$, 215 $[M+H-BuNH_2]^+$, 172 $[M+H-BuNH_2-NHCO]^+$. Positive-ion APCI-MS/MS of m/z 288: m/z 271 $[M+H-NH_3]^+$ (100%), 243 $[M+H-NH_3-CO]^+$, 215 $[M+H-BuNH_2]^+$, 172 $[M+H-BuNH_2-NHCO]^+$. Negative-ion APCI-MS: m/z 286 $[M-H]^-$ (100%). Negative-ion APCI-MS/MS of m/z 286: m/z 243 $[M-H-NHCO]^-$, 229 $[M-H-butane]^-$, 186 $[M-H-butane-NHCO]^-$ (100%), 143 $[M-H-butane-2\times NHCO]^-$.

Anal. calcd (found) for $C_{17}H_{25}N_3O$: C 71.04 (71.20); H 8.77 (8.56); N 14.62 (14.49).

3.2.2. 1-(2-Butyl-1*H*-indol-3-yl)-1-phenylurea (4b). Compound was prepared from **2b** (yield 7%). Colourless crystals; mp 204–208 °C (ethyl acetate); IR: 3463, 3322, 3254, 3197, 2957, 2934, 1662, 1580, 1491, 1458, 1406, 1266, 1243, 1046, 769, 743, 695, 628, 512, 435 cm^{-1}. Positive-ion APCI-MS: m/z 308 $[M+H]^+$, 291 $[M+H-NH_3]^+$, 263 $[M+H-NH_3-CO]^+$, 221 $[M+H-NH_3-CO-NCO]^{+\bullet}$, 172 $[M+H-PhNCO-NH_3]^+$ (100%), 143 $[M+H-PhNCO-NH_3-HCO]^{+\bullet}$, 130 $[M+H-PhNCO-NH_3-NCO]^{+\bullet}$. Positive-ion APCI-MS/MS of m/z 308: m/z 265 $[M+H-NHCO]^+$, 263 $[M+H-NH_3-CO]^+$, 189 $[M+H-PhNCO]^+$, 172 $[M+H-PhNCO-NH_3]^+$ (100%), 130 $[M+H-PhNCO-NH_3-NCO]^{+\bullet}$. Negative-ion APCI-MS: m/z 306 $[M-H]^-$ (100%), 263 $[M-H-NHCO]^-$, 221 $[M-H-NHCO-NCO]^{-\bullet}$, 170 $[M-H-PhNCO-NH_3]^-$. Negative-ion APCI-MS/MS of m/z 306: m/z 263 $[M-H-NHCO]^-$, 170 $[M-H-PhNCO-NH_3]^-$ (100%).

Anal. calcd (found) for $C_{19}H_{21}N_3O$: C 74.24 (74.12); H 6.89 (6.97); N 13.67 (13.49).

3.2.3. 1-(2-Butyl-1*H*-indol-3-yl)-3-methyl-1-phenylurea (4f). Compound was prepared from **3f** in 39% yield besides **5f**. Colourless crystals; mp 204–208 °C (benzene–hexane); IR: 3426, 3227, 3202, 2955, 2930, 2869, 1657, 1622, 1514, 1498, 1486, 1461, 1410, 1288, 1199, 1183, 1157, 760, 742, 695, 622, 510 cm^{-1}. Positive-ion APCI-MS: m/z 322 $[M+H]^+$ (100%), 264 $[M+H-butene]^+$, 172 $[M+H-PhNHCONHCH_3]^+$. Positive-ion APCI-MS/MS of m/z 322: m/z 264 $[M+H-butene]^+$, 172 $[M+H-PhNHCONHCH_3]^+$ (100%), 130 $[M+H-PhNHCONHCH_3-C_3H_6]^+$. Negative-ion APCI-MS: m/z 320 $[M-H]^-$ (100%). Negative-ion APCI-MS/MS of m/z 320: m/z 263 $[M-H-Bu]^{-\bullet}$ (100%), 170 $[M-H-PhNHCONHCH_3]^{-\bullet}$.

Anal. calcd (found) for $C_{20}H_{23}N_3O$: C 74.74 (74.59); H 7.21 (7.38); N 13.07 (12.89).

3.2.4. 3-Butyl-1-(2-butyl-1*H*-indol-3-yl)-1-phenylurea (4h). Compound was prepared from **3h** in 48% yield besides **5h**. Colourless crystals; mp 168–171 °C (benzene); IR: 3426, 3228, 3201, 3064, 2952, 2932, 2869, 1648, 1586, 1505, 1489, 1459, 1353, 1319, 1292, 1264, 1246, 1027, 966, 920, 891, 742, 695, 674, 624, 572, 520, 508 cm^{-1}. Positive-ion APCI-MS: m/z 364 $[M+H]^+$ (100%), 263 $[M+H-BuNHCOH]^+$, 172 $[M+H-BuNHCONHBu]^+$. Positive-ion APCI-MS/MS of m/z 364: m/z 263 $[M+H-BuNHCOH]^+$, 172 $[M+H-BuNHCONHBu]^+$ (100%), 130 $[M+H-BuNHCONHBu-C_3H_6]^+$. Negative-ion APCI-MS: m/z 362 $[M-H]^-$ (100%), 262 $[M-H-BuNHCO]^-$. Negative-ion APCI-MS/MS of m/z 362: m/z 263 $[M-H-BuNCO]^-$ (100%), 170 $[M-H-BuNHCONHBu]^-$.

