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Dedicated to Full Member of the Russian Academy of Sciences G.A. Tolstikov on his 80th anniversary

Activated Sterically Strained C=N Bond in N-Substituted *p*-Quinone Mono- and Diimines: XIV.* Reaction of Some 3,5-Dimethyl-1,4-benzoquinone Monoimines with Alcohols

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Abstract—Steric strain in the C=N–C fragment in 3,5-disubstituted *N*-acyl-1,4-benzoquinone monoimines, unlike their *N*-arylsulfonyl analogs, leads to increase of the C=N–C angle above 130° or twisting of the double C=N bond and loss of planarity of the quinoid ring. This structural transformation enhances the reactivity of the C=N bond so that 1,2-addition of alcohols becomes possible with formation of sterically unstrained cyclohexadienone structure with sp^3-hybridized C^4 carbon atom.

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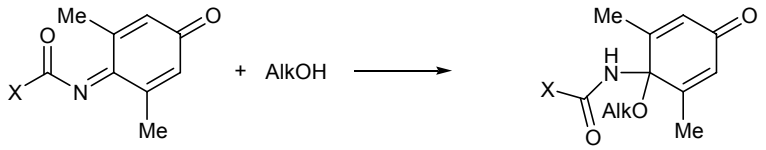
N-Substituted 3,5-dimethyl(chloro)-1,4-benzoquinone monoimines are known to readily react with alcohols [1–4], hydrazines, primary aromatic amines, dialkyl hydrogen phosphites, and bis(4-dimethylaminophenyl)phosphinite [5] according to the 1,2-addition pattern (i.e., at the C=N bond). The nature of substituents on the nitrogen atom [$ArSO_2N{=}C(Me)$, $ArSO_2$, $ArSO_2N{=}C(Ph)$] and in positions *3* and *5* of the quinoid ring (Me, Cl) does not affect the reactivity of the C=N bond [4, 6], while orientation of the substituent on the nitrogen atom and the size of the entering AlkO group are crucial [4].

It was presumed that 1,2-addition becomes possible due to activation of the C=N bond as a result of steric strain appearing upon increase of the C=N–X bond angle above 130° [4]. However, according to the X-ray diffraction data, the C=N–C angle in 3,5-dimethyl-*N*-(phenylaminocarbonyl)-1,4-benzoquinone monoimine

Scheme 1.



Ia–Ig **IIa–IIh** **IIIa–IIIe**, **IIIg**, **IVa–IVd**, **Va–Vh**, **VIa–VIe** **VIIa–VIIh**, **VIIIa–VIIIc**, **IXa**, **IXb**, **IXg**

I, X = Me (**a**), $PhCH_2$ (**b**), $4\text{-}MeC_6H_4CH_2$ (**c**), $PhOCH_2$ (**d**), (*E*)-PhCH=CH (**e**), Ph (**f**), $4\text{-}MeC_6H_4$ (**g**); **II**–**IX**, Alk = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), Bu (**e**), *i*-Bu (**f**), C_5H_{11} (**g**), *cyclo*-C_6H_{11} (**h**); **III**, X = Me; **IV**, X = $PhCH_2$; **V**, X = $4\text{-}MeC_6H_4CH_2$; **VI**, X = $PhOCH_2$; **VII**, X = (*E*)-PhCH=CH; **VIII**, X = Ph; **IX**, X = $4\text{-}MeC_6H_4$.

* For communication XIII, see [1].

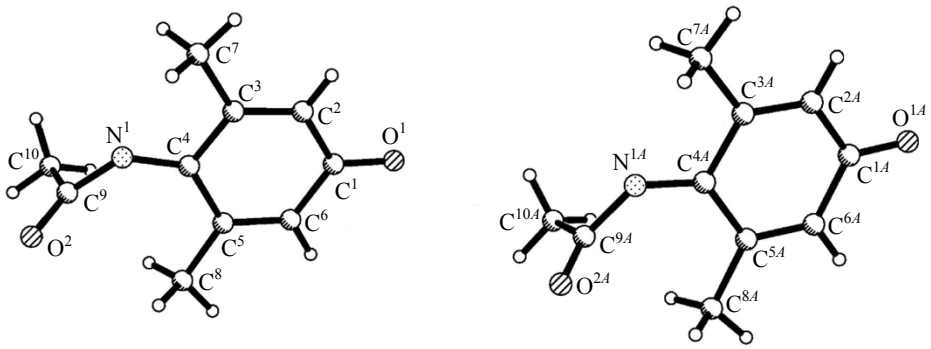


Fig. 1. Structure of the molecule of *N*-acetyl-3,5-dimethyl-1,4-benzoquinone imine (**Ia**) according to the X-ray diffraction data.

