ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 5, pp. 674–680. © Pleiades Publishing, Ltd., 2009.
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Reaction of *N*-Alkyl(aryl)aminocarbonyl-1,4-benzoquinone Monoimines with Alcohols

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Received May 6, 2008

Abstract—— Reactions of *N*-alkyl(aryl)aminocarbonyl-3,5-dimethyl-1,4-benzoquinone monoimines with alcohols led to the formation of products of 1,2-addition, quinolide compounds. They are the final products in reactions with alkyl derivatives, but in event of aryl derivatives they underwent cyclization with the subsequent elimination of the alcohol molecule to provide 4,7a-dimethyl-1-aryl-7,7a-dihydro-1*H*-benzimidazole-2,6-diones.

DOI: 10.1134/S1070428009050054

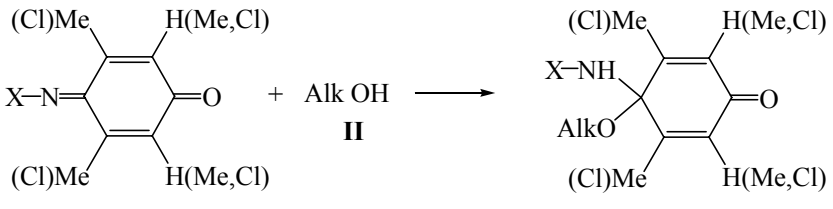
We formerly reported on a synthesis of a new class of quinone imines, *N*-alkyl(aryl)aminocarbonyl-1,4-benzoquinone monoimines [1], whose structure combined elements of quinone imines and substituted ureas extending the range of reactivity of these compounds.

A characteristic feature of various N-substituted 3,5-dimethyl-1,4-benzoquinone monoimines **I** containing an activated sterically strained C=N bond is a ready occurrence of 1,2-addition to give products of quinolide structure **III** [2, 3] (Scheme 1).

Owing to the spatial effect of substituents in the positions *3* and *5* of the quinoid ring the 3,5-disubstituted 1,4-benzoquinone monoimines contain an enhanced bond angle C=N–X resulting in the activation of the C=N bond [3–6] and the nucleophile addition occurs by the path of the 1,2-addition. The character of the substituent at the nitrogen atom of the N-substituted *p*-quinone imine [$ArSO_2$, $ArSO_2N{=}C(Me)$, $ArSO_2N{=}C(Ph)$, MeCO] and the character of substituents in the positions *3* and *5* quinoid ring (Me, Cl) do not affect the activity of the C=N bond in the reaction with alcohols [4, 5]. The governing influence belongs to the spatial arrangement of the substituent at the nitrogen ring and the bulk of the incoming AlkO group; these factors produce important effect on the reaction rate and the possibility of the process to occur [4, 5].

We formerly suggested that the activated sterically strained C=N bond of quinone imines was present at the values of the bond angle C=N–X > 130 deg [5]. In the ^{1}H NMR spectra of 3,5-dimethyl(3,5-dichloro)-1,4-benzoquinone imines which characteristically are involved into the 1,2-addition the signals of protons $H^{2,6}$ appear as one singlet. This fact is due to the large inversion rate around the C=N bond in the ^{1}H NMR time scale and also may

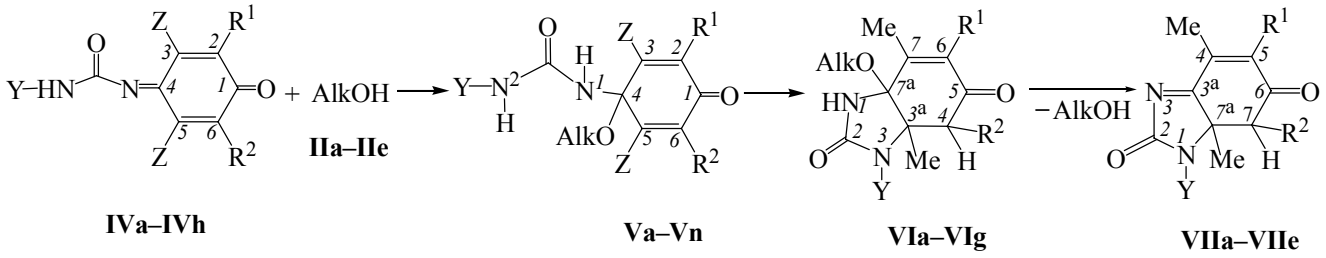
Scheme 1.



I **III**

X = $ArSO_2$, $ArSO_2NC(Me)$, $ArSO_2N{=}C(Ph)$, Ac; Alk = Me, Et, Pr, *i*-Pr.

Scheme 2.