Anal. calcd (found) for $C_{23}H_{29}N_3O$: C 76.00 (76.13); H 8.04 (7.93); N 11.56 (11.38).

3.2.5. 3-Benzyl-1-butyl-1-(2-butyl-1*H*-indol-3-yl)-urea (4i). Compound was prepared from **3i** in 18% yield besides **5i**. Colourless crystals; mp 137–142 °C (benzene–ethyl acetate); IR: 3422, 3225, 3197, 3082, 2955, 2930, 2870, 1638, 1586, 1515, 1456, 1419, 1383, 1338, 1293, 1266, 1225, 1172, 1128, 1028, 923, 767, 740, 695, 624, 600, 570, 487 cm^{-1}. Positive-ion APCI-MS: m/z 378

$[M+H]^+$ (100%), 271 $[M+H-BnNH_2]^+$, 243 $[M+H-BnNHCOH]^+$, 215 $[M+H-BnNHCOH-CO]^+$, 172 $[M+H-BuNHCONHCH_2Ph]^+$. Positive-ion APCI-MS/MS of *m/z* 378: *m/z* 361 $[M+H-NH_3]^+$, 333 $[M+H-NHCO]^+$, 305 $[M+H-BuNH_2]^+$, 271 $[M+H-BnNH_2]^+$, 243 $[M+H-BnNHCOH]^+$ (100%), 215 $[M+H-BnNHCOH-CO]^+$, 172 $[M+H-BuNHCONHCH_2Ph]^+$, 130 $[M+H-BuNHCONHCH_2Ph-C_3H_6]^+$. Negative-ion APCI-MS: *m/z* 376 $[M-H]^-$ (100%), 241 $[M-H-BnNHCOH]^-$. Negative-ion APCI-MS/MS of *m/z* 376: *m/z* 319 $[M-H-Bu]^{-\bullet}$, 275 $[M-H-Bu-NH_2CO]^-$, 243 $[M-H-BnNCO]^-$ (100%), 186 $[M-H-BnNCO-Bu]^{-\bullet}$, 170 $[M-H-BuNHCONHCH_2Ph]^-$, 143 $[M-H-BnNCO]^-$.

Anal. calcd (found) for $C_{24}H_{31}N_3O$: C 76.35 (76.18); H 8.28 (8.39); N 11.13 (11.02).

3.2.6. 3-Benzyl-1-(2-butyl-1*H*-indol-3-yl)-1-phenylurea (4j). Compound was prepared from **3j** in 7% yield besides **5j**. Colourless crystals; mp 153–157 °C (hexane); IR: 3416, 3264, 3233, 3062, 2954, 2931, 2869, 1653, 1509, 1494, 1457, 1295, 1075, 1028, 889, 744, 694, 627, 511 cm^{-1}. Positive-ion APCI-MS: *m/z* 398 $[M+H]^+$ (100%), 263 $[M+H-BnNHCOH]^+$. Positive-ion APCI-MS/MS of *m/z* 398: *m/z* 264 $[M+H-BuNHCO]^{+\bullet}$, 172 $[M+H-BuNHCONHBn]^+$ (100%), 130 $[M+H-BuNHCONHBn-C_3H_6]^+$. Negative-ion APCI-MS: *m/z* 396 $[M-H]^-$ (100%), 262 $[M-H-BnNHCO]^{-\bullet}$. Negative-ion APCI-MS/MS of *m/z* 396: *m/z* 263 $[M-H-BnNCO]^-$ (100%), 170 $[M-H-BuNHCONHBn]^-$.

Anal. calcd (found) for $C_{26}N_{27}N_3O$: C 78.56 (78.39); H 6.85 (6.97); N 10.57 (10.41).

3.2.7. 3-Butyl-1-(2-phenyl-1*H*-indol-3-yl)-1-phenylurea (4l). Compound was prepared from **3l** in 5% yield besides **5l**. Colourless crystals; mp 226–230 °C (acetic acid); IR: 3421, 3216, 3189, 3069, 2957, 2934, 2870, 1646, 1507, 1455, 1376, 1322, 1295, 1257, 761, 738, 693, 630, 608, 565, 511 cm^{-1}. Positive-ion APCI-MS: *m/z* 384 $[M+H]^+$ (100%), 311 $[M+H-BuNH_2]^+$, 283 $[M+H-BuNHCOH]^+$, 193 $[M+H-PhNHCONHBu]^+$. Positive-ion APCI-MS/MS of *m/z* 384: *m/z* 311 $[M+H-BuNH_2]^+$, 285 $[M+H-BuNCO]^+$ (100%), 193 $[M+H-PhNHCONHBu]^+$. Negative-ion APCI-MS: *m/z* 382 $[M-H]^-$ (100%), 283 $[M-H-BuNCO]^-$. Negative-ion APCI-MS/MS of *m/z* 382: *m/z* 283 $[M+H-BuNCO]^+$ (100%).