is 126.26° [7] which is typical of quinone imines having no substituent on C^3 and C^5 [6], and this compound did react with alcohols at the C=N bond [8]. No X-ray diffraction data are available on other 3,5-disubstituted 1,4-benzoquinone monoimines with a carbonyl group on the nitrogen, though 1,2-additions of alcohols to *N*-acetyl-3,5-dimethyl- [3] and *N*-acetyl-2,3,5,6-tetrachloro-1,4-benzoquinone monoimines [4] were reported.

The goal of the present work was to examine reactions of alcohols with previously synthesized *N*-acyl-3,5-dimethyl-1,4-benzoquinone monoimines and elucidate structural specificities of the latter.

The reactions of *N*-acyl-3,5-dimethyl-1,4-benzoquinone monoimines **Ia**–**Ig** with methanol (**IIa**) and ethanol (**IIb**) gave expected 1,2-addition products **III**–**IX** (Scheme 1). In the reactions with propan-1-ol, propan-2-ol, butan-1-ol, and pentan-1-ol, the corresponding 1,2-addition products were isolated from quinone imines **Ia** and **Ic**–**Ie**, and with 2-methylpropan-1-ol and cyclohexanol, from quinone imines **Ic** and **Ie**. The reaction time increased in parallel with the size of the alkyl group (Alk) in **IIa**–**IIh** (MeOH < EtOH < PrOH < BuOH < $C_5H_{11}OH$ < *i*-PrOH < *i*-BuOH, *cyclo*-$C_6H_{11}OH$). Analogous relation was observed for other quinone imine series [4]. The above alcohol series coincides with the series of their steric constants E_S^0 calculated with account taken of hyperconjugation between C–H and C–C bonds [9]. This means that the reaction rate is determined by steric factor, i.e., steric hindrance to attack by alcohol molecule on the C=N bond in quinone imine. *tert*-Butyl alcohol characterized by the highest negative value of E_S^0 (–2.14) failed to react with compounds **Ia**–**Ig**.

The structure of quinone imines **Ia**, **Ib**, and **Id**–**If** was determined by X-ray analysis (Figs. 1–5). All the examined molecules were found to suffer a considerable steric strain in the C^4=N–C^9=O fragment due to the presence of two methyl groups in positions *3* and *5* of the quinoid ring (Table 1). Unlike 2,6-dimethyl-substituted analogs [10], quinone imines **Ia**, **Ib**, and **Id**–**If** are characterized by increased bond angle C^4NC^9, torsion angle $C^3C^4NC^9$, dihedral angle formed by the N–C^9 bond and C^1–C^6 plane, and deviation of the C^9 atom from the C^1–C^6 plane; in addition, the quinoid ring C^1–C^6 becomes less planar. There exists a correlation between the C^4NC^9 bond angle and variations in the quinoid ring and C^4=N–C^9=O fragment.

Detailed analysis of the geometry variation pattern showed that steric strain in molecules **I** relaxes in two

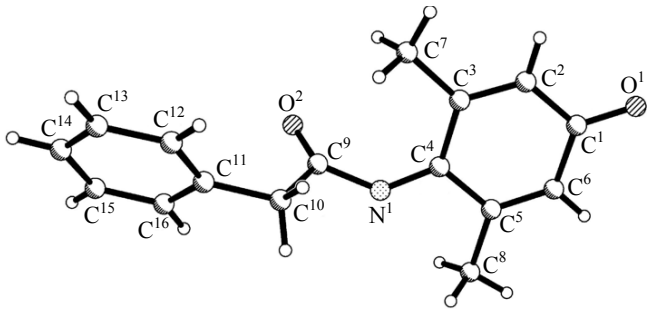


Fig. 2. Structure of the molecule of 3,5-dimethyl-*N*-phenylacetyl-1,4-benzoquinone imine (**Ib**) according to the X-ray diffraction data.