II, Alk = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), Bu (**e**); **IV**, Y = Ph (**a–d**), 4-LeC$_6$M$_4$ (**e**), Bu (**f**), *t*-Bu (**g**), Cy (**h**), Z = Me (**a–c**, **e–h**), Cl (**d**), $R^1 = R^2 = H$ (**a, d–h**), Cl (**c**); R^1 = Cl, R^2 = H (**b**); **V, VI**, Y = Ph (**a–d, g, h**), 4-LeC$_6$M$_4$ (**e, f**), Bu (**i, j**), *t*-Bu (**k, l**), Cy (**m, n**), Z = Me (**a–g, i–n**), Cl (**h**), $R^1 = R^2 = H$ (**a–f, h–n**), $R^1 = R^2$ = Cl (**g**), Alk=Me (**a, e, g–i, k, m**), Et (**b, f, l, n**), Pr (**c, j**), Bu (**d**); **VII**, Y = Ph (**a**, **c–e**), 4-LeC$_6$M$_4$ (**b**), $R^1 = R^2 = H$ (**a, b**), Cl (**e**); R^1 = Cl, R^2 = H (**c**), R^1 = H, R^2 = Cl (**d**).

indicate the presence of the activated sterically strained C=N bond [3, 4, 6].

According to XRD findings 3,5-dimethyl-*N*-phenylaminocarbonyl-1,4-benzoquinone monoimine contains the angle C=N–C of 126.26 deg [1], considerably less than the suggested limit for the demonstration of the reactivity of the activated sterically strained C=N bond. This value is close to those of the angles C=N–X (of the order of magnitude 126 deg) of many N-substituted 1,4-benzoquinone imines lacking substituents in the positions *3* and *5* of the quinoid ring and consequently lacking the activated sterically strained C=N bond [7, 8]. But in the ^{1}H NMR spectrum of *N*-alkyl-(aryl)aminocarbonyl-3,5-dimethyl-1,4-benzoquinone monoimines (in contrast to the 2,6-dimethyl-substituted derivatives) the protons H^{2,6} give rise to a singlet [1], indicating the fast process of *Z*,*E*-isomerization in the NMR time scale and therefore the possibility of the 1,2-addition reaction with alcohols.

Aiming at the revealing the presence of the activated sterically strained C=N bond in *N*-alkyl-(aryl)aminocarbonyl-3,5-dimethyl-1,4-benzoquinone monoimines we investigated in this research the reaction of *N*-alkyl(aryl)-aminocarbonyl-1,4-benzoquinone monoimines **IVa–IVh** with substituents Me or Cl in the positions *3* and *5* of the quinoid ring with alcohols **IIa–IIe** (see the scheme).

The reaction was carried out by boiling the quinone imine in anhydrous alcohol till the disappearance of the yellow color of the initial quinone imine solution. The reaction duration depended on the structure of the quinone imine. For instance, in reaction with methanol it took 1–2 min with 3,5-dimethyl-*N*-phenylamino-carbonyl-1,4-benzoquinone monoimine (**IVa**) and 5 h with 2,6-dichloro derivative **IV**c. In the case of *N*-alkyl(cyclohexyl)amino-carbonyl-3,5-dimethyl-1,4-benzoquinone monoimines **IVf–IVh** the required time did not exceed 1–2 h. The reaction completion was checked by TLC by the absence in the mixture of the initial quinone imine. It was found that in reactions of *N*-arylaminocarbonyl-3,5-dimethyl-1,4-benzoquinone monoimines **IVa–IVc**, and **IVe** up to four compounds were present in the mixture during the process, including the initial quinone imine.

N-Alkyl(cyclohexyl)aminocarbonyl-3,5-dimethyl-1,4-benzoquinone monoimines **IVf–IVh** in reaction with alcohols afforded only the products of 1,2-addition, quinolide structures 4-[alkyl-(cyclohexyl)aminocarbonyl]-4-alkoxy-3,5-dimethylcyclohexa-2,5-dien-1-ones **Vi–Vn**. The characteristic feature of the ^{1}H NMR spectra of these compounds is the presence of a singlet from the protons H^{2,6} in the region δ 6.24–6.30 ppm, of a singlet of protons of the OMe group (in the case of methanol addition) at δ 2.99–3.01 ppm, and of signals of two NH groups at δ 5.16–5.40 and 4.42–4.88 ppm.

The reactions of N-arylaminocarbonyl-1,4-benzoquinone monoimines **IVa–IVc** and **IVe** yielded as final products 1-aryl-4,7a-dimethyl-7,7a-dihydro-1*H*-benzimidazole-2,6-diones **VIIa–VIIe**. The characteristic feature of the ^{1}H NMR spectra of these compounds is the presence of a doublet of doublets in the region δ 2.87–3.15 ppm corresponding to two hydrogen atoms attached to the *sp*^{3}-hybridized atom C^7. In the ^{13}C NMR spectrum of compound **VIIa** appear signals of two nonequivalent methyl groups: one of them is linked to the *sp*^{3}-hybridized atom C^{7a} (δ 69.88 ppm) and its signal is observed at δ 17.38 ppm, the other methyl group is attached to the *sp*^{2}-hybridized atom C^4 and its peak appears at δ 24.30 ppm. *sp*^{3}-Hybridized atom C^7 gives rise to the signal at

δ 50.67 ppm. The IR spectra of compounds **VIIa–VIIe** demonstrated that the NH and OH groups were lacking in their structure. It should be noted that the formation of benzimidazoles **VIIa–VIIe** is unusual for the class of quinone imines.

