Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron
ELSEVIER
Tetrahedron 60 (2004) 9953–9961

Reaction of 3-aminoquinoline-2,4-diones with nitrourea. Synthetic route to novel 3-ureidoquinoline-2,4-diones and imidazo[4,5-*c*]quinoline-2,4-diones

Antonín Klásek,[a,*] Antonín Lyčka,[b] Michal Holčapek[c] and Ignác Hoza[a]

[a]*Department of Food Engineering and Chemistry, Faculty of Technology, Tomas Bata University, CZ-762 72 Zlín, Czech Republic*
[b]*Research Institute for Organic Syntheses, Rybitví 296, CZ-53218 Pardubice 20, Czech Republic*
[c]*Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, CZ-53210 Pardubice, Czech Republic*

Received 24 May 2004; revised 20 July 2004; accepted 12 August 2004

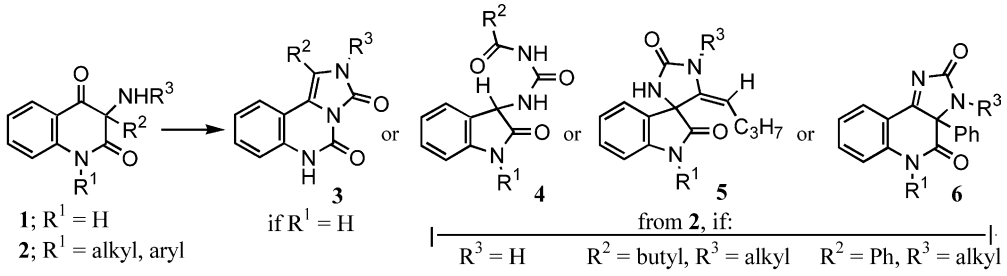
Available online 11 September 2004

Abstract—1-Unsubstituted 3-alkyl/aryl-3-amino-1*H*,3*H*-quinoline-2,4-diones react with 1-substituted and 1,1-disubstituted ureas in boiling acetic acid to give 2,6-dihydro-imidazo[1,5-*c*]quinazoline-3,5-diones. In contrast, the reaction of these amines with nitrourea in dioxane affords novel 3-alkyl/aryl-3-ureido-1*H*,3*H*-quinoline-2,4-diones or 9b-hydroxy-3a-alkyl/aryl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones, which can smoothly be dehydrated to 3a-alkyl/aryl-3,3a-dihydro-5*H*-imidazo[4,5-*c*]quinoline-2,4-diones. All three types of products can be converted to 2,6-dihydro-imidazo[1,5-*c*]quinazoline-3,5-diones by refluxing in acetic acid.

1. Introduction

Recently, an unprecedented reaction of 3-amino-1*H*,3*H*-quinoline-2,4-diones **1** with urea in boiling acetic acid has been described by us.[1] The expected 3,3a-dihydro-5*H*-imidazo[4,5-*c*]-quinoline-2,4-diones **6** ($R^1 = H$) do not arise but a molecular rearrangement takes place, producing novel 2,6-dihydro-imidazo[1,5-*c*]quinazoline-3,5-diones **3** (Scheme 1). In contrast, the study of the reaction of urea with compounds **1** containing a tertiary lactam group in the quinoline ring showed that these compounds react to give three different types of compounds.[2] Depending on the character of substitution in the starting compounds **2**, either a molecular rearrangement of the quinolone system to indolinone system occurs with formation of previously undescribed 3-(3-acylureido)-2,3-dihydro-1*H*-indol-2-ones **4** or 4-alkylidene-1′*H*-spiro[imidazolidine-5,3′-indole]-2,2′-diones **5**, or the expected 3,3a-dihydro-5*H*-imidazo[4,5-*c*]quinoline-2,4-diones **6** arise (Scheme 1). A reaction mechanism for these transformations was proposed.[2]

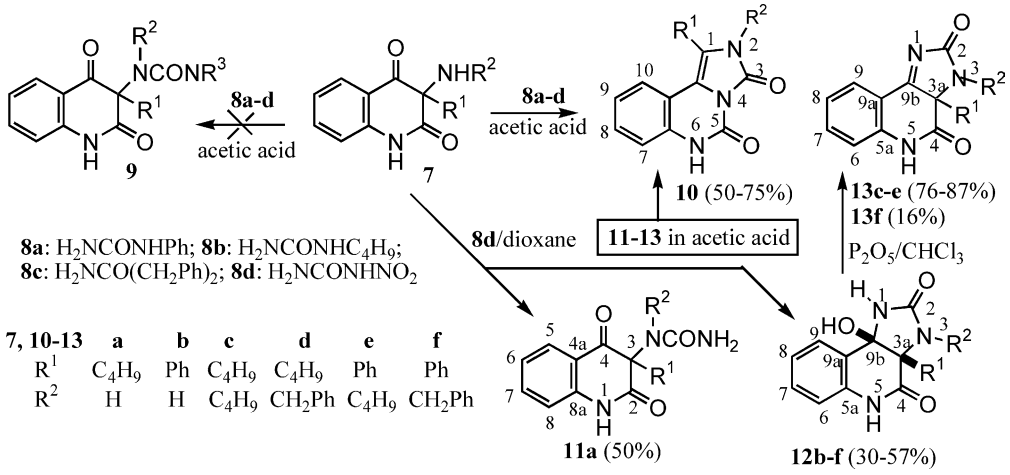
Owing to the unexpected course of substances **1** and **2** reacting with urea to produce new heterocyclic systems, we



Scheme 1.

Keywords: Molecular rearrangement; Nitrourea; Urea derivatives; α-Aminoketones; α-Ureidoketones.
* Corresponding author. Tel.: +420-576-031-413; fax: +420-577-210-722; e-mail: klasek@ft.utb.cz

0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.07.106



Scheme 2.

also decided to study reactions of these α-aminoketones with some substituted ureas. We demonstrate in this work that differently substituted 3-amino-1*H*,3*H*-quinoline-2,4-diones **7** react with 1-substituted and 1,1-disubstituted ureas in acetic acid in the same manner as with urea[1] forming 2,6-dihydro-imidazo(1,5-*c*(quinazoline-3,5-diones **10**. With nitrourea, however, substances **7** react in various manners depending on the character of reaction medium.