Anal. calcd (found) for $C_{25}H_{25}N_3O$: C 78.30 (78.22); H 6.57 (6.71); N 10.96 (10.77).

3.2.8. 1,3-Bis[2-(3,5-dibutyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5a). Compound was obtained from **2a** (yield 36%) and **3a** (yield 34%) besides **4a**. Colourless crystals; mp 182–188 °C (hexane); IR: 3276, 3236, 3187, 2959, 2933, 2872, 1678, 1607, 1579, 153.0, 1454, 1403, 1287, 1189, 941, 757, 670, 629, 473 cm^{-1}. Positive-ion APCI-MS: *m/z* 601 $[M+H]^+$ (100%), 314 $[F+26]^+$, 288 $[F]^+$, 243 $[F-NH_3-CO]^+$. Positive-ion APCI-MS/MS of *m/z* 601: *m/z* 558 $[M+H-NHCO]^+$, 314 $[F+26]^+$ (100%), 288 $[F]^+$, 245 $[F-NHCO]^+$, 202 $[F-2\times NHCO]^+$, 172 $[F-NHCO-BuNH_2]^+$. Negative-ion APCI-MS: *m/z* 599 $[M-H]^-$ (100%), 312 $[F+26-2H]^-$, 286 $[F-2H]^-$. Negative-ion APCI-MS/MS of *m/z* 599: *m/z* 312 $[F+26-2H]^-$ (100%), 286 $[F-2H]^-$, 269 $[F+26-2H-NHCO]^-$, 255 $[F-2H-Bu]^{-\bullet}$, 212 $[F-2H-Bu-NH_3]^{-\bullet}$.

Anal. calcd (found) for $C_{35}H_{48}N_{z6}O_3$: C 69.97 (69.79); H 8.05 (8.23); N 13.99 (13.80).

3.2.9. 1,3-Bis[2-(3-butyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5c). Compound was prepared from **3c** (52% yield). Colourless crystals; mp 173–179 °C (ethyl acetate); IR: 3348, 3281, 3214, 3177, 3058, 2959, 2936, 2873, 1679, 1604, 1579, 1523, 1449, 1401, 1376, 1284, 1189, 1115, 1044, 936, 844, 759, 693, 670, 629, 553, 493 cm^{-1}. Positive-ion APCI-MS: *m/z* 641 $[M+H]^+$ (100%), 615 $[M+H-C_2H_2]^+$, 334 $[F+26]^+$, 308 $[F]^+$, 263 $[F-NH_3-CO]^+$. Positive-ion APCI-MS/MS of *m/z* 641: *m/z* 598 $[M+H-NHCO]^+$, 334 $[F+26]^+$ (100%), 308 $[F]^+$, 291 $[F+26-NHCO]^+$, 278 $[F+26-butene]^+$, 263 $[F-NH_3-CO]^+$, 252 $[F-butene]^+$, 235 $[F-BuNH_2]^+$, 209 $[F-BuNH_2-C_2H_2]^+$. Negative-ion APCI-MS: *m/z* 639 $[M-H]^-$ (100%), 332 $[F+26-2H]^-$, 306 $[F-2H]^-$, 261 $[F-NH_3-CO-2H]^-$. Negative-ion APCI-MS/MS of *m/z* 639: *m/z* 332 $[F+26-2H]^-$ (100%), 306 $[F-2H]^-$, 275 $[F-Bu-2H]^{-\bullet}$.

Anal. calcd (found) for $C_{39}H_{40}N_6O_3$: C 73.10 (73.25); H 6.29 (6.09); N 13.12 (12.95).

3.2.10. 1,3-Bis[2-(3,5-dibutyl-1-methyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5e). Compound was prepared from **3e** (57% yield). Yellowish oil; IR: 3274, 3241, 2957, 2931, 2871, 1669, 1646, 1578, 1529, 1455, 1401, 1286, 1190, 1160, 750, 668, 654, 629, 596, 548 cm^{-1}. Positive-ion APCI-MS: *m/z* 629 $[M+H]^+$ (100%), 328 $[F+26]^+$, 302 $[F]^+$. Positive-ion APCI-MS/MS of *m/z* 629: *m/z* 572 $[M+H-Bu]^{+\bullet}$, 328 $[F+26]^+$ (100%), 302 $[F]^+$, 272 $[F+26-Bu]^{+\bullet}$, 245 $[F-Bu]^{+\bullet}$, 216 $[F+26-Bu-butene]^+$. Negative-ion APCI-MS: *m/z* 627 $[M-H]^-$ (100%), 325 $[F+26-2H]^-$, 300 $[F-2H]^-$. Negative-ion APCI-MS/MS of *m/z* 627: *m/z* 300 $[F-2H]^-$ (100%), 243 $[F-2H-Bu]^{-\bullet}$, 186 $[F-2H-2Bu]^-$.

Anal. calcd (found) for $C_{37}H_{52}N_6O_3$: C 70.67 (70.49); H 8.33 (8.49); N 13.36 (13.26).