As already mentioned, in the reactions of aryl derivatives **IVa–IVc** and **IVe** TLC revealed in the reaction mixture three reaction products. In order to establish their structure we sampled the reaction mixture every 3–5 min in the course of the process between quinone imines **IVa** and **IVe** and alcohols **IIa–IIe**. We selected the samples containing one of the components in the maximum amount, recrystallized them, and investigated the product by ^{1}H NMR spectroscopy. Owing to this procedure we succeeded to isolate in the individual state inter-mediate compounds except for compounds of quinolide structure **Va–Vg** that were obtained only in the mixtures with compounds **VIa–VIg**. This is evidently due to the close values of the reaction rates of the formation of compounds **Va–Vg** and of cyclic products 7a-alkoxy-3-aryl-3a,7-dimethyl-3a,7a-dihydro-1*H*-benzimidazole-2,5(3*H*,4*H*)-diones **VIa–VIg**. The attempts to separate these compounds by crystallization failed because of their similar solubility. It was also impossible to isolate individual quinolide compounds **Va–Vg** by column chromatography for their R_f values were close to those of compounds **VIa–VIg** and **VIIa**–**VIIg**. The transition to the final cyclic structure **VII** apparently occurred only after accumulation of intermediate product **VI**, therefore we succeeded in isolation of individual compounds **VIa**, **VIe**, and **VIf** and in establishing their characteristics. In the reactions of quinone imine **IVa** with 1-propanol and 1-butanol analogous compounds **VIc** and **VId** were only detected by TLC. Compounds **VIg** and **VIIe** were obtained as a mixture with each other. Their separation was impossible because of low yields for alongside the cyclization quinone imine **IVc** suffered a hydrolysis. Quinone imines **IV** did not react with 2-propanol due to the large volume of the isopropyl group.

Hence we established that in the reaction of quinone imines **IVa–IVc** and **IVe** with alcohols the products of the first stage of the process were 1,2-addition products of quinolide structure, 4-alkoxy-4-(aryl-aminocarbonyl)-3,5-dimethyl(3,5-dichloro)cyclohexa-2,5-dien-1-ones **Va–Vg**. Further they readily underwent cyclization giving 7a-alkoxy-3-aryl-3a,7-dimethyl-3a,7a-dihydro-1*H*-benzimidazole-2,5(3*H*,4*H*)-diones **VIa–VIg**. The latter eliminated a molecule of alcohol converting finally into dihydrobenzimidazole derivatives **VIIa–VIIe**. In the case of *N*-phenylaminocarbonyl-3,5-dichloro-1,4-benzoquinone monoimine (**IVd**) the compound of quinolide structure **Vh** was the final product analogously to alkyl derivatives **Vi–Vn**.

The reaction of quinone imine **IVb** with methanol provided two isomeric products **VIIc** and **VIId** in the ratio 3:7, namely, the cyclization occurred at both C=C bonds of the quinolide ring, prevailingly at the C=C bond containing the chlorine atom in the position *2* of the initial quinone imine **IVb** revealing the regioselectivity of the process. It is possible to presume based on the data in [5] that the alkoxy group in quinolide compounds **V** is located above the plane of the quinolide ring, and the Y–$N^2HC(O)N^1H$ moiety, below this plane. As a result of the rotation around the N^1–C(O) bond in compounds **V** the second nitrogen atom (N^2H) might occur either close in the space to atom C^3 or to atom C^5 leading to the regioselectivity of cyclization.

In the ^{1}H NMR spectra of compounds **VIa–VIf** appear the following signals: a characteristic doublet of doublets belonging to two hydrogen atoms linked to C^4 in the region δ 2.73–2.76 ppm, signals of alkoxy groups protons, and a singlet of the NH group in the region δ 6.40–6.69 ppm. According to the ^{13}C NMR spectra one of the methyl groups is attached to the sp^3-hybridized atom C^{3a} (δ 47.90 ppm).

In order to reliably establish the structure of the cyclic products obtained XRD analysis was performed on a single crystal of 3a,7-dimethyl-7a-methoxy-3-phenyl-3a,7a-dihydro-1*H*-benzimidazole-2,5(3*H*,4*H*)-dione (**VIa**) (see the figure). The six-membered ring of compound **VIa** C^1–C^6 is in the conformation intermediate between *semichair* and *sofa* (folding parameters S 0.61, Θ 43.95, Ψ 16.44 [9]). Atoms $C^{2–5}$ are located in the same plane with an accuracy of 0.006 Å, atoms C^1 and C^6 deviate from the plane by –0.189(6) and –0.662(6) Å respectively. The five-membered heterocycle $C^4C^5N^2C^7N^1$ is present in a *twist*-conformation (atoms C^4 and C^5 deviate from the least-mean-squares plane of the other atoms of the ring by –0.237 and –0.272 Å). The two rings are joined by the *cis*-type [torsion angle $O^3C^4C^5C^8$ 33.9(2) deg].

Atoms N^1 and N^2 have strongly flattened trigonal-pyramidal configuration. The sum of bond angles at the nitrogen atoms amounted to 354 and 353.6 deg respectively.