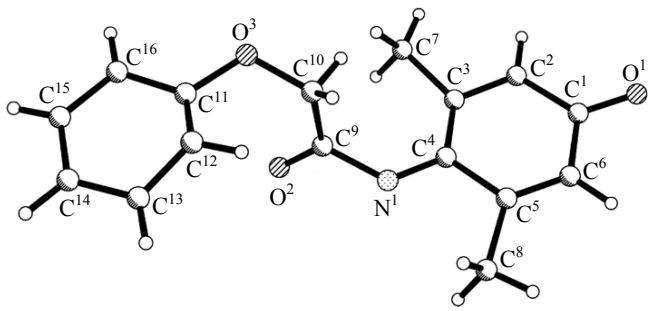


Fig. 3. Structure of the molecule of 3,5-dimethyl-*N*-phenoxyacetyl-1,4-benzoquinone imine (**Id**) according to the X-ray diffraction data.

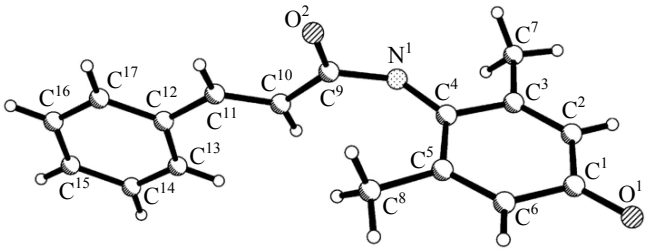


Fig. 4. Structure of the molecule of *N*-benzylideneacetyl-3,5-dimethyl-1,4-benzoquinone imine (**Ie**) according to the X-ray diffraction data.

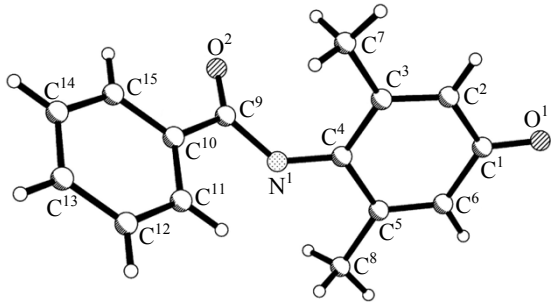
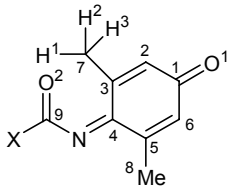


Fig. 5. Structure of the molecule of *N*-benzoyl-3,5-dimethyl-1,4-benzoquinone imine (**If**) according to the X-ray diffraction data.

ways. First of all, the C^9NC^4 bond angle in **Ia**, **Ib**, **Ie**, and **If** is larger by 8–12° than the corresponding angle in 2,6-dimethyl-1,4-benzoquinone imines [10], which is typical of quinone imines; this is accompanied by relatively small twisting of the double C=N bond (by less than 6°) and small distortion of planarity of the quinoid ring (Table 1). The C^9NC^4 bond angle in **Ia**, **Ib**, **Ie**, and **If** exceeds 130°, which is consistent with previous interpretations of high reactivity of the C=N bond in 1,2-addition reactions.

However, the C^9NC^4 angle in quinone imine **Id**, as well as in *N*-(phenylaminocarbonyl)-3,5-dimethyl-1,4-benzoquinone imine [7], is considerably smaller than 130° (Table 1). Nevertheless, compound **Id** takes up alcohols at the C=N bond. Detailed analysis of the geometric parameters of molecule **Id** revealed another

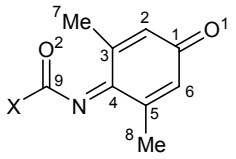
Table 1. X-Ray diffraction data for 3,5-dimethyl-1,4-benzoquinone imines **Ia**, **Ib**, and **Id**–**If**[a]