2. Results and discussion

The starting amines **7** were obtained from the corresponding 3-chloro derivatives in accordance with procedures described in the literature.[3] We first dealt with reactions of compounds **7** with substituted ureas **8a–c**. Reactions were performed in the same manner as in our previous papers,[1,2] that is, by boiling amines **7** with **8** in a solution of acetic acid. The reaction of **7a** with phenylurea (**8a**) yielded the

Table 1. ^{1}H, ^{13}C, and ^{15}N NMR shifts (δ, ppm) of compounds **10f** and **11a** in DMSO-d_6

Position	**10f**		**11a**	
	δ_H	δ_C or δ_N	δ_H	δ_C or δ_N
1	—	117.8	10.81	−246.2[a]
2	—	−241.3	—	172.4
3	—	148.4	—	66.9
4	—	−230.6	—	194.7
4a	—	—	—	119.1
5	—	145.0	7.79	126.9
6	10.51	−263.8[b]	7.13	122.2
6a	—	134.5	—	—
7	7.04	115.3	7.62	135.8
8	7.18	128.3	7.12	116.3
8a			—	141.8
9	6.79	122.6	—	—
10	6.73	121.3	—	—
10a	—	112.9	—	—
10b	—	113.8	—	—
1′(3)			2.79	36.4
2′(3)			1.21	24.6
3′(3)			1.21	22.2
4′(3)			0.80	13.8
*NH*CONH$_2$			7.00	−284.7[c]
NH*C*ONH$_2$			—	157.9
NHCO*NH*$_2$			5.70	−306.1[d]
NH$_2$(CO)			5.70	—
i-Ph (1)	—	128.1	—	—
o-Ph (1)	7.40	131.0	—	—
m-Ph (1)	7.54	128.5	—	—
p-Ph (1)	7.60	130.1	—	—
CH$_2$Ph	4.72	43.9	—	—
i-PhCH$_2$	—	137.0		
o-PhCH$_2$	6.99	126.8		
m-PhCH$_2$	7.26	129.5		
p-PhCH$_2$	7.38	127.3		

[a] $^{1}J(^{15}N, ^{1}H)$ (Hz): 90.7.
[b] $^{1}J(^{15}N, ^{1}H)$ (Hz): 92.7.
[c] $^{1}J(^{15}N, ^{1}H)$ (Hz): 90.5.
[d] $^{1}J(^{15}N, ^{1}H)$ (Hz): 87.2.

Table 2. ^{1}H, ^{13}C, and ^{15}N NMR shifts (δ, ppm) of compounds **12b–f** in DMSO-d_6

Position	**12b**		**12c**		**12d**		**12e**		**12f**	
	δ_H	δ_C or δ_N	δ_H	δ_C or δ_N	δ_H	δ_C or δ_N	δ_H	δ_C or δ_N	δ_H	δ_C or δ_N
1	7.54	−264.3[a]	7.27	−267.6[b]	7.51	−267.4[c]	7.54	−268.4[d]	7.87	−268.3[e]
2	—	160.5	—	158.9	—	159.2	—	160.6	—	160.7
3	7.66	−290.8[f]	—	−283.8	—	−284.2	—	−285.4	—	−287.2
3a	—	70.4	—	68.8	—	69.1	—	75.2	—	75.3
4	—	171.1	—	171.2	—	171.4	—	170.4	—	170.6
5	10.83	−247.6[g]	10.50	−245.7[h]	10.59	−244.9[i]	10.94	−243.6[j]	11.06	−242.9[k]
5a	—	135.3	—	134.7	—	134.7	—	134.9	—	135.8
6	7.07	115.4	6.90	114.9	6.94	115.0	7.05	115.3	7.09	115.4
7	7.37	129.8	7.27	129.4	7.29	129.6	7.32	129.8	7.37	129.9
8	7.11	122.9	7.06	122.5	7.09	122.6	7.02	122.9	7.08	122.8
9	7.61	127.3	7.64	126.2	7.70	126.3	7.51	127.5	7.58	127.6
9a	—	123.4	—	124.6	—	124.5	—	123.0	—	123.1
9b	—	85.5	—	83.6	—	83.8	—	84.1	—	85.0
1′(3)	—	—	3.52, 3.34	40.5	—	—	3.27, 3.03	44.1	—	—
2′(3)	—	—	1.60, 1.48	32.7	—	—	2.01, 1.56	31.0	—	—
3′(3)	—	—	1.35, 1.32	20.0	—	—	1.26, 1.20	20.2	—	—
4′(3)	—	—	0.94	14.0	—	—	0.88	14.0	—	—
OH	6.29	—	6.54	—	6.59	—	6.44	—	6.55	—
1′(3a)	—	135.8	1.92, 1.89	31.2	1.77, 1.73	31.0	—	133.7	—	133.3
2′(3a)	7.26	126.4	1.12, 0.94	24.5	1.14, 0.93	24.5	7.35	128.3	7.48	127.1
3′(3a)	7.29	128.0	0.94	22.7	1.12	22.5	7.37	128.1	7.35	127.9
4′(3a)	7.29	127.7	0.75	13.8	0.62	13.5	7.37	128.3	7.29	126.2
CH_2	—	—	—	—	4.89, 4.75[l]	43.7	—	—	4.69, 4.43[m]	46.8
i-Ph(CH_2)	—	—	—	—	—	140.8			—	139.8
o-Ph(CH_2)	—	—	—	—	7.45	126.8			7.24	128.0
m-Ph(CH_2)	—	—	—	—	7.35	128.1			7.24	128.1
p-Ph(CH_2)	—	—	—	—	7.25	126.4			7.25	128.3

[a] $^{1}J(^{15}N, ^{1}H)$ (Hz): 92.2.
[b] $^{1}J(^{15}N, ^{1}H)$ (Hz): 92.6.
[c] $^{1}J(^{15}N, ^{1}H)$ (Hz): 92.3.
[d] $^{1}J(^{15}N, ^{1}H)$ (Hz): 92.0.
[e] $^{1}J(^{15}N, ^{1}H)$ (Hz): 92.7.
[f] $^{1}J(^{15}N, ^{1}H)$ (Hz): 92.2.
[g] $^{1}J(^{15}N, ^{1}H)$ (Hz): 90.2.
[h] $^{1}J(^{15}N, ^{1}H)$ (Hz): 90.3.
[i] $^{1}J(^{15}N, ^{1}H)$ (Hz): 89.8.
[j] $^{1}J(^{15}N, ^{1}H)$ (Hz): 90.4.
[k] $^{1}J(^{15}N, ^{1}H)$ (Hz): 90.0.
[l] AB system, $^{2}J(H,H)=17.0$ Hz.
[m] AB system, $^{2}J(H,H)=17.0$ Hz.

same product **10a** as reaction with urea.[1] The analogous product **10b** was obtained through reaction of **7b** with butylurea (**8b**), but also through reaction of **7b** with 1,1-dibenzylurea (**8c**) (Scheme 2).

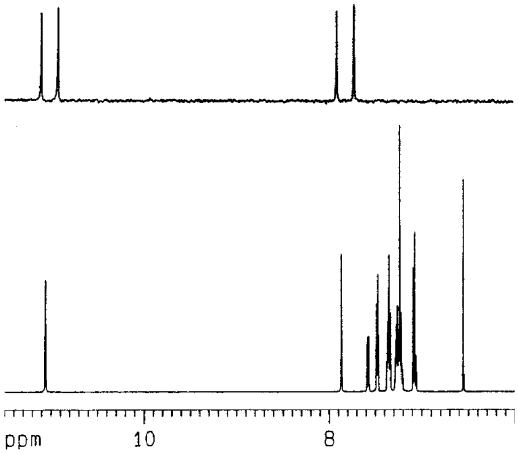


Figure 1. Part of ^{1}H NMR spectrum of compound **12f** (bottom trace) and 1D gs ^{1}H–^{15}N HMBC spectrum optimised for $^{1}J(^{15}N, ^{1}H)=95$ Hz (upper trace).