The methoxy group is practically coplanar with the N^1–C^4 bond [torsion angle $N^1C^4O^3C^{16}$ 9.0(2) deg]. The

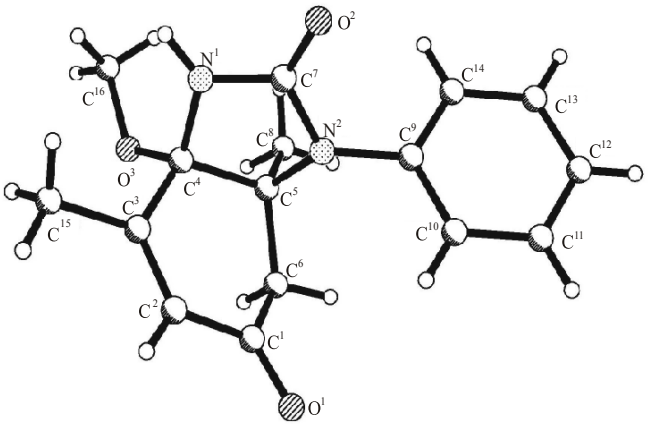
phenyl substituent is turned with respect to the amide fragment [torsion angle $C^7N^2C^9C^{14}$ 58.3(2) deg] resulting in breaking of the conjugation and in elongation of the N^2–C^9 bond to 1.442(2) Å compared to the average value of 1.426 E [10].

In the crystal the molecules of compound **VIa** form centrosymmetric dimers owing to the intermolecular hydrogen bond N^1–H^{1A}…O^{22} (1–*x*,–*y*,1–*z*) (H…O distance 2.02 A, N–H…O angle 165 deg).

Hence we established in this study that although the angle C=N–C is not typical for N-substituted 3,5-dimethyl-1,4-benzoquinone imines (in the 3,5-dimethyl-N-phenylamino-carbonyl-1,4-benzoquinone monoimine the C=N–C angle was 126.6 deg [1]), these quinone imines readily entered with alcohols into the 1,2-addition reaction. This may originate from the more significant deviation of atoms C^4 and N from the plane of the quinoid ring than in the quinone imines lacking substituents in the positions *3* and *5* of the quinoid ring. Therefore the enhanced angle (> 130 deg) is not a necessary condition for the 1,2-addition to proceed. On 8 of indicators of the presence of an activated sterically strained C=N bond alongside the existence of a fast *Z*,*E*-isomerization in the NMR time scale may be the deviation of atoms C^4 and N from the plane of the quinoid ring. For instance, in 3,5-dimethyl-substituted quinone imines the atoms C^4 and N deviate from the least-mean-squares plane $C^1C^2C^3C^5C^6$ by 0.043 and 0.136 Å for 3,5-dimethyl-*N*-phenyl-aminocarbonyl-1,4-benzoquinone monoimine [1], for 3,5-dimethyl-*N*-[(4-chlorophenyl)sulfonyl]-1,4-benzoquinone monoimine, by 0.054 and 0.133 Å respectively [5]. In the quinone imines without substituents in the positions *3* and *5* of the quinoid ring the deviation of atoms C^4 and N from the least-mean-squares plane $C^1C^2C^3C^5C^6$ amounts respectively to 0.026 and 0.047 Å for 2,6-di-*tert*-butyl-*N*-(4-chlorobenzoyl)-1,4-benzoquinone monoimine [7], 0.031 and 0.010 Å for 2,6-di-*tert*-butyl-*N*-[(4-nitro-phenyl)sulfinyl]-1,4-benzoquinone monoimine [8], the values significantly less that for 3,5-dimethyl-substituted 1,4-benzo-quinone onoimines.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Varian VXR-300 at operating frequency 300 MHz in $CDCl_3$ solutions, internal reference TMS. IR spectrum of compound **VIIa** was recorded on a spectrophotometer UR-20 in KBr. The reaction progress was monitored and the purity of products was checked by TLC on Silufol UV-254 plates, solvent chloroform, eluent ethanol–chloroform, 1:10, spots visualized under UV irradiation.



The structure of 3a,7-dimethyl-7a-methoxy-3-phenyl-3a,7a-dihydro-1*H*-benzimidazole-2,5(3*H*,4*H*)-dione (**VIa**) according to XRD findings.

XRD study of a single crystal of compound **VIa** was carried out at 293 K on a diffractometer Xcalibur-3 (MoK_α radiation, CCD-detector, graphite monochromator, ω-scanning, $2\theta_{max}$ 50 deg).

Crystals of compound **VIa** triclinic, $C_{16}H_{18}N_2O_3$, at 293 K *a* 7.425(3), *b* 9.788(3), *c* 11.262(2) Å, α 65.35(3), β 85.68(2), γ 74.85(3) deg, V 717.5(4) Å^3, M_r 286.32, *Z* 2, space group P$\bar{1}$, d_{calc} 1.325 g/cm^3, μ(MoK_α) 0.093 mm^{-1}, *F*(000) 304. Parameters of the unit cell and intensities of 4682 reflections were measured (2479 independent reflections, R_{int} 0.016).