3.2.11. 1,3-Bis[2-(5-butyl-1-methyl-2-oxo-3-phenyl-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5f). Compound was prepared from **3f** in 21% yield besides **4f**. Colourless crystals; mp 133–138 °C (cyclohexane); IR: 3319, 3058, 2957, 2930, 2861, 1676, 1598, 1579, 1527, 1503, 1446, 1395, 1285, 1193, 1108, 1072, 756, 694, 652, 631, 508 cm^{-1}. Positive-ion APCI-MS: *m/z* 669 $[M+H]^+$ (100%), 612 $[M+H-Bu]^{+\bullet}$, 348 $[F+26]^+$, 322 $[F]^+$. Positive-ion APCI-MS/MS of *m/z* 669: *m/z* 612 $[M+H-Bu]^{+\bullet}$, 348 $[F+26]^+$ (100%), 322 $[F]^+$, 292 $[F+26-butene]^+$, 265 $[F-Bu]^{+\bullet}$, 235 $[F+26-butene-Bu]^{+\bullet}$, 208 $[F-2\times Bu]^+$. Negative-ion APCI-MS: *m/z* 667 $[M-H]^-$ (100%), 320 $[F-2H]^-$. Negative-ion APCI-MS/MS of *m/z* 667: *m/z* 320 $[F-2H]^-$ (100%), 263 $[F-2H-Bu]^{-\bullet}$.

Anal. calcd (found) for $C_{41}H_{44}N_6O_3$: C 73.63 (73.49); H 6.63 (6.79); N 12.57 (12.49).

3.2.12. 1,3-Bis[2-(1,3,5-tributyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5g). Compound was prepared from **3g** in 79% yield. Yellowish oil; IR: 3280, 2958, 2932, 2872, 1667, 1642, 1578, 1527, 1454, 1415, 1373, 1285, 1192, 1113, 1062, 1038, 945, 755, 654, 629, 549 cm^{-1}. Positive-ion APCI-MS: *m/z* 713 $[M+H]^+$, 370 $[F+26]^+$, 344 $[F]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 713: *m/z* 370 $[F+26]^+$ (100%), 344 $[F]^+$. Negative-ion APCI-MS: *m/z* 711 $[M-H]^-$, 342 $[F-2H]^-$ (100%).

Anal. calcd (found) for $C_{43}H_{64}N_6O_3$: C 72.43 (72.31); H 9.05 (9.23); N 11.79 (11.62).

3.2.13. 1,3-Bis[2-(1,5-dibutyl-2-oxo-3-phenyl-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5h). Compound was prepared from **3h** in 16% yield besides **4h**. Colourless crystals; mp 183–187 °C (hexane); IR: 3303, 3063, 2957, 2932, 2871, 1695, 1669, 1643, 1579, 1526, 1503, 1449, 1409, 1380, 1286, 1193, 1112, 945, 886, 755, 693, 651, 543, 508 cm^{-1}. Positive-ion APCI-MS: *m/z* 753 $[M+H]^+$ (100%), 390 $[F+26]^+$, 364 $[F]^+$. Positive-ion APCI-MS/MS of *m/z* 753: *m/z* 654 $[M+H-BuNCO]^+$, 390 $[F+26]^+$ (100%), 364 $[F]^+$, 334 $[F+26-butene]^+$, 278 $[F+26-2\times butene]^+$, 235 $[F+26-2\times butene-NHCO]^+$. Negative-ion APCI-MS: *m/z* 751 $[M-H]^-$ (100%), 362 $[F-2H]^-$. Negative-ion APCI-MS/MS of *m/z* 751: *m/z* 362 $[F-2H]^-$ (100%), 263 $[F-2H-BuNCO]^-$.

Anal. calcd (found) for $C_{47}H_{56}N_6O_3$: C 74.97 (74.79); H 7.50 (7.67); N 11.16 (11.02).

3.2.14. 1,3-Bis[2-(1-benzyl-3,5-dibutyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5i). Compound was prepared from **3i** in 50% yield besides **4i**. Yellowish oil; IR: 3221, 3030, 2957, 2930, 2871, 1673, 1643, 1578, 1527, 1496, 1453, 1411, 1400, 1285, 1192, 1111, 1076, 1029, 946, 785, 753, 732, 700, 654, 577, 550 cm^{-1}. Positive-ion APCI-MS: *m/z* 781 $[M+H]^+$ (100%), 404 $[F+26]^+$, 378 $[F]^+$. Positive-ion APCI-MS/MS of *m/z* 781: *m/z* 690 $[M+H-Bn]^{+\bullet}$, 648 $[M+H-BnNCO]^+$, 404 $[F+26]^+$ (100%), 378 $[F]^+$, 360 $[F+26-NH_2CO]^{+\bullet}$, 348 $[F+26-butene]^+$, 313 $[F+26-Bn]^{+\bullet}$, 270 $[F+26-BnNHCO]^{+\bullet}$, 245 $[F-BnNCO]^+$. Negative-ion APCI-MS: *m/z* 779 $[M-H]^-$ (100%), 376 $[F-2H]^-$. Negative-ion APCI-MS/MS of *m/z* 779: *m/z* 376 $[F-2H]^-$ (100%), 320 $[F-2H-butene]^{-\bullet}$, 243 $[F-2H-BnNCO]^+$.