Parameter	Ia		Ib	Id	Ie	If
	conformer **A**	conformer **B**				
Bond angle C^9NC^4, deg	131.3(2) (+9.0)	132.0(2) (+8.2)	132.8(1) (+9.4)	124.1(2) (+4.8)	130.4(2) (+12.4)	132.0(1) (+8.9)
Bond length C^4=N, Å	1.277(2)	1.282(2)	1.276(2)	1.314(3)	1.272(2)	1.283(2)
Bond length C^9–N, Å	1.389(2)	1.385(3)	1.384(2)	1.477(2)	1.399(2)	1.385(2)
Torsion angle $C^3C^4NC^9$, deg	–4.2(4) (+3.7)	–5.6(3) (+6.0)	+6.4(4) (+3.6)	–22.8(5) (+8.6)	+7.2(4) (+3.1)	+10.8(3) (+5.9)
Planarity of the quinoid fragment C^1–C^6	±0.039 (+0.029)	±0.032 (+0.026)	±0.006 (–0.008)	±0.049 (+0.038)	±0.016 (+0.015)	±0.037 (+0.018)
Dihedral angle between the N–C bond and C^1–C^6 plane, deg	9.6 (+9.0)	10.0 (+8.1)	4.8 (+3.5)	14.7 (+7.5)	9.1 (+3.5)	13.8 (+11.7)
Deviation of the C^9 atom from the C^1–C^6 plane, Å	+0.474 (+0.400)	+0.464 (+0.395)	–0.137 (+0.097)	+0.594 (+0.347)	+0.349 (+0.063)	+0.561 (+0.514)
Shortened intramolecular contacts						
$C^9\cdots C^7$, Å (3.42 Å)[b]	2.88	2.92	2.94	2.84	2.89	2.92
$C^9\cdots H^1$, Å (2.87 Å)[b]	2.51	2.52	2.60	2.44	2.56	2.66

[a] The difference from the corresponding parameter of analogous 2,6-dimethyl-1,4-benzoquinone imine [10] is given in parentheses.
[b] The sum of the van der Waals radii [11].

Table 2. Calculated orbital and orbital interaction energies and hybridization of the nitrogen LEP in *N*-acyl-3,5-dimethyl-1,4-benzoquinone monoimines **Ia**, **Ib**, and **Id**–**If**[a]



Parameter	**Ia**	**Ib**	**Id**	**Ie**	**If**	**Ih**
Energy of $\pi(C^4{=}N)$, kJ/mol	–951.8 (–32.2)	–954.7 (–31.6)	–968.4 (–34.0)	–938.5 (–33.4)	–947.4 (–33.0)	–1008.0 (–88.3)
Energy of $\pi^*(C^4{=}N)$, kJ/mol	–17.0 (–12.4)	–17.3 (–10.0)	–37.1 (–12.3)	–17.2 (–27.1)	–11.9 (–13.0)	–63.7 (–59.0)
Energy of n(N) , kJ/mol	–919.2 (+51.8)	–908.4 (+62.3)	–938.3 (+47.8)	–910.2 (+49.8)	–916.0 (+50.0)	–961.1 (+9.8)
Energy of $\pi(C^4{=}N)\rightarrow\pi^*(C^9{=}O^2)$ interaction, kJ/mol	24.5 (–17.1)	29.1 (–12.7)	28.8 (–27.0)	13.3 (–30.0)	21.7 (–22.4)	17.3 (–24.3)
Energy of $\pi^*(C^4{=}N)\rightarrow\pi^*(C^9{=}O^2)$ interaction, kJ/mol	17.4 (–23.5)	17.5 (–14.9)	21.5 (–41.2)	30.4 (–70.1)	36.03 (–56.8)	9.8 (–31.1)
Energy of $n_N\rightarrow\pi^*(C^9{=}O^2)$ interaction, kJ/mol	60.1 (+18.3)	48.8 (+12.4)	62.8 (+29.7)	86.9 (+40.4)	91.2 (+42.3)	52.9 (+11.1)
Hybridization of n(N)[b]	$sp^{3.50}$ ($sp^{2.60}$)	$sp^{3.71}$ ($sp^{2.66}$)	$sp^{3.61}$ ($sp^{2.66}$)	$sp^{3.38}$ ($sp^{2.54}$)	$sp^{3.45}$ ($sp^{2.60}$)	$sp^{3.45}$ ($sp^{2.60}$)
Energy of $\pi(C^4{=}N)\rightarrow\pi^*(C^2{=}C^3)$ interaction, kJ/mol	34.7 (–0.8)	34.3 (–1.1)	33.6 (–0.4)	34.1 (–1.3)	34.1 (–0.8)	34.7 (–0.1)
Energy of $\pi(C^2{=}C^3)\rightarrow\pi^*(C^4{=}N)$ interaction, kJ/mol	72.7 (–8.5)	73.6 (–8.2)	74.8 (–9.4)	72.2 (–8.6)	73.0 (–8.6)	63.8 (–17.8)
Energy of $\pi(C^4{=}N)\rightarrow\pi^*(C^5{=}C^6)$ interaction, kJ/mol	39.2 (–1.3)	38.7 (–1.6)	38.0 (–1.2)	38.9 (–2.0)	38.8 (–1.4)	39.3 (–1.0)
Energy of $\pi(C^5{=}C^6)\rightarrow\pi^*(C^4{=}N)$ interaction, kJ/mol	67.2 (–7.5)	67.5 (–7.6)	69.0 (–8.1)	66.4 (–7.6)	67.2 (–7.6)	59.4 (–15.5)