The 3′-substituted ureido derivative **9** was obtained in no case. In accord with expectations, it thus seems that substituted ureas **8a–c** fragment under given reaction conditions only to the respective amine and isocyanic acid and not to isocyanate and ammonia. Isocyanic acid subsequently reacts with amines **7a**,**b** to give products **10a**,**b** through the anticipated[1] intermediate **13a**,**b**. Compounds **10** may hence be obtained by boiling amines **7** with an arbitrary 1-substituted or 1,1-disubstituted urea in a solution of acetic acid. As expected, we also obtained compounds **10** by reacting amines **7a** and **7b** with nitrourea (**8d**) in a solution of acetic acid.

Owing to the well-known fact that nitrourea decomposes into isocyanic acid with simultaneous formation of water and N_2O far more easily than urea, we set about studying its reaction with amines **7** in a non-acidic environment. Performing the reaction in dioxane or aqueous dioxane, completely different products were surprisingly obtained (Scheme 2).

When comparing the ^{13}C NMR spectra of products from the reaction of **7a–f** with nitrourea in dioxane, it followed that two different types of products were originating.

Compounds of the first group are represented in the set under study by only one compound (from starting compound **7a**), which exhibits in the ^{13}C NMR spectrum, beside signals of sp^2 hybridised carbon atoms, a signal pertaining to a carbon atom in sp^2 hybridisation (apart from carbons of the butyl group) and three signals of carbonyl groups (Table 1), which is in accord with the anticipated structure **11a**. In the ^1H NMR spectrum of **11a** (Table 1), there appear discernible signals of an aromatic ABCD system in the 7.12–7.79 ppm range, and signals corresponding to hydrogen atoms of a butyl group. In addition, signals of four NH protons are to be found at 5.70 (2H), 7.00, and 10.81 ppm. The presence of an $-NHCONH_2$ group was also confirmed by results of ^{15}N NMR spectra. Based on a 2D experiment, all signals were assigned to their respective atoms (Table 1).

The product of reaction of **7b** with nitrourea displays in the ^{13}C NMR spectra signals fundamentally different from that of compound **11a**. Structure **12b** resulted for this compound mainly from the appearance of two signals of sp^3 hybridised carbon atoms in the ^{13}C NMR spectrum (apart from sp^3 hybridised carbon atoms of butyl or benzyl group) at 85.5 and 70.4 ppm (Table 2). The last signal corresponds to the carbon atom C-3 of starting amine **7b**, and the signal at 85.5 ppm must correspond to a carbon that arose through transformation of the initial CO group in position 4 of starting amine **7b** because no signal of the keto group in the ^{13}C NMR spectrum of product **7b** with urea is present, and signals of amide groups at 160.5 and 171.1 ppm are to be found (Table 2). As the signal of an OH group at 7.61 ppm was also found in the ^1H NMR spectrum of this compound, besides signals of three NH protons at 7.54, 7.66 and 10.83 ppm, the product of reaction of **7b** with nitrourea must possess structure **12b**. This structure was confirmed by results of a NOE experiment proving interactions of the hydroxyl group at C-9b with the proton at the nitrogen atom in position 1, with proton at C-9, and with *o*-protons of the phenyl group. The latter proved interaction is to certify that the hydroxyl group at C-9b and the phenyl group at C-3a are *cis*-oriented. Also proved was the interaction of proton N(5)–H with the proton at C-6 as well as interaction of hydrogen at N(3) with *o*-protons of the phenyl group. The ^{15}N NMR spectrum (Table 2) of the product is in accordance with structure **12b**.

It is noteworthy that both products of the reaction of **7a**,**b** with nitrourea displayed two well discernible spots by TLC. Their ratio in different crystallisation fractions varied, but dependence of this ratio on crystallisation conditions could not be found. All our attempts at separating the individual compounds through repeated crystallisation or column chromatography met with failure. We suppose an equilibrium exists between tautomeric forms **11a**,**b** and **12a**,**b**, however, with only one form of greater stability being preferred in the solution of strongly polar DMSO-d_6. The formation of an equilibrium mixture of cyclic and acyclic tautomers during hydration of 4-oxoazetidines substituted with carbamoylthioacetyl group in position 2 was described by Sápi et al.[4] Unfortunately, due to insolubility of compounds **11a** and **12b** in non-polar solvents, the tautomeric equilibrium could not be more closely investigated.

All secondary amines **7c–f** yield merely cyclic carbinolamide forms **12c–f** as products of the reaction with nitrourea in dioxane or aqueous dioxane. Based on results of 2D experiments, all signals in ^1H, ^{13}C and ^{15}N NMR spectra of compounds **12c–f** were assigned to particular atoms (Table 2).

Figure 1 shows a part of the ^1H NMR spectrum of compound **12f** in which three broadened singlets ($\delta(^1H)=$ 11.06, 7.87, 6.55) are visible, two of them giving doublets in 1D gs ^1H–^{15}N HMBC spectrum due to the existence of $^1J(^{15}N, ^1H)=95$ Hz and, thus, these protons must belong to NH fragments. The third signal resonating at 6.55 ppm gave neither any doublet in 1D gs ^1H–^{15}N HMBC nor any correlation in 2D gs ^1H–^{13}C HSQC spectrum optimised for $^1J(^{13}C, ^1H)$. Taking the above-mentioned results as well as results following from mass spectra into account, the signal resonating at 6.55 ppm must belong to an OH group proton.

Analysis of 2D gs ^1H–^{15}N HMBC spectrum of compound **12f** optimised for $^nJ(^{15}N, ^1H)=7$ Hz allowed us to assign all three ^{15}N resonances undoubtedly and confirm the structure proposal. The ^{15}N signal at -242.9 ppm represents a resonance of nitrogen of N(5)HCO group because residual doublet due to $^1J(^{15}N(5), ^1H)$ coupling constant and the cross-peak due to $^3J(^{15}N, C(6)^1H)$ were observed. Residual doublet due to $^1J(^{15}N(1), ^1H)$ coupling constant and the cross-peak due to $^3J(^{15}N, O^1H)$ belong to nitrogen in position 1 ($\delta(^{15}N)=-268.3$). Nitrogen atom of $N(3)CH_2C_6H_5$ group ($\delta(^{15}N)=-287.2$) showed correlations with both prochiral methylene protons of benzyl group and N(1)H proton via $J(^{15}N, C(=O)N^1H)$.

Similarly as in compound **12b**, the two signals of sp^3 hybridised carbon atoms C-3a and C-9b can be found in the ^{13}C NMR spectrum of **12f**. Protonated carbons were assigned by gs-HMQC and quaternary carbons were assigned by gs-HMBC.

The ^1H, ^{13}C and ^{15}N NMR spectra of compounds **12c–e** were analysed in the same manner.

Compounds **11a** and **12c–f** are quite stable in a solution of acetic acid up to a temperature of approx. 50 °C, when boiling, however, their rapid rearrangement to imidazoquinazolines **10a–f** takes place.