Anal. calcd (found) for $C_{49}H_{60}N_6O_3$: C 75.35 (75.16); H 7.74 (7.82); N 10.76 (10.59).

3.2.15. 1,3-Bis[2-(1-benzyl-5-butyl-2-oxo-3-phenyl-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5j). Compound was prepared from **3j** in 41% yield besides **4j**. Colourless crystals; mp 110–115 °C (hexane); IR: 3298, 3062, 3030, 2957, 2930, 2869, 1676, 1598, 1580, 1524, 1501, 1451, 1407, 1359, 1287, 1195, 1074, 1029, 960, 750, 697, 581, 540, 506 cm^{-1}. Positive-ion APCI-MS: *m/z* 821 $[M+H]^+$ (100%), 424 $[F+26]^+$, 398 $[F]^+$. Positive-ion APCI-MS/MS of *m/z* 821: *m/z* 730 $[M+H-Bn]^{+\bullet}$, 688 $[M+H-BnNCO]^+$, 424 $[F+26]^+$ (100%), 398 $[F]^+$, 368 $[F+26-butene]^+$, 333 $[F+26-Bn]^{+\bullet}$, 290 $[F+26-BnNHCO]^{+\bullet}$, 265 $[F-BnNCO]^+$. Negative-ion APCI-MS: *m/z* 819 $[M-H]^-$ (100%), 396 $[F-2H]^-$. Negative-ion APCI-MS/MS of *m/z* 819: *m/z* 396 $[F-2H]^-$ (100%), 305 $[F-2H-Bn]^{-\bullet}$.

Anal. calcd (found) for $C_{53}H_{52}N_6O_3$: C 77.53 (77.41); H 6.38 (6.51); N 10.24 (10.14).

3.2.16. 1,3-Bis[2-(1,3-dibutyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5k). Compound was prepared from **3k** in 63% yield. Colourless crystals; mp 154–164 °C; IR: 3287, 3057, 2959, 2933, 2872, 1686, 1660, 1578, 1526, 1451, 1406, 1369, 1285, 1192, 1075, 939, 873, 756, 701, 655, 629 cm^{-1}. Positive-ion APCI-MS: *m/z* 753 $[M+H]^+$ (100%), 390 $[F+26]^+$, 364 $[F]^+$. Positive-ion APCI-MS/MS of *m/z* 753: *m/z* 390 $[F+26]^+$ (100%), 364 $[F]^+$, 334 $[F+26-butene]^+$, 278 $[F+26-2\times butene]^+$, 235 $[F+26-2\times butene-NHCO]^+$. Negative-ion APCI-MS: *m/z* 751 $[M-H]^-$ (100%). Negative-ion APCI-MS/MS of *m/z* 751: *m/z* 362 $[F+26-2H]^-$ (100%), 306 $[F-2H]^-$, 263 $[F+26-2H-BuNCO]^+$, 206 $[F+26-2H-BuNCO-Bu]^{+\bullet}$.

Anal. calcd (found) for $C_{47}H_{56}N_6O_3$: C 74.97 (74.79); H 7.50 (7.68); N 11.16 (11.01).

3.2.17. 1,3-Bis[2-(1-butyl-3,5-diphenyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5l). Compound was prepared from **3l** in 54% yield besides **4l**. Colourless crystals; mp 258–264 °C (benzene); IR: 3338, 3177, 3061, 3043, 2957, 2932, 2872, 1697, 1671, 1598, 1579, 1517, 1499, 1448, 1383, 1288, 1227, 1192, 1091, 1073, 1027, 946, 806, 758, 698, 651, 632, 525, 505 cm^{-1}. Positive-ion APCI-MS: *m/z* 793 $[M+H]^+$ (100%), 410 $[F+26]^+$, 384 $[F]^+$. Positive-ion APCI-MS/MS of *m/z* 793: *m/z* 410 $[F+26]^+$ (100%), 384 $[F]^+$, 354 $[F+26-butene]^+$, 285 $[F-BuNCO]^+$, 235 $[F+26-butene-PhNCO]^+$. Negative-ion APCI-MS: *m/z* 791 $[M-H]^-$ (100%). Negative-ion APCI-MS/MS of *m/z* 791: *m/z* 382 $[F-2H]^-$ (100%), 326 $[F-2H-butene]^-$, 283 $[F-2H-BuNCO]^-$.

Anal. calcd (found) for $C_{51}H_{48}N_6O_3$: C 77.25 (77.31); H 6.10 (6.21); N 10.60 (10.42).