[a] Increase (+) or decrease (–) of the corresponding parameter relative to that of 2,6-dimethyl-1,4-benzoquinone monoimine [10] is given in parentheses.

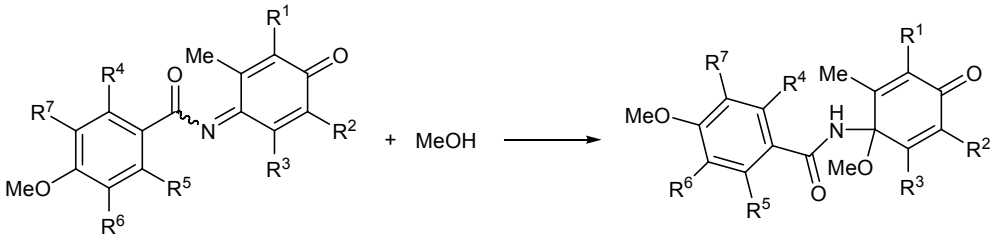
[b] Hybridization of the nitrogen LEP in 2,6-dimethyl derivative [10] is given in parentheses.

way of structural relaxation with retention of an appreciable steric strain (see shortened intramolecular contacts in Table 1). Instead of increase of the C^9NC^4 bond angle we observed considerable twisting of the C=N bond [the torsion angle $C^3C^4NC^9$ is –22.8(5)°] and some distortion of the quinoid ring from planar structure (Table 1). In addition, the C^9–N^1 bond is extended to 1.477(2) Å against 1.384(2)–1.399(2) Å in other compounds of the same series, and the C^4=N bond is extended to 1.314(3) Å against 1.272(2)–1.283(2) Å.

Thus, analysis of the X-ray diffraction data shows that the C=N–X angle cannot be regarded as the only parameter indicating that the C=N bond in the C=N–C fragment of quinone imines is sterically strained and activated. Steric strain is also reflected in considerable twisting (by more than 20°) of the double C=N bond.

According to quantum-chemical calculations, steric strain in the C^4=N–C^9=O fragment of 3,5-dimethyl-1,4-benzoquinone imines **Ia**, **Ib**, and **Id**–**If** leads to reduction of the energy of the $\pi(C^4{=}N)$ and $\pi^*(C^4{=}N)$ orbitals and energy of the orbital donor–acceptor interactions $\pi(C^4{=}N^1)\rightarrow\pi^*(C^9{=}O^2)$ and $\pi^*(C^4{=}N^1)\rightarrow\pi^*(C^9{=}O^2)$, increase of the energy of the lone electron pair (LEP) on the nitrogen atom n(N), and the energy of the donor–acceptor interaction $n_N\rightarrow\pi^*(C^9{=}O^2)$ (Table 2) as compared to 2,6-dimethyl-substituted analogs [10]. As a result, the LEP on the nitrogen atom acquires a higher *p*-character, and the nitrogen atom becomes more nucleophilic and capable of abstracting hydrogen from an alcohol molecule. This is confirmed by the mass spectra of N-substituted 1,4-benzoquinone monoimines [12]. Only 3,5-disubstituted 1,4-benzo-

Scheme 2.