The APCI mass spectra of all compounds **11** and **12** under study yielded the peaks of $[M+H]^+$ ions in the positive-ion mode and $[M-H]^-$ ions in the negative-ion mode. Mostly, these ions are base peaks or at least very intensive peaks in the spectra. The typical neutral loss for all compounds containing the tertiary hydroxyl group (**12b–12f**) is the loss of water. The other characteristic neutral loss, NHCO ($\Delta m/z$ 43), is observed for all compounds containing third 5-membered cycle (**12b–12f**) and also for **11a**, where the NHCO moiety can be lost from the side $-NHCONH_2$ chain as well.

Yields of compounds **11** or **12** (Table 3) depend mainly on the character of substitution in starting compounds **7**, but also on reaction conditions. In the cases where primary amines **7a**,**b** are used as starting compounds, they reach

Table 3. Results of the reaction of amines **7** with nitrourea in dioxane (method A) or aqueous dioxane (method B)

Entry	Starting compound	Method	Reaction time (h)	Isolated compounds (%)
1	**7a**	A	1.5	**11a** (43)
2	**7a**	A	1.5	**11a** (50)
3	**7b**	A	2	**12b** (55)
4	**7b**	A	2	**12b** (51)
5	**7b**	A	2.5	**12b** (57)
6	**7b**	B	2.5	**12b** (58)
7	**7c**	A	4	**12c** (49), **10c** (16)
8	**7d**	A	5	**12d** (31), **7d** (17)
9	**7d**	A	9	**12d** (11), **7d** (37)
10	**7d**	A	15	**12d** (35), **7d** (19)
11	**7e**	A	5.5	**12e** (52), **7e** (4), **10e** (5)
12	**7e**	B	2.5	**7e** (21), **10e** (52), **13e** (6)
13	**7f**	A	6	**12f** (30), **7f** (49), **10f** (2)
14	**7f**	B	5.5	**12f** (16), **7f** (33)[a]

[a] 4-Hydroxy-3-phenyl-1*H*-quinolin-2-one (2%) was also isolated.

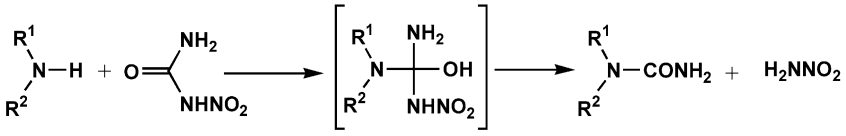
levels around 50%, are not overly affected by character of reaction medium and display good reproducibility (entries 1–6). When secondary amines **7c–f** are employed, yields of compounds **12**, as expected, are lower. In these cases, as is obvious in Table 3, non-reacted starting compounds **7** and products of rearrangement **10** were also isolated from the reaction mixture. Employing here non-aqueous dioxane as reaction medium (Method A) is more appropriate. Isocyanic acid arising during the reaction in aqueous dioxane slowly reacts with a secondary amine and breaks down at the same time, to disappear from the reaction mixture in a short time. During the reaction, bubbles of escaping N_2O may be observed, and their production soon comes to a stop. During the reaction in non-aqueous dioxane, however, bubbles of N_2O do not arise. A possible explanation may be found in the anhydrous conditions, under which nitrourea does not directly decompose to isocyanic acid and N_2O but under which the reaction proceeds as a nucleophilic addition of amine to activated carbonyl group of nitrourea (Scheme 3). The intermediate thus created then breaks down to the corresponding substituted urea and nitramide, which is destroyed only during subsequent processing of the reaction mixture.

The reaction of amines **7** with nitrourea in dioxane or aqueous dioxane runs quite unambiguously. Apart from products **11a** and **12b–f**, only non-reacted starting amines **7** and rearranged compounds **10** were isolated, and other minor products were successfully obtained in just two cases (Table 3). The first side product is 4-hydroxy-3-phenyl-1*H*-quinolin-2-one, arising through hydrolysis of starting amine **7f** in a reaction in aqueous dioxane.

The second minor compound isolated is 3-butyl-3a-phenyl-3,3a-dihydro-5*H*-imidazo(4,5-*c*(quinoline-2,4-dione (**13e**), isolated from the reaction of **7e** with urea in aqueous dioxane. This compound showed a completely different melting point and different IR spectrum than compound **10e** but its ^1H and ^{13}C NMR spectra measured in DMSO-d_6 were identical with NMR spectra of compound **10e**. Only after measuring NMR spectra of this minor compound in $CDCl_3$ was it determined that the substance in question really was a new compound **13e**, which is so unstable that it already rearranges to compound **10e** through merely standing in a solution of DMSO-d_6. The NMR spectra of compound **13e** (Table 4) were very similar to those for analogous substances having methyl or phenyl groups in position 5 instead of a proton.[2]

We also attempted to prepare the other 3a-alkyl/aryl-3,3a-dihydro-5*H*-imidazo-(4,5-*c*(quinoline-2,4-diones **13** through dehydration of carbinolamides **12c–f**. Our first attempts (using acetic anhydride, acetic anhydride in pyridine, or thionyl chloride in pyridine) proved unsuccessful, and on processing the reaction mixture, rearranged compounds **10c–f** were always obtained. Only action of phosphorus pentoxide on the suspension of compounds **12c–f** in chloroform produced the corresponding products **13c–f** (NMR data in Table 4). These are very unstable compounds, which already rearrange to compounds **10c–f** through mild heating up in methanol or standing for several hours in a DMSO solution. The reverse addition of water to compounds **13** was not observed, though this reaction was described in 1-methoxy-1,5-dihydroimidazol-2-one series.[5]

Our attempts at preparing compounds **13a**,**b** were not successful. According to TLC monitoring, compounds **11a** and **12a** do not undergo dehydration through action of P_2O_5 in chloroform at room temperature. Compounds whose characteristic yellow fluorescence at UV irradiation (366 nm) of TLC chromatograms is analogous to that displayed by compounds **13c–f**, arise only when boiling. Nevertheless, all attempts at isolating them failed, and rearranged products **10a** and **10b** were obtained after processing the reaction mixture. The high instability of compounds **13** is surprising, because their N(5)-substituted derivatives are stable[2] as well as their 3-sulfa analogues.[6] Measurements of APCI-MS spectra of compounds **13c–f**



Scheme 3.