3.2.18. 1,3-Bis[2-(1-benzyl-3-butyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5m). Compound was prepared from **3m** in 83% yield. Colourless crystals; mp 95–100 °C; IR: 3331, 3231, 3190, 3060, 3030, 2957, 2932, 2871, 1687, 1667, 1579, 1526, 1497, 1450, 1401, 1359, 1285, 1226, 1195, 113, 1074, 1028, 972, 946, 919, 872, 818, 751, 700, 660, 629, 582, 552, 509 cm^{-1}. Positive-ion APCI-MS: *m/z* 821 $[M+H]^+$, 424 $[F+26]^+$, 398 $[F]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 821: *m/z* 424 $[F+26]^+$, 398 $[F]^+$ (100%), 368 $[F+26-butene]^+$, 333 $[F+26-Bn]^{+\bullet}$, 276 $[F+26-Bn-Bu]^+$, 234 $[F+26-Bn-BuNCO]^{+\bullet}$. Negative-ion APCI-MS: *m/z* 819 $[M-H]^-$ (100%). Negative-ion APCI-MS/MS of *m/z* 819: *m/z* 396 $[F-2H]^-$ (100%), 340 $[F-2H-butene]^-$, 263 $[F-2H-BnNCO]^+$.

Anal. calcd (found) for $C_{53}H_{52}N_6O_3$: C 77.53 (77.38); H 6.38 (6.52); N 10.24 (10.08).

3.2.19. 1,3-Bis[2-(1-benzyl-3,5-diphenyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-urea (5n). Compound was prepared from **3n** in 74% yield. Colourless crystals; mp 227–232 °C; IR: 3340, 3285, 3221, 3058, 3032, 2947, 1688, 1671, 1598, 1580, 1519, 1497, 1448, 1388, 1288,

1229, 1190, 1075, 1028, 921, 877, 819, 782, 760, 697, 650, 589, 520, 501 cm^{-1}. Positive-ion APCI-MS: *m/z* 861 $[M+H]^+$, 444 $[F+26]^+$, 418 $[F]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 861: *m/z* 770 $[M+H-Bn]^+$, 444 $[F+26]^+$, 418 $[F]^+$, 353 $[F+26-Bn]^{+\bullet}$, 325 $[F+26-toluene]^+$, 283 $[F+26-toluene-C_3H_6]^+$. Negative-ion APCI-MS: *m/z* 859 $[M-H]^-$ (100%), 416 $[F-2H]^-$. Negative-ion APCI-MS/MS of *m/z* 859: *m/z* 416 $[F-2H]^-$ (100%), 325 $[F-2H-Bn]^{-\bullet}$.

Anal. calcd (found) for $C_{57}H_{44}N_6O_3$: C 79.51 (79.39); H 5.15 (5.31); N 9.76 (9.59).

3.3. General procedure for the conversion of (1*H*-indol-3-yl)-ureas (4) to 4-(2-aminophenyl)-1,3-dihydroimidazol-2-ones (6) in concd hydrochloric acid

The mixture of **4** (0.2 mmol) and concd hydrochloric acid (6 mL) was refluxed for the time given below. The course of the reaction was monitored by TLC. The reaction mixture was evaporated in vacuo to dryness and the residue was triturated with a 6% solution of sodium hydrogencarbonate (5 mL). The precipitate was filtered off and crystallised from appropriate solvent or extracted with benzene. The benzene portion was evaporated and the residue was crystallised from appropriate solvent or column chromatographed. In several cases, the crude reaction product was dissolved in chloroform, the solution was stirred with solid potassium carbonate, filtered and evaporated. Unstable compounds **6a**,**b** were obtained by evaporation of the reaction mixture and triturating the residue with hexane.

3.3.1. 4-(2-Aminophenyl)-3,5-dibutyl-1,3-dihydroimidazol-2-one (6a). Compound was prepared from **4a** in 74% yield, reaction time 1 h. Lightly pink crystals; mp 135–140 °C (without recrystallisation); IR: 3421, 3149, 2956, 2931, 2860, 2608, 1661, 1548, 1495, 1453, 1407, 1377, 1312, 1192, 1099, 1040, 945, 765, 656, 553 cm^{-1}. Positive-ion APCI-MS: *m/z* 288 $[M+H]^+$ (100%), 271 $[M+H-NH_3]^+$, 244 $[M+H-NH_2CO]^{+\bullet}$, 172 $[M+H-BuNHCONH_2]^+$. Positive-ion APCI-MS/MS of *m/z* 288: *m/z* 270 $[M+H-H_2O]^+$, 258 $[M+H-H_2CO]^+$, 244 $[M+H-NH_2CO]^{+\bullet}$, 232 $[M+H-butene]^+$ (100%), 215 $[M+H-butene-NH_3]^+$, 189 $[M+H-butene-NHCO]^+$, 172 $[M+H-BuNHCONH_2]^+$, 130 $[M+H-BuNHCONH_2-C_3H_6]^+$. Negative-ion APCI-MS: *m/z* 286 $[M-H]^-$ (100%), 256 $[M-H-H_2CO]^-$, 241 $[M-H-CO-NH_3]^-$, 229 $[M-H-butene]^-$. Negative-ion APCI-MS/MS of *m/z* 286: *m/z* 243 $[M-H-NHCO]^-$ (100%), 229 $[M-H-butene]^-$, 186 $[M-H-NHCO-Bu]^{-\bullet}$, 170 $[M-H-NHCO-BuNH_2]^-$.

Anal. calcd (found) for $C_{17}H_{25}N_3O$: C 71.04 (71.12); H 8.77 (8.58); N 14.62 (14.55).