The structure was solved by the direct method using SHELXTL software [11]. The hydrogen atoms positions were revealed from the difference synthesis of the electron density and were refined isotropically. The structure was refined for F^2 by full-matrix least-mean-squares method in the anisotropic approximation for nonhydrogen atoms till wR_2 0.084 for 4600 reflections [R_1 0.033 for 1882 reflections with $F > 4\sigma(F)$, *S* 1.030]. The final atomic coordinates, geometrical parameters of the molecule, and the crystallographic data are deposited to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambgidge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk) and are available to the request under the no. CCDC 681167.

***N*-(Alkyl)arylaminocarbonyl-1,4-benzoquinone monoimines IVa, IVd–IVh** were prepared by procedure [1]. Characteristics of compounds **IVa, IVd–IVh** were identical to the corresponding data published in [1].

3,5-Dimethyl-*N*-phenylaminocarbonyl-2-chloro-1,4-benzoquinone monoimine (IVb), 3,5-dimethyl-*N*-phenylaminocarbonyl-2,6-dichloro-1,4-benzoquinone monoimine (IVc). Through a solution of 0.07 mol of *p*-quinone monoimine **IVa, IVb** in 30 ml of dry chloroform was passed a flow of gaseous hydrogen chloride till the reaction mixture turned colorless, and a colorless precipitate settled of 3,5-dimethyl-*N*-phenylaminocarbonyl-2-chloro(2,6-dichloro)-1,4-aminophenol. The precipitate was filtered off, washed with chloroform, and recrystallized from the glacial acetic acid. Into the dispersion of 0.01 mol of recrystallized 3,5-dimethyl-*N*-phenylaminocarbonyl-2-chloro-(2,6-dichloro)-1,4-aminophenol in 5 ml of glacial acetic acid was charged 0.011 mol of lead tetraacetate at cooling and stirring of the reaction mixture. The initial colorless precipitate dissolved, and orange substance precipitated of 3,5-dimethyl-*N*-phenyl-aminocarbonyl-2-chloro(2,6-dichloro)-1,4-benzoquinone monoimine **IVb, IVc**. Into the reaction mixture 1 ml of ethylene glycol was added, the mixture was thoroughly stirred, cooled, and filtered. The precipitate was washed with a little acetic acid, dried, and recrystallized from benzene.

3,5-Dimethyl-*N*-phenylaminocarbonyl-2-chloro-1,4-benzoquinone monoimine (IVb). Yield 70%, mp 145–146°C. ^{1}H NMR spectrum, δ, ppm: 2.26 d (3H, C^5H_3), 2.37 s (3H, C^3H_3), 6.53 q (1H, H^6), 7.10 br.s (1H, NH), 7.14–7.52 m (5H, Ph). Found, %: N 9.60, 9.75. $C_{15}H_{13}ClN_2O_2$. Calculated, %: N 9.70.

3,5-Dimethyl-*N*-phenylaminocarbonyl-2,6-dichloro-1,4-benzoquinone monoimine (IVc). Yield 42%, mp 128–129°C. ^{1}H NMR spectrum, δ, ppm: 2.40 s (6H, $C^{3,5}H_3$), 7.29 br.s (1H, NH), 7.11–7.60 m (5H, Ph). Found, %: N 8.64, 8.71. $C_{15}H_{12}Cl_2N_2O_2$. Calculated, %: N 8.67.

Reactions of N-(alkyl)arylaminocarbonyl-1,4-benzoquinone monoimines IVa–IVh with alcohols. A solution of 2 mmol of quinone imine **IVa–IVh** in 8 ml of an appropriate anhydrous alcohol was boiled in a flask with a reflux condenser equipped with an outlet tube packed with calcium chloride till decoloration of the solution (TLC monitoring till the disappearance of the initial quinone imine). The crystals precipitated on cooling were filtered off and washed with the corresponding alcohol. The filtrate was evaporated in order to increase the yield of the product. The residue after the evaporation was recrystallized from benzene.

3,5-Dimethyl-4-methoxy-4-phenylaminocarbonylaminocyclohexa-2,5-dien-1-one (Va). Yield 62%. ^{1}H NMR spectrum, δ, ppm: 1.95 s (6H, $C^{3,5}H_3$), 3.02 s (3H, OMe), 5.62 br.s (1H, N^2H), 6.31 s (2H, $H^{2,6}$), 7.08 br.s (1H, N^1H), 7.14–7.45 m (5H, Ph).

3,5-Dimethyl-4-phenylaminocarbonylamino-4-ethoxycyclohexa-2,5-dien-1-one (Vb). Yield 5%. ^{1}H NMR spectrum, δ, ppm: 0.85–0.90 t (3H, OCH_2CH_3), 2.11 s (6H, $C^{3,5}H_3$), 3.72–3.79 d.d (2H, OCH_2CH_3), 5.99 br.s (1H, N^2H), 6.30 s (2H, $H^{2,6}$), 7.18 br.s (1H, N^1H), 7.26–7.50 m (5H, Ph).