Table 4. ^{1}H and ^{13}C NMR shifts (δ, ppm) of compounds **13c–f** in $CDCl_3$

Position	**13c**		**13d**		**13e**		**13f**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
2	—	166.7	—	166.8	—	166.8	—	167.2
3a	—	75.6	—	75.3	—	78.4	—	78.3
4	—	170.0	—	170.3	—	168.1	—	168.5
5	9.27	—	9.08	—	9.04	—	9.47	—
5a	—	139.0	—	138.7	—	138.4	—	138.3
6	7.11	11666.4	6.90	116.5	6.98	116.4	6.73	116.6
7	7.56	135.2	7.52	135.4	7.44	135.0	7.40	135.2
8	7.24	124.6	7.21	124.7	7.15	124.6	7.13	124.6
9	7.96	127.0	7.95	127.0	7.94	127.3	7.94	128.0
9a	—	115.7	—	115.7	—	116.7	—	116.6
9b	—	184.6	—	184.8	—	183.9	—	184.4
1′(3)	3.67, 3.40	42.2	—	—	3.48, 3.21	42.9	—	—
2′(3)	1.88	31.0	—	—	1.67, 1.41	30.4	—	—
3′(3)	1.44	20.4	—	—	1.23	20.3	—	—
4′(3)	0.99	13.9	—	—	0.83	13.7	—	—
1′(3a)	2.24, 1.94	30.5	2.06, 1.82	36.9	—	132.4	—	131.9
2′(3a)	0.96, 0.89	24.5	0.89, 0.66	21.7	7.22	126.5	7.14	126.6
3′(3a)	1.19	21.9	0.68	24.5	7.33	129.7	7.26	129.6
4′(3a)	0.79	13.6	0.58	13.5	7.33	130.1	7.26	130.0
CH_2	—	—	5.02, 4.96[a]	45.6	—	—	4.73, 4.47[b]	46.3
i-Ph(NCH_2)	—	—	—	137.5	—	—	—	137.3
o-Ph(NCH_2)	—	—	7.54	129.0	—	—	7.14	128.0
m-Ph(NCH_2)	—	—	7.31	128.4	—	—	7.26	128.4
p-Ph(NCH_2)	—	—	7.27	127.6	—	—	7.14	126.9

[a] AB system, $^{2}J(H,H)=15.0$ Hz.
[b] AB system, $^{2}J(H,H)=15.3$ Hz.

indicated their spectra are completely identical with spectra of compounds **10c–f** and it cannot be judged whether conversion of **13c–f** to **10c–f** takes place during dissolution in acetonitrile or only later during ionisation.

Compounds **11**, **12** and also **13** exhibit a relatively wide range of melting points despite being chromatographically pure. Some of them first melt at a lower temperature, and after re-crystallisation of the melt they exhibit another melting point corresponding to pertaining compound **10**, some of them even melt at the same temperature as **10**. In all cases, the TLC analysis of the rests after melting point determination of compounds **11**, **12**, and **13** proved that their thermal transformation to compounds **10** proceeds.

In our earlier work[1] we expressed the assumption that the reaction of amines **7** with urea in boiling acetic acid produces, as primary reaction intermediates, compounds **11**, which are cyclodehydrated to intermediates **13**. The following base-catalysed breaking of bond C(3a)–C(4) in **13** creates an isocyanate group to which nitrogen atom N(1) of the imidazole nucleus adds, thus giving rise to product **10**. This concept is impaired by our discovery that compounds **11** and **12** rearrange in acetic acid to **10** in the absence of any basic compound, and undergo thermal rearrangement as well. Compound **12f** also rearranges to **10f** by boiling in pyridine, but much more slowly than in acetic acid hence ruling out basic catalysis. We found, however, that rearrangement of compound **12d** to **10d** also occurs through boiling in cyclohexanol. This rules out formation of the corresponding intermediate isocyanate because such an intermediate would have to react with cyclohexanol to the respective carbamic acid ester at least in part. Based on hitherto obtained knowledge of the stability of prepared compounds as reaction intermediates,[1] we may assume that transformation of amines **7** through their reaction with urea in acetic acid to final product **10** really proceeds via intermediates **11**, **12** and **13**. In strongly unstable intermediates **13**, the nucleophilic migration of the whole ArNHCO group has to take place. Whether the action in question is direct 1,3-migration to nitrogen atom N(1) or two successive 1,2-migrations is an issue that will be decided only through results of experiments on N(1)-substituted analogues of compounds **7**, which we are presently starting.

The described reaction of 3-amino-1*H*,3*H*-quinoline-2,4-diones **7** with nitrourea is not merely interesting from a theoretical point of view but, owing to the simple reaction protocol, presents an easy pathway to preparing novel heterocyclic systems. Compounds **11** and **12** can serve as suitable starting materials for studying the equilibrium between α-ureido ketones (or hitherto undescribed α-ureido-β-dicarbonyl compounds) and their cyclic carbinolamide forms. Analogues of **13**, containing the C═N–C(O)–N grouping, are not described in the literature with only the exception of our recent paper.[2] Only several simple imidazolin-2-ones were prepared,[5,7–10] but just one reaction of them has previously been described.[5]

3. Experimental

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. ^{15}N

chemical shifts were referred to external neat nitromethane in co-axial capillary ($\delta=0.0$). All 2D experiments (gradient-selected (gs)-COSY, NOESY, gs-HMQC, gs-HMBC) were performed using manufacturer's software. Proton signals 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 analyser Esquire 3000 (Bruker Daltonics, Bremen, Germany) within the mass range $m/z=50$–600. 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, 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 0.7–0.9 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–isopropylalcohol, 9:1 (S6) on Alugram® SIL G/UV_{254} foils (Macherey–Nagel). Elemental analyses (C, H, N) were performed with a EA 1108 Elemental Analyzer (Fisons Instrument).

3-Amino-1*H*,3*H*-quinoline-2,4-diones (**7a**–**f**) were prepared according to the general procedure described in the literature.[3]

3.1. General procedures for the preparation of 2,6-dihydro-imidazo[1,5-*c*]quinazoline-3,5-diones (10a–f)

Method A. A mixture of appropriate 3-amino-1*H*,3*H*-quinoline-2,4-dione (**7a**,**b**) (3 mmol) and substituted urea **8a**–**d** (6 mmol) in acetic acid (10 mL) was refluxed for 1–2.5 h and the course of the reaction was monitored by TLC. After cooling, the reaction mixture was diluted with water. The precipitated products **10a**,**b** were filtered off with suction and crystallized from appropriate solvent or column chromatographed.

Method B. A solution of appropriate compound **11** or **12** (0.5 mmol) in acetic acid (5 mL) was refluxed for 1 h. The reaction mixture was evaporated to dryness in vacuo and the residue was crystallized from appropriate solvent or column chromatographed.

Method C. A solution of appropriate compound **12** (0.5 mmol) in appropriate solvent (see below) was refluxed for 6–10 h. The reaction mixture was evaporated to dryness and the residue was crystallized from ethanol.