3.3.2. 4-(2-Aminophenyl)-5-butyl-3-phenyl-1,3-dihydroimidazol-2-one (6b). Compound was prepared from **4b** in 94% yield. Lightly pink crystals; mp 138–141 °C (without recrystallisation); IR: 3405, 3019, 2958, 2931, 2871, 2552, 1677, 1596, 1522, 1498, 1453, 1393, 1340, 1125, 1038, 870, 765, 709, 655, 555 cm^{-1}. Positive-ion APCI-MS: *m/z* 308 $[M+H]^+$, 263 $[M+H-CO-NH_3]^+$, 172 $[M+H-PhNHCONH_2]^+$ (100%), 130 $[M+H-PhNHCONH_2-C_3H_6]^+$. Positive-ion APCI-MS/MS of *m/z* 308: *m/z* 265 $[M+H-NHCO]^+$, 189 $[M+H-PhNCO]^+$, 172 $[M+H-PhNHCONH_2]^+$ (100%), 130 $[M+H-PhNHCONH_2-C_3H_6]^+$. Negative-ion APCI-MS: *m/z* 306 $[M-H]^-$ (100%), 263 $[M-H-NHCO]^-$, 233 $[M-H-BuNH_2]^-$, 206 $[M-H-BuNHCO]^{-\bullet}$, 170 $[M-H-PhNHCONH_2]^-$. Negative-ion APCI-MS/MS of *m/z* 306: *m/z* 263 $[M-H-NHCO]^-$ (100%), 170 $[M-H-PhNHCONH_2]^-$.

Anal. calcd (found) for $C_{19}H_{21}N_3O$: C 74.24 (74.11); H 6.89 (6.98); N 13.67 (13.42).

3.3.3. 4-(2-Aminophenyl)-5-butyl-1-methyl-3-phenyl-1,3-dihydroimidazol-2-one (6f). Compound was prepared from **4f** in 51% yield, reaction time 1.5 h. Colourless crystals; mp 154–162 °C (benzene–hexane); IR: 3435, 3324, 3206, 2959, 2932, 2862, 1680, 1650, 1621, 1597, 1494, 1455, 1439, 1392, 1310, 1158, 891, 767, 755, 742, 696, 651, 619, 508, 475 cm^{-1}. Positive-ion APCI-MS: *m/z* 322 $[M+H]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 322: *m/z* 278 $[M+H-NH_2CO]^{+\bullet}$, 265 $[M+H-Bu]^{\bullet}$ (100%), 203 $[M+H-PhNCO]^+$, 172 $[M+H-PhNHCONHCH_3]^+$, 130 $[M+H-PhNHCONHCH_3-C_3H_6]^+$. Negative-ion APCI-MS: *m/z* 320 $[M-H]^-$ (100%). Negative-ion APCI-MS/MS of *m/z* 320: *m/z* 263 $[M-H-Bu]^{-\bullet}$ (100%), 206 $[M-H-2\times Bu]^-$, 170 $[M-H-PhNHCONHCH_3]^-$.

Anal. calcd (found) for $C_{20}H_{23}N_3O$: C 74.74 (74.58); H 7.21 (7.37); N 13.07 (13.01).

3.3.4. 4-(2-Aminophenyl)-1,5-dibutyl-3-phenyl-1,3-dihydroimidazol-2-one (6h). Compound was prepared from **4h** in 58% yield, reaction time 3 h. Colourless crystals; mp 115–122 °C (hexane–ethyl acetate); IR: 3428, 3341, 3234, 2954, 2928, 2870, 1690, 1677, 1650, 1626, 1599, 1501, 1465, 1410, 1385, 1314, 1158, 749, 691, 651, 504 cm^{-1}. Positive-ion APCI-MS: *m/z* 364 $[M+H]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 364: *m/z* 265 $[M+H-BuNCO]^+$ (100%), 245 $[M+H-PhNCO]^+$, 172 $[M+H-PhNHCONHBu]^+$, 130 $[M+H-PhNHCONHBu-C_3H_6]^+$. Negative-ion APCI-MS: *m/z* 362 $[M-H]^-$ (100%). Negative-ion APCI-MS/MS of *m/z* 362: *m/z* 263 $[M-H-BuNCO]^-$ (100%), 170 $[M-H-PhNHCONHBu]^-$.

Anal. calcd (found) for $C_{23}H_{29}N_3O$: C 76.00 (75.82); H 8.04 (8.17); N 11.56 (11.41).

3.3.5. 4-(2-Aminophenyl)-1-benzyl-3,5-dibutyl-1,3-dihydroimidazol-2-one (6i). Compound was prepared from **4i** in 72% yield, reaction time 2 h. Colourless crystals; mp 98–105 °C (hexane); IR: 3420, 3332, 3229, 2953, 2864, 1675, 1650, 1621, 1574, 1496, 1458, 1414, 1361, 1312, 1262, 1158, 1106, 1028, 975, 939, 850, 746, 697, 652, 511 cm^{-1}. Positive-ion APCI-MS: *m/z* 378 $[M+H]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 378: *m/z* 334 $[M+H-NH_2CO]^{+\bullet}$, 300 $[M+H-C_6H_6]^+$, 287 $[M+H-Bn]^{+\bullet}$, 243 $[M+H-Bn-NH_2CO]^{+\bullet}$ (100%), 186 $[M+H-Bn-NH_2CO-Bu]^+$, 172 $[M+H-BuNHCONHCH_2Ph]^+$, 130 $[M+H-BuNHCONHCH_2Ph-C_3H_6]^+$. Negative-ion APCI-MS: *m/z* 376 $[M-H]^-$ (100%), 320 $[M-H-butene]^-$. Negative-ion APCI-MS/MS of *m/z* 376: *m/z* 320 $[M-H-butene]^-$, 243 $[M-H-butene-phenyl]^{-\bullet}$ (100%), 186 $[M-H-butene-phenyl-Bu]^-$.