3,5-Dimethyl-4-propoxy-4-phenylaminocarbonylaminocyclohexa-2,5-dien-1-one (Vc). Yield 94%. ^{1}H NMR spectrum, δ, ppm: 0.88–0.93 t (3H, $OCH_2CH_2CH_3$), 1.52–1.64 d.d (2H, $OCH_2CH_2CH_3$), 1.98 s (6H, $C^{3,5}H_3$), 3.04–3.08 t (2H, $OCH_2CH_2CH_3$), 5.42 br.s (1H, N^2H), 6.29 br.s (2H, $H^{2,6}$), 6.84 br.s (1H, N^1H), 7.07–7.30 m (5H, Ph).

4-Butoxy-3,5-dimethyl-4-phenylaminocarbonylaminocyclohexa-2,5-dien-1-one (Vd). Yield 35%. ^{1}H NMR spectrum, δ, ppm: 0.87–3.12 m (9H, Bu), 1.98 s (6H, $C^{3,5}H_3$), 5.55 br.s (1H, N^2H), 6.29 s (2H, $H^{2,6}$), 7.03 br.s (1H, N^1H), 7.06–7.30 m (5H, Ph).

3,5-Dimethyl-4-[(4-methylphenyl)aminocarbonylamino]-4-methoxycyclohexa-2,5-dien-1-one (Ve). Yield 82%. ^{1}H NMR spectrum, δ, ppm: 1.95 br.s (6H, $C^{3,5}H_3$), 2.32 s (3H, 4-$CH_3C_6H_4$), 3.01 s (3H, OMe), 5.35 br.s (1H, N^2H), 6.31 br.s (2H, $H^{2,6}$), 6.53 br.s (1H, N^1H), 7.14 s (4H, 4-$CH_3C_6H_4$).

3,5-Dimethyl-4-[(4-methylphenyl)aminocarbonylamino]-4-ethoxycyclohexa-2,5-dien-1-one (Vf). Yield 3%. ^{1}H NMR spectrum, δ, ppm: 0.85–0.90 t (3H, OCH_2CH_3), 1.97 s (6H, $C^{3,5}H_3$), 2.34 s (3H, 4-$CH_3C_6H_4$), 3.72–3.79 d.d (2H, OCH_2CH_3), 5.33 br.s (1H, N^2H), 6.27 s (2H, $H^{2,6}$), 6.84 br.s (1H, N^1H), 7.00–7.21 d.d ($4H_{arene}$, *J* 8.4 Hz).

3,5-Dimethyl-4-methoxy-4-(phenylaminocarbonylamino)-2,6-dichlorocyclohexa-2,5-dien-1-one (Vg). Yield 15%. ^{1}H NMR spectrum, δ, ppm: 2.10 s (6H, $C^{3,5}H_3$), 3.00 s (3H, OMe), 6.15 br.s (1H, N^2H), 7.03 br.s (1H, N^1H), 7.34–7.52 m (5H, Ph).

4-Methoxy-4-phenylaminocarbonylamino-3,5-dichlorocyclohexa-2,5-dien-1-one (Vh). Yield 95%, mp 182–184°C. ^{1}H NMR spectrum, δ, ppm: 3.19 s (3H, OMe), 5.52 br.s (1H, N^2H), 6.52 br.s (1H, N^1H), 6.70 s (2H, $H^{2,6}$), 7.13–7.37 m (5H, Ph). Found, %: N 8.43, 8.60. $C_{14}H_{12}Cl_2N_2O_3$. Calculated, %: N 8.56.

4-Butylaminocarbonylamino-3,5-dimethyl-4-methoxycyclohexa-2,5-dien-1-one (Vi). Yield 82%, mp 129–130°C. ^{1}H NMR spectrum, δ, ppm: 0.87–

3.15 m (9H, Bu), 1.94 s (6H, $C^{3,5}H_3$), 3.00 s (3H, OMe), 4.88 q (1H, N^2H), 5.48 br.s (1H, N^1H), 6.29 s (2H, $H^{2,6}$). Found, %: N 10.45, 10.61. $C_{14}H_{22}N_2O_3$. Calculated, %: N 10.52.

4-Butylaminocarbonylamino-3,5-dimethyl-4-propoxycyclohexa-2,5-dien-1-one (Vj). Yield 45%, mp 121–122°C. ^{1}H NMR spectrum, δ, ppm: 0.87–0.92 t (3H, $OCH_2CH_2CH_3$), 0.93–3.16 m (9H, Bu), 1.50–1.57 d.d (2H, $OCH_2CH_2CH_3$), 1.94 s (6H, $C^{3,5}H_3$), 3.00–3.04 t (2H, $OCH_2CH_2CH_3$), 4.81 q (1H, N^2H), 5.24 br.s (1H, N^1H), 6.25 s (2H, $H^{2,6}$). Found, %: N 9.41, 9.59. $C_{16}H_{26}N_2O_3$. Calculated, %: N 9.52.