3.1.1. 1-Butyl-2,6-dihydro-imidazo[1,5-*c*]quinazoline-3,5-dione (10a). Compound was prepared from **7a** and **8a** (Method A, 2.5 h, yield 58%), from **7a** and **8d** (Method A, 30 min, yield 65%), and from **11a** (Method B, 1 h, yield 68%). Colourless crystals, identical in all respects with authentic sample.[1]

3.1.2. 1-Phenyl-2,6-dihydro-imidazo[1,5-*c*]quinazoline-3,5-dione (10b). Compound was prepared from **7b** and **8b** (1.5 h, yield 37%), from **7b** and **8c** (1.5 h, yield 64%), and from **7b** and **8d** (2.5 h, yield 58%) by Method A, and from **12b** by Method B (yield 84%). Colourless crystals, identical in all respects with authentic sample.[1]

3.1.3. 1,2-Dibutyl-2,6-dihydro-imidazo[1,5-*c*]quinazoline-3,5-dione (10c). Compound was prepared from **12c** by Method B (yield 50%). Colourless crystals, identical in all respects with authentic sample.[1]

3.1.4. 2-Benzyl-1-butyl-2,6-dihydro-imidazo[1,5-*c*]-quinazoline-3,5-dione (10d). Compound was prepared from **12d** by Method B (yield 52%) and by Method C (cyclohexanol, 10 mL, 10 h, yield 53%). Colourless crystals, identical in all respects with authentic sample.[1]

3.1.5. 2-Butyl-1-phenyl-2,6-dihydro-imidazo[1,5-*c*]-quinazoline-3,5-dione (10e). Compound was prepared from **12e** by Method B (53%) and by Method C (acetic anhydride, 10 mL, 10 h, yield 52%). Colourless crystals, identical in all respects with authentic sample.[1]

3.1.6. 2-Benzyl-1-phenyl-2,6-dihydro-imidazo[1,5-*c*]-quinazoline-3,5-dione (10f). Compound was prepared by refluxing of the solution of **7f** (0.5135 g, 1.5 mmol) and urea (0.5405 g, 9 mmol) in acetic acid (2 mL) for 60 min. After evaporation in vacuo, the residue was washed with water and crystallized from ethanol. Yield 417 mg (75%). By the same procedure, but using pyridine instead of acetic acid, 340 mg (62%) of **10f** was obtained after 5 h. Colourless crystals, mp 291–294 °C (ethanol). IR: 3295, 3250, 3065, 3003, 2932, 1764, 1753, 1679, 1613, 1589, 1482, 1444, 1376, 1366, 1347, 1326, 1315, 1266, 1173, 923, 755, 741, 697, 669, 654, 598, 582 cm^{-1}. Positive-ion APCI-MS: *m/z* 368 $[M+H]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 368: 290 $[M+H-C_6H_6]^+$, 276 $[M+H-C_6H_5CH_3]^+$, 250 $[(C_6H_5CH_2)NCH(C_6H_5)CHNCO]^+$ (100%), 234 $[M+H-C_6H_5CH_3-NCO]^+$. Negative-ion APCI-MS: 366 $[M-H]^-$ (100%), 275 $[M-H-C_6H_5CH_2]^-$. Negative-ion APCI-MS/MS of *m/z* 366: 275 $[M-H-C_6H_5CH_2]^-$ (100%). Anal. Calcd (found) for $C_{23}H_{17}N_3O_2$: C 75.19 (75.34); H 4.66 (4.73); N 11.44 (11.15).

3.2. General procedure for the preparation of 3-ureido-1*H*,3*H*-quinoline-2,4-dione (11a) and 9b-hydroxy-3a-alkyl/aryl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]-quinoline-2,4-diones (12b–f)

Method A. A mixture of appropriate 3-amino-1*H*,3*H*-quinoline-2,4-dione (**7a**–**f**) (3 mmol) and nitrourea (0.631 g, 6 mmol) in dioxane (11 mL) was stirred at 80 °C for the time given in Table 3 and the course of the reaction was monitored by TLC. After cooling, the reaction mixture was evaporated to dryness in vacuo. The residue was extracted with water, the insoluble portion was filtered off with suction and crystallized from appropriate solvent. In some cases, mother liquors after crystallization of the product were column chromatographed.

Method B. A mixture of appropriate 3-amino-1*H*,3*H*-quinoline-2,4-dione (**7a**–**f**) (3 mmol) and nitrourea

(0.631 g, 6 mmol) in aqueous dioxane (70%, 10 mL) was stirred at 100 °C for the time given in Table 3. The work up of the reaction mixture was carried out in the same way as in Method A.

3.2.1. 3-Butyl-3-ureido-1*H*,3*H*-quinoline-2,4-dione (11a). Yield 50% (Method A, 90 min). Colourless crystals, mp 220–224 °C, IR: 3408, 3335, 3236, 3092, 2960, 2930, 2871, 1712, 1666, 1613, 1548, 1523, 1486, 1433, 1365, 1256, 1192, 1116, 951, 940, 775, 753, 668, 623, 548, 529 cm^{-1}. Positive-ion APCI-MS: *m/z* 276 $[M+H]^+$, 233 $[M+H–NHCO]^+$ (100%), 215 $[M+H–NHCO–H_2O]^+$, 188 $[M+H–NHCO–NH_2CHO]^+$, 177 $[M+H–NHCO\text{-butene}]^+$. Positive-ion APCI-MS/MS of *m/z* 276: 259 $[M+H–NH_3]^+$, 233 $[M+H–NHCO]^+$ (100%), 215 $[M+H–NHCO–H_2O]^+$. Negative-ion APCI-MS: 274 $[M-H]^-$ (100%), 231 $[M-H–NHCO]^-$, 161 $[C_6H_4NHCOCH_2CO]^-$, 146 $[C_6H_4(CO)NCO]^-$. Negative-ion APCI-MS/MS of *m/z* 274: 256 $[M-H–H_2O]^-$, 231 $[M-H–NHCO]^-$ (100%), 213 $[M-H–NHCO–H_2O]^-$. Anal. Calcd (found) for $C_{14}H_{17}N_3O_3$: C 61.08 (60.88); H 6.22 (6.35); N 15.26 (15.03).

3.2.2. 9b-Hydroxy-3a-phenyl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (12b). Yield 57% (Method A, 150 min) or 58% (Method B, 135 min). Colourless crystals, mp 269–274 °C (methanol), IR: 3365, 3262, 3195, 3078, 2991, 2919, 1712, 1690, 1617, 1598, 1494, 1441, 1402, 1231, 1058, 998, 894, 880, 848, 763, 700, 649, 602, 570 cm^{-1}. Positive-ion APCI-MS: *m/z* 296 $[M+H]^+$, 278 $[M+H–H_2O]^+$, 253 $[M+H–NHCO]^+$ (100%), 236 $[M+H–NH_2CONH_2]^+$, 223 $[M+H–NHCO–HCHO]^+$, 208 $[M+H–NH_2CONH_2–CO]^+$. Positive-ion APCI MS/MS of *m/z* 296: 278 $[M+H–H_2O]^+$, 253 $[M+H–NHCO]^+$ (100%), 236 $[M+H–NH_2CONH_2]^+$. Negative-ion APCI-MS and MS/MS of *m/z* 294 are the same: 294 $[M-H]^-$ (100% for MS), 276 $[M-H–H_2O]^-$, 251 $[M-H–NHCO]^-$, 233 $[M-H–NHCO–H_2O]^-$ (100% for MS/MS), 207, 161. Anal. Calcd (found) for $C_{16}H_{13}N_3O_3$: C 65.08 (64.83); H 4.44 (4.65); N 14.23 (14.09).