Anal. calcd (found) for $C_{24}H_{31}N_3O$: C 76.35 (76.16); H 8.28 (8.17); N 11.13 (11.28).

3.3.6. 4-(2-Aminophenyl)-1-benzyl-5-butyl-3-phenyl-1,3-dihydroimidazol-2-one (6j). Compound was prepared from **4j** in 50% yield, reaction time 2 h. Colourless crystals; mp 88–94 °C (hexane); IR: 3448, 3416, 3343, 3027, 2956, 2930, 2870, 1678, 1640, 1622, 1598, 1496, 1454, 1404, 1356, 1311, 1156, 1073, 1028, 955, 749, 694, 652, 552, 503 cm^{-1}. Positive-ion APCI-MS: *m/z* 398 $[M+H]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 398: *m/z* 265 $[M+H-BnNCO]^+$ (100%), 248 $[M+H-BnNCO-NH_3]^+$, 221 $[M+H-BnNCO-NH_2CO]^{+\bullet}$, 208 $[M+H-BnNCO-Bu]^{+\bullet}$, 172 $[M+H-PhNHCONHCH_2Ph]^+$, 130 $[M+H-PhNHCONHCH_2Ph-C_3H_6]^+$. Negative-ion APCI-MS: *m/z* 396 $[M-H]^-$ (100%). Negative-ion APCI-MS/MS of *m/z* 396: *m/z* 305 $[M-H-Bn]^{-\bullet}$, 263 $[M-H-BnNCO]^-$ (100%), 170 $[M-H-PhNHCONHCH_2Ph]^-$.

Anal. calcd (found) for $C_{26}H_{27}N_3O$: C 78.56 (78.38); H 6.85 (6.93); N 10.57 (11.41).

3.3.7. 4-(2-Aminophenyl)-1-butyl-3,5-diphenyl-1,3-dihydroimidazol-2-one (6l). Compound was prepared from **4l** in 59% yield, reaction time 3 h. Colourless crystals; mp 54–57 °C (without recrystallisation); IR: 3465, 3337, 3241, 2956, 2928, 2870, 1689, 1619, 1598, 1499, 1454, 1384, 1311, 1226, 1156, 1027, 749, 697, 652, 525, 508 cm^{-1}. Positive-ion APCI-MS: *m/z* 384 $[M+H]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 384: *m/z* 366 $[M+H-H_2O]^+$, 311 $[M+H-BuNH_2]^+$, 285 $[M+H-BuNCO]^+$ (100%), 265 $[M+H-PhNCO]^+$. Negative-ion APCI-MS: *m/z* 382 $[M-H]^-$ (100%). Negative-ion APCI-MS/MS of *m/z* 382: *m/z* 283 $[M-H-BuNH_2]^-$ (100%).

Anal. calcd (found) for $C_{25}H_{25}N_3O$: C 78.30 (78.12); H 6.57 (6.75); N 10.96 (10.81).

3.4. General procedure for the synthesis of 1,3-bis[2-(2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)-phenyl]-ureas (5)

Triphosgene (0.035 mmol=1.06 equiv, 10.4 mg) was added under stirring at rt to the solution of **6** (0.2 mmol), triethylamine (0.25 mmol, 25.4 mg) and 4-dimethylaminopyridine (5 mg) in 5 mL of benzene. After 1 h at rt, the reaction mixture was refluxed for 2.5 h. After cooling, the mixture was filtered and evaporated to dryness in vacuo. The residue was column chromatographed on silica gel using chloroform as eluent. The following compounds **5**, identical in all respects with those prepared by refluxing of **2** or **3** in acetic acid (see Section 3.1), were prepared: **5a** (6%), **5f** (52%), **5h** (58%), **5i** (65%), **5j** (50%), **5l** (49%).

Acknowledgements

This study was supported by the Ministry of Education, Youth and Sports of the Czech Republic (Grant No. MSM 7088352101) and Czech Science Foundation (Grant No. 203/07/0320). M.H. acknowledges the support of grant projects MSM 0021627502 (the Ministry of Education, Youth and Sports of the Czech Republic) and 203/05/2106 (Czech Science Foundation). A.K. is indebted to Dr. Robert Vicha (Faculty of Technology, Tomas Bata University in Zlín) for fruitful discussions on the stereochemistry of diarylureas. The authors thank Mrs. H. Geržová (Faculty of Technology, Tomas Bata University in Zlín) and Mr. Robert Jirásko (University of Pardubice) for technical help.

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