Xa–Xc **XIa–XIc**

$R^1 = R^3 = R^7 = Cl$, $R^2 = Me$, $R^4 = R^5 = R^6 = H$ (**a**); $R^1 = R^2 = R^3 = R^4 = R^5 = Cl$, $R^6 = R^7 = MeO$ (**b**); $R^1 = R^5 = H$, $R^2 = R^3 = R^4 = Br$, $R^6 = R^7 = MeO$ (**c**).

quinone monoimines displayed in the mass spectra strong peaks of $[M + 1]^+$ ions formed via addition of one hydrogen atom.

Furthermore, unlike 2,6-dimethyl analogs, 3,5-dimethyl derivatives **Ia**, **Ib**, and **Id**–**If** are characterized by considerably lower energies of the following orbital donor–acceptor interactions: $\pi(C^4{=}N)\rightarrow\pi^*(C^2{=}C^3)$, $\pi(C^2{=}C^3)\rightarrow\pi^*(C^4{=}N)$, $\pi(C^4{=}N)\rightarrow\pi^*(C^5{=}C^6)$, and $\pi(C^5{=}C^6)\rightarrow\pi^*(C^4{=}N)$, indicating weakened conjugation along the N=C–C=C bond sequence.

We can conclude that steric strain in the C=N–C fragment of *N*-acyl-3,5-dimethyl-1,4-benzoquinone imines increases the energy of the nitrogen LEP, reduces the energy of the π-C=N bond, and weakens conjugation of the latter with the quinoid C=C bonds and carbonyl bond. As a result, the C=N bond becomes more reactive toward 1,2-addition of nucleophiles.

Quantum-chemical calculations for model *N*-acetyl-3,5-dichloro-1,4-benzoquinone imine (**Ih**) showed that its energy parameters differ from those of 2,6-disubstituted analog in a way similar to compounds **Ia**, **Ib**, and **Id**–**If** (Table 2). Presumably, such compounds should also react with alcohols according to the 1,2-addition pattern. Insofar as *N*-acyl-3,5-dichloro-1,4-benzoquinone monoimines are very unstable, the above assumption was verified using *N*-aroyl derivatives **Xa**–**Xc**. As expected, compounds **Xa**–**Xc** fairly readily reacted with methanol to give the corresponding 1,2-addition products **XIa**–**XIc** (Scheme 2).

EXPERIMENTAL

Quantum-chemical calculations were performed in terms of the density functional theory using B3LYP functional [13–18] and standard 6-31+G(*d*) basis set [19, 20] with the aid of Gaussian 03 software package [21]. Conjugative and hyperconjugative interactions were simulated in terms of the natural bond orbitals (NBO) theory [22] (NBO 5.0 [23]). The X-ray diffraction data were used as starting geometric parameters for optimization, and the optimized parameters of **Ia**, **Ib**, and **Id**–**If** were consistent with the experimental values.

X-Ray analysis of compounds **Ia** ($C_{10}H_{11}NO_2$, *M* 177.20), **Ib** ($C_{16}H_{15}NO_2$, *M* 253.29), **Ie** ($C_{17}H_{15}NO_2$, *M* 265.30), and **If** ($C_{15}H_{13}NO_2$, *M* 239.26) was performed at 293 K on an Xcalibur 3 four-circle automatic diffractometer with a CCD detector (MoK_α irradiation, graphite monochromator, ω-scanning). The structures were solved by the direct method using SHELXTL software package [24]. The positions of non-hydrogen atoms were refined in anisotropic approximation. The positions of hydrogen atoms were determined by difference synthesis of electron density and were refined according to the riding model with $U_{iso} = n U_{equiv}$ for non-hydrogen atom linked to a given hydrogen atom (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms) with fixed thermal vibration parameters.