3.2.3. 3,3a-Dibutyl-9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (12c). Yield 49% (Method A, 4 h). Colourless crystals, mp 170–176 °C and 281–285 °C (ethyl acetate), IR: 3384, 3263, 3202, 3067, 2958, 2932, 2870, 1696, 1677, 1601, 1496, 1466, 1432, 1384, 1245, 1122, 1063, 849, 755, 658, 625, 543, 524 cm^{-1}. Positive-ion APCI-MS: *m/z* 332 $[M+H]^+$ (100%), 314 $[M+H–H_2O]^+$, 289 $[M+H–NHCO]^+$. Positive-ion APCI-MS/MS of *m/z* 332: 289 $[M+H–NHCO]^+$ (100%). Negative-ion APCI-MS: 330 $[M-H]^-$ (100%), 312 $[M-H–H_2O]^-$, 269 $[M-H–H_2O–NHCO]^-$, 255 $[M-H–H_2O\text{-butyl}]^-$. Negative-ion APCI-MS/MS of *m/z* 330: 312 $[M-H–H_2O]^-$, 287 $[M-H–NHCO]^-$, 230 $[M-H–NHCO\text{-butyl}]^-$. Anal. Calcd (found) for $C_{18}H_{25}N_3O_3$: C 65.23 (65.12); H 7.60 (7.42); N 12.68 (12.73).

3.2.4. 3-Benzyl-3a-butyl-9b-hydroxy-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (12d). Yield 35% (Method A, 15 h). Colourless crystals, mp 178–187 °C and 280–283 °C (ethyl acetate), IR: 3368, 3349, 3199, 3098, 2962, 2930, 2868, 1710, 1664, 1598, 1486, 1441, 1416, 1384, 1229, 1123, 1061, 947, 886, 800, 773, 763, 712, 658, 613, 540 cm^{-1}. Positive-ion APCI-MS: *m/z* 366 $[M+H]^+$ (100%), 348 $[M+H–H_2O]^+$, 323 $[M+H–NHCO]^+$. Positive-ion APCI-MS/MS of *m/z* 366: 323 $[M+H–NHCO]^+$, 233 $[M+H–C_6H_5CH_2NCO]^+$ (100%), 216 $[M+H–C_6H_5CH_2NCO–NH_3]^+$, 177 $[M+H–C_6H_5CH_2NCO\text{-butene}]^+$, 146. Negative-ion APCI-MS: 364 $[M-H]^-$ (100%), 346 $[M-H–H_2O]^-$, 316 $[M-H–H_2O–HCHO]^-$, 255, 161. Negative-ion APCI-MS/MS of *m/z* 364: 346 $[M-H–H_2O]^-$, 321 $[M-H–NHCO]^-$ (100%), 229 $[M-H–NHCO–C_6H_5CH_3]^-$, 216 $[M-H–NHCO–C_6H_5–CO]^-$. Anal. Calcd (found) for $C_{21}H_{23}N_3O_3$: C 69.02 (69.15); H 6.34 (6.09); N 11.50 (11.33).

3.2.5. 3-Butyl-9b-hydroxy-3a-phenyl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (12e). Yield 52% (Method A, 5.5 h). Colourless crystals, mp 174–183 °C and 294–297 °C (2-propanol), IR: 3411, 3334, 3195, 3066, 2957, 2928, 1705, 1678, 1599, 1496, 1446, 1413, 1371, 1217, 1135, 1071, 952, 865, 762, 751, 701, 680, 656, 633, 597 cm^{-1}. Positive-ion APCI-MS: *m/z* 352 $[M+H]^+$, 334 $[M+H–H_2O]^+$ (100%), 309 $[M+H–NHCO]^+$. Positive-ion APCI-MS/MS of *m/z* 352: 309 $[M+H–NHCO]^+$ (100%). Negative-ion APCI-MS: 350 $[M-H]^-$, 332 $[M-H–H_2O]^-$ (100%), 306 $[M-H–NH_2CO]^-$, 249 $[M-H–NH_2CHO\text{-butene}]^-$. Negative-ion APCI-MS/MS of *m/z* 350: 332 $[M-H–H_2O]^-$, 306 $[M-H–NHCO]^-$ (100%), 293 $[M-H\text{-butyl}]^-$, 275 $[M-H–H_2O\text{-butyl}]^-$, 249 $[M-H–NH_2CHO\text{-butene}]^-$. Anal. Calcd (found) for $C_{20}H_{21}N_3O_3$: C 68.36 (68.51); H 6.02 (6.23); N 11.96 (11.71).

3.2.6. 3-Benzyl-9b-hydroxy-3a-phenyl-3,3a,5,9b-tetrahydro-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione (12f). Yield 30% (Method A, 6 h) or 16% (Method B, 5.5 h). Colourless crystals, mp 186–196 °C (ethanol), IR: 3384, 3351, 3198, 3095, 2907, 1712, 1675, 1597, 1485, 1434, 1399, 1368, 1349, 1231, 1125, 1078, 934, 896, 802, 773, 747, 717, 697, 671, 655, 607, 593, 576 cm^{-1}. Positive-ion APCI-MS: *m/z* 386 $[M+H]^+$ (100%), 368 $[M+H–H_2O]^+$, 343 $[M+H–NHCO]^+$, 253 $[M+H–C_6H_5CH_2NCO]^+$. Positive-ion APCI-MS/MS of *m/z* 386: 343 $[M+H–NHCO]^+$ (100%), 278, 253 $[M+H–C_6H_5CH_2NCO]^+$, 236 $[M+H–C_6H_5CH_2NCO–NH_3]^+$, 208 $[M+H–C_6H_5CH_2NCO–NH_3–CO]^+$. Negative-ion APCI-MS and MS/MS of *m/z* 384 are the same: 384 $[M-H]^-$ (100% for MS), 366 $[M-H–H_2O]^-$, 340 $[M-H–NH_2CO]^-$, 275 $[M-H–H_2O–C_6H_5CH_2]^-$ (100% for MS/MS), 249, 236. Anal. Calcd (found) for $C_{23}H_{19}N_3O_3$: C 71.67 (71.45); H 4.97 (5.21); N 10.90 (10.69).

3.3. General procedure for the preparation of 3,3a-dihydro-5*H*-imidazo[4,5-*c*]quinoline-2,4-diones (13c–f)

To the stirred suspension of compound 12c–f (0.5 mmol) in chloroform (25 mL), powdered phosphorus pentoxide (107 mg, 0.75 mmol) was added in one portion at rt. After 10 min, the mixture was filtrated through a column filled with silica gel (7.5 g). Column was washed with chloroform (250 mL), collected filtrates were evaporated to dryness in vacuo and the residue was crystallized from benzene or benzene–hexane.