4-(*tert*-Butyl)aminocarbonylamino-3,5-dimethyl-4-methoxycyclohexa-2,5-dien-1-one (Vk). Yield 80%, mp 192–194°C. ^{1}H NMR spectrum, δ, ppm: 1.27 s (9H, *t*-Bu), 1.95 s (6H, $C^{3,5}H_3$), 2.99 s (3H, OMe), 4.68 br.s (1H, N^2H), 5.31 br.s (1H, N^1H), 6.31 s (2H, $H^{2,6}$). Found, %: N 10.46, 10.62. $C_{14}H_{22}N_2O_3$. Calculated, %: N 10.52.

4-(*tert*-Butyl)aminocarbonylamino-4-ethoxycyclohexa-2,5-dien-1-one (Vl). Yield 81%, mp 185–186°C. ^{1}H NMR spectrum, δ, ppm: 1.10–1.15 t (3H, OCH_2CH_3), 1.33 s (9H, *t*-Bu), 1.95 s (6H, $C^{3,5}H_3$), 3.09–3.13 d.d (2H, OCH_2CH_3), 4.42 br.s (1H, N^2H), 5.33 br.s (1H, N^1H), 6.24 s (2H, $H^{2,6}$). Found, %: N 9.82, 10.04. $C_{15}H_{24}N_2O_3$. Calculated, %: N 9.99.

3,5-Dimethyl-4-methoxy-4-cyclohexylaminocarbonylaminocyclohexa-2,5-dien-1-one (Vm). Yield 79%, mp 177–179°C. ^{1}H NMR spectrum, δ, ppm: 1.00–3.53 m (11H, *cyclo*-C_6H_{11}), 1.94 s (6H, $C^{3,5}H_3$), 3.00 s (3H, OMe), 4.77 d (1H, N^2H, *J* 8.1 Hz), 5.40 br.s (1H, N1H), 6.30 br.s (2H, $H^{2,6}$). Found, %: N 9.46, 9.69. $C_{16}H_{24}N_2O_3$. Calculated, %: N 9.58.

3,5-Dimethyl-4-cyclohexylaminocarbonylamino-4-ethoxycyclohexa-2,5-dien-1-one (Vn). Yield 35%, mp 140–141°C. ^{1}H NMR spectrum, δ, ppm: 1.08–3.51 m (11H, *cyclo*-C_6H_{11}), 1.12–1.17 t (3H, OCH_2CH_3), 1.95 s (6H, $C^{3,5}H_3$), 3.11–3.16 d.d (2H, OCH_2CH_3), 4.66 d (1H, N^2H, *J* 9 Hz), 5.16 s (1H, N1H), 6.26 s (2H, $H^{2,6}$). Found, %: N 9.03, 9.21. $C_{17}H_{26}N_2O_3$. Calculated, %: N 9.14.

3a,7-Dimethyl-7a-methoxy-3-phenyl-3a,7a-dihydro-1*H*-benzimidazole-2,5(3*H*,4*H*)-dione (VIa). Yield 93%, mp 180–182°C. ^{1}H NMR spectrum, δ, ppm: 1.35 s (3H, $C^{3a}H_3$), 2.03 d (3H, C^7H_3), 2.53–2.73 d.d (2H, C^4H_2, *J* 15.6 Hz), 3.50 s (3H, OMe), 6.09 q (1H, H^6), 6.69 br.s (1H, NH), 7.14–7.42 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 17.68 (Me–C^7), 19.51 (Me–C^{3a}), 47.90 (C^4), 52.03 (OMe), 67.33 (C^{3a}), 87.93 (C^{7a}), 128.22 ($C^{2'}$), 128.37 (C^{22}), 129.27 (C^{12}), 129.41 (C^{32}), 134.34 (C^{42}), 146.68 (C^6), 153.51 (C^7), 157.68 (C^2), 195.03 (C^5). Found, %: N 9.64, 9.87. $C_{16}H_{18}N_2O_3$. Calculated, %: N 9.78.

3a,7-Dimethyl-3-phenyl-7a-ethoxy-3a,7a-dihydro-1*H*-benzimidazole-2,5(3*H*,4*H*)-dione (VIb). Yield 96%, mp 218–219°C. ^{1}H NMR spectrum, δ, ppm: 1.22–1.27 t (3H, OCH_2CH_3), 1.33 s (3H, $C^{3a}H_3$), 2.21 d (3H, C^7H_3), 2.58–2.71 d.d (2H, C^4H_2, *J* 15 Hz), 3.68–3.75 d.d (2H, OCH_2CH_3), 5.91 br.s (1H, NH), 6.00 br.s (1H, H^6), 7.26–7.50 m (5H, Ph). Found, %: N 9.28, 9.40 . $C_{17}H_{20}N_2O_3$. Calculated, %: N 9.33.

3a,7-Dimethyl-3-(4-methylphenyl)-7a-methoxy-3a,7a-dihydro-1*H*-benzimidazole-2,5(3*H*,4*H*)-dione (VIe). Yield 69%, mp 156–157°C. ^{1}H NMR spectrum, δ, ppm: 1.34 s (3H, $C^{3a}H_3$), 2.03 d (3H, C^7H_3), 2.36 s (3H, 4-$CH_3C_6H_4$), 2.52–2.71 d.d (2H, C^4H_2, *J* 15.6 Hz), 3.49 s (3H, OMε), 6.10 q (1H, H^6), 6.40 br.s (1H, NH), 7.02–7.21 d.d (4H, 4-$CH_3C_6H_4$, *J* 8.4 Hz). Found, %: N 9.25, 9.39. $C_{17}H_{20}N_2O_3$. Calculated, %: N 9.33.