3.3.1. 3,3a-Dibutyl-3,3a-dihydro-5*H*-imidazo[4,5-*c*]-quinoline-2,4-dione (13c). Yield 87%. Colourless crystals,

mp 139–147 °C and 277–283 °C (benzene), IR: 3416, 3241, 2958, 2932, 2871, 1709, 1615, 1596, 1477, 1343, 1260, 1237, 1158, 779, 768, 650, 566 cm^{-1}. Positive-ion APCI-MS: *m/z* 314 $[M+H]^+$ (100%), 258 $[M+H\text{-butene}]^+$. Positive-ion APCI-MS/MS of *m/z* 314: 258 $[M+H\text{-butene}]^+$ (100%), 241 $[M+H\text{-butene-}NH_3]^+$, 215 $[M+H\text{-butene-NHCO}]^+$, 202 $[M+H\text{-2*butene}]^+$. Negative-ion APCI-MS: 312 $[M-H]^-$ (100%), 256 $[M-H\text{-butene}]^-$. Negative-ion APCI-MS/MS of *m/z* 312: 284 $[M-H-CO]^+$, 269 $[M-H-NHCO]^-$, 255 $[M-H\text{-butyl}]^-$ (100%), 212 $[M-H\text{-butyl-NHCO}]^-$. Anal. Calcd (found) for $C_{18}H_{23}N_3O_2$: C 68.98 (68.73); H 7.40 (7.59); N 13.41 (13.23).

3.3.2. 3-Benzyl-3a-butyl-3,3a-dihydro-5*H*-imidazo[4,5-*c*]-quinoline-2,4-dione (13d). Yield 77%. Yellow crystals, mp 278–282 °C (benzene–hexane), IR: 3241, 3211, 2931, 1720, 1614, 1591, 1475, 1427, 1365, 1344, 1290, 1237, 1151, 1126, 1102, 1051, 951, 841, 773, 748, 721, 666, 651, 565. Positive-ion APCI-MS: *m/z* 348 $[M+H]^+$ (100%), 292 $[M+H\text{-butene}]^+$. Positive-ion APCI-MS/MS of *m/z* 348: 331 $[M+H-NH_3]^+$, 305 $[M+H-NHCO]^+$, 292 $[M+H\text{-butene}]^+$, 256 $[M+H-C_6H_5CH_3]^+$ (100%), 230, 214 $[M+H\text{-butene-}C_6H_6]^+$, 202. Negative-ion APCI-MS: 346 $[M-H]^-$ (100%), 290 $[M-H\text{-butene}]^-$, 255 $[M-H-C_6H_5CH_2]^-$. Negative-ion APCI-MS/MS of *m/z* 346: 290 $[M-H\text{-butene}]^-$, 255 $[M-H-C_6H_5CH_2]^-$ (100%). Anal. Calcd (found) for $C_{21}H_{21}N_3O_2$: C 72.60 (72.41); H 6.09 (6.20); N 12.10 (11.96).

3.3.3. 3-Butyl-3a-phenyl-3,3a-dihydro-5*H*-imidazo[4,5-*c*]-quinoline-2,4-dione (13e). Yield 76%. Yellow crystals, mp 89–102 °C (benzene–hexane), IR: 3475, 3416, 2960, 2931, 2872, 1713, 1615, 1600, 1477, 1448, 1360, 1331, 1241, 1073, 779, 761, 695, 680, 653, 573. Positive-ion APCI-MS: *m/z* 334 $[M+H]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 334: 316 $[M+H-H_2O]^+$, 290 $[M+H-NH_2CO]^+$, 278 $[M+H\text{-butene}]^+$ (100%), 235 $[M+H\text{-butene-NHCO}]^+$, 203, 160. Negative-ion APCI-MS: 332 $[M-H]^-$ (100%). Negative-ion APCI-MS/MS of *m/z* 332: 289 $[M-H-NHCO]^-$, 275 $[M-H\text{-butyl}]^-$ (100%). Anal. Calcd (found) for $C_{20}H_{19}N_3O_2$: C 72.05 (71.90); H 5.74 (5.87); N 12.60 (12.45).

3.3.4. 3-Benzyl-3a-phenyl-3,3a-dihydro-5*H*-imidazo-[4,5-*c*]quinoline-2,4-dione (13f). Yield 16%. Yellow crystals, mp 161–167 °C (benzene–hexane), IR: 3446, 3227, 3175, 2994, 2930, 2865, 1711, 1616, 1596, 1478, 1449, 1370, 1357, 1322, 1238, 1131, 1061, 1032, 774, 710, 695, 655, 568. Positive-ion APCI-MS: *m/z* 368 $[M+H]^+$ (100%). Positive-ion APCI-MS/MS of *m/z* 368: 290 $[M+H-C_6H_6]^+$, 276 $[M+H-C_6H_5CH_3]^+$ (100%), 250 $[(C_6H_5\text{-}CH_2)NCH(C_6H_5)CHNCO]^+$, 234 $[M+H-C_6H_5CH_3-NCO]^-$. Negative-ion APCI-MS: 366 $[M-H]^-$ (100%), 275 $[M-H-C_6H_5CH_2]^-$. Negative-ion APCI-MS/MS of *m/z* 366: 275 $[M-H-C_6H_5CH_2]^-$ (100%). Anal. Calcd (found) for $C_{23}H_{17}N_3O_2$: C 75.19 (75.32); H 4.66 (4.51); N 11.44 (11.26).

Acknowledgements

This study was supported by the Ministry of Education, Youth and Sports of the Czech Republic (Grant No. MSM 265200015). M. H. acknowledges the support of grant project No. 203/02/0023 sponsored by the Grant Agency of the Czech Republic. The authors thank Mrs. H. Geržová (Faculty of Technology, Tomas Bata University in Zlín) for technical help.

References and notes

1. Klásek, A.; Koristek, K.; Lyčka, A.; Holčapek, M. *Tetrahedron* **2003**, *59*, 1283–1288.
2. Klásek, A.; Koristek, K.; Lyčka, A.; Holčapek, M. *Tetrahedron* **2003**, *59*, 5279–5288.
3. Kafka, S.; Klásek, A.; Polis, J.; Košmrlj, J. *Heterocycles* **2002**, *57*, 1659–1682.
4. Sápi, A.; Fetter, J.; Lempert, K.; Kajtár-Peredy, M.; Czira, G. *Tetrahedron* **1997**, *53*, 12729–12738.
5. Bakunova, S. M.; Grigoŕev, I. A.; Kirilyuk, I. A.; Volodarsky, L. B. *Izv. Akad. Nauk Ser. Khim.* **1999**, *11*, 2160–2167.
6. Klásek, A.; Mrkvička, V.; Pevec, A.; Košmrlj, J. *J. Org. Chem.* **2004**, *69*, 5646–5651.
7. Sasaki, T.; Eguchi, S.; Okano, T. *Synthesis* **1980**, *6*, 472–475.
8. Zaher, H. A.; Ibrahim, Y. A.; Sherif, O.; Mohammady, R. *Indian J. Chem.* **1983**, *22B*, 559–561.
9. Schwellkopf, U.; Lau, H.-H.; Scheunemann, K.-H.; Blume, E.; Matawinata, K. *Liebigs Ann. Chem.* **1980**, 600–610.
10. Boehme, H.; Schneider, H. *Chem. Ber.* **1958**, *91*, 988–996.