3a,7-Dimethyl-3-(4-methylphenyl)-7a-ethoxy-3a,7a-dihydro-1*H*-benzimidazole-2,5(3*H*,4*H*)-dione (VIf). Yield 82%, mp 174–175°C. ^{1}H NMR spectrum, δ, ppm: 1.12–1.17 t (3H, OCH_2CH_3), 1.34 s (3H, $C^{3a}H_3$), 2.05 d (3H, C^7H_3), 2.36 s (3H, 4-$CH_3C_6H_4$), 2.52–2.69 d.d (2H, C^4H_2, *J* 15.6 Hz), 3.64–3.70 d.d (2H, OCH_2CH_3), 6.11 q (1H, H^6), 6.42 br.s (1H, NH), 7.00–7.21 d.d (4H, 4-$CH_3C_6H_4$, *J* 8.4 Hz). Found, %: N 8.86, 9.01. $C_{18}H_{22}N_2O_3$. Calculated, %: N 8.91.

3a,7-Dimethyl-7a-methoxy-3-phenyl-4,6-dichloro-3a,7a-dihydro-1*H*-benzimidazole-2,5(3*H*,4*H*)-dione (VIg). Yield 30%. ^{1}H NMR spectrum, δ, ppm: 1.46 s (3H, $C^{3a}H_3$), 2.57 s (3H, C^7H_3), 3.56 s (3H, OMe), 4.60 s (1H, H^4), 7.24–7.50 m (5H, Ph), 7.34 br.s (1H, NH).

4,7a-Dimethyl-1-phenyl-7,7a-dihydro-1*H*-benzimidazole-2,6-dione (VIIa). Yield 98%, mp 248–250°C. ^{1}H NMR spectrum, δ, ppm: 1.40 d (3H, $C^{7a}H_3$), 2.40 d (3H, CH_3, *J* 1.5 Hz), 2.92–3.12 d.d (2H, C^7H_2, *J* 15.6 Hz), 6.50 q (1H, H^5), 7.29–7.50 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 17.38 (Me–C^{7a}), 24.30 (Me–C^4), 50.67 (C^7), 69.88 (C^{7a}), 126.64 (C^{22}),128.00 (C^{42}), 129.47 (C^{32}), 134.49 (C^5), 135.67 (C^{12}), 146.42 (C^4), 163.92 (C^{3a}), 188.56 (C^2), 192.92 (C^6). Found, %: N 10.97, 11.13. $C_{15}H_{14}N_2O_2$. Calculated, %: N 11.02.

4,7a-Dimethyl-1-(4-methylphenyl)-7,7a-dihydro-1*H*-benzimidazole-2,6-dione (VIIb). Yield 88%, mp 192–194°C. ^{1}H NMR spectrum, δ, ppm: 1.38 s (3H,

$C^{7a}H_3$), 2.39 s (3H, 4-$CH_3C_6H_4$), 2.39 d (3H, C^4H_3, $J_{4,5}$ 1.5 Hz), 2.90–3.09 d.d (2H, $2H^7$, J 15.0 Hz), 6.49 br.s (1H, H^5), 7.13–7.25 d.d (4H, 4-$CH_3C_6H_4$, J 8.1 Hz). Found, %: N 10.35, 10.50. $C_{16}H_{16}N_2O_2$. Calculated, %: N 10.44.

4,7a-Dimethyl-1-phenyl-5-chloro-7,7a-dihydro-1*H*-benzimidazole-2,6-dione (VIIc). Yield 60%. ^{1}H NMR spectrum, δ, ppm: 1.41 s (3H, $C^{7a}H_3$), 2.55 s (3H, C^4H_3), 2.99–3.34 d.d (2H, C^7H_2, J 1.5 Hz), 7.26–7.48 m (5H, Ph).

4,7a-Dimethyl-1-phenyl-7-chloro-7,7a-dihydro-1*H*-benzimidazole-2,6-dione (VIId). Yield 26%. ^{1}H NMR spectrum, δ, ppm: 1.54 s (3H, $C^{7a}H_3$), 2.45 d (3H, C^4H_3, $J_{4,5}$ 1.2 Hz), 4.81 s (1H, H^7), 6.73 q (1H, H^5, $J_{4,5}$ 1.2 Hz), 7.26–7.48 m (5H, Ph).

4,7a-Dimethyl-1-phenyl-5,7-dichloro-7,7a-dihydro-1*H*-benzimidazole-2,6-dione (VIIe). Yield 55%. ^{1}H NMR spectrum, δ, ppm: 1.56 s (3H, $C^{7a}H_3$), 2.57 s (3H, C^4H_3), 4.85 s (1H, H^7), 7.24–7.50 m (5H, Ph).

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