The X-ray powder diffraction pattern for a sample of **Id** ($C_{16}H_{15}NO_3$, *M* 269.29) was obtained on a Siemens D500 diffractometer (Cu irradiation, graphite monochromator for the reflected beam, θ–2θ scanning, Bregg–Brentano geometry). The full-profile diffraction patterns were measured in the 2θ range from 2 to 84° with a step of 0.02°; measurement time 60 s; LaB_6 was used as calibration standard. The X-ray powder diffraction pattern was processed with the aid of PowderX [25], ITO [26], and DICVOL [27]; the structure was resolved using Fox program [28] and was refined by the Rietveld method using FullProf [29]. The positions of hydrogen atoms were set on the basis of geometry considerations and were refined according to the riding model. The principal crystallographic parameters are given in Table 3. The complete sets of crystallographic data for compounds **Ia**,

Table 3. Principal crystallographic parameters of *N*-acyl-3,5-dimethyl-1,4-benzoquinone monoimines **Ia**, **Ib**, and **Id**–**If**

Parameter	**Ia**	**Ib**	**Id**	**Ie**	**If**
a, Å	5.0575(3)	7.9649(2)	13.7055(7)	12.999(5)	8.1584(2)
b, Å	12.5593(7)	11.4653(5)	9.4015(5)	7.311(3)	8.1584(2)
c, Å	14.3550(9)	14.6182(5)	5.2867(3)	14.918(6)	32.5732(14)
α, deg	85.974(5)	90	90	90	90
β, deg	86.198(5)	92.940(3)	98.567(5)	103.66(4)	90
γ, deg	82.919(5)	90	90	90	120
V, Å^3	901.10(9)	1333.18(8)	673.61(6)	1377.7(10)	1877.59(10)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Hexagonal
Space group	*P*-1	*P*21/*n*	*P*21	*P*21/*n*	*P*61
Z	4	4	2	4	6
F(000)	376	536	284	560	756
D_{calc}, g/cm^3	1.306	1.262	1.328	1.279	1.270
μ(MoK_α), mm^{-1}	0.092	0.083	0.092	0.084	0.085
$2\theta_{max}$, deg	60	60	84	50	60
Total number of reflections	9662	21146	6886	8003	17145
Number of independent reflections	5172	3866	3580	2412	3601
R_{int}	0.1492	0.1011	0.0551	0.0754	0.0675
Number of reflections with $F > 4\sigma(F)$	2202	2503		1257	2233
Number of variables	239	174	49	183	166
wR_2	0.0531	0.1522	0.076	0.0923	0.1003
R_1 [$F > 4\sigma(F)$]	0.0542	0.0577		0.0445	0.0478
Goodness of fit	0.816	1.047		0.846	0.906
Entry no. in CCDC	874659	874661	874663	874660	874662

Ib, and **Id**–**If** were deposited to the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; e-mail: *deposit@ccdc.cam.ac.uk*).

The ^{1}H and ^{13}C NMR spectra were measured on a Varian VXR-300 instrument at 300 and 75.4 MHz, rspectively, using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates; spots were applied from solutions in chloroform, plates were eluted with hexane–benzene (1 : 10), and spots were visualized under UV light.

Initial quinone imine (**Ia**) was synthesized by oxidation of *N*-(4-hydroxy-2,6-dimethylphenyl)acetamide with silver(I) oxide in chloroform according to the procedure described in [2]. Quinone imines **Ib**–**Ig** were prepared by oxidation of the corresponding 4-aminophenols with lead tetraacetate in acetic acid according to [10]. The properties of compounds **If** and **Ig** were consistent with published data [30]. Quinone imines **Xa**–**Xc** were obtained by halogenation of *N*-aroyl-1,4-benzoquinone imines as reported in [31].

Reaction of *N*-acyl-3,5-dimethyl-1,4-benzoquinone monoimines Ia–Ig and Xa–Xc with alcohols (*general procedures*). *a*. A solution of 1.1 mmol of quinone imine **Ib**–**Ig** in 5 ml of anhydrous alcohol **IIa**–**IId** was heated for 1–3 h under reflux with protection from atmospheric moisture. When the reaction was complete (TLC), the mixture was cooled, and the white crystalline solid was filtered off and recrystallized from petroleum ether (40–65°C). We thus isolated compounds **IVa**–**IVd**, **Va**–**Vd**, **VIa**–**VId**, **VIIa**–**VIId**, **VIIIa**–**VIIIc**, **IXa**, **IXb**, and **IXg**.

b. Anhydrous alcohol **IIa**, **IIc**, and **IIe**–**IIh**, 3 ml, was added to a solution of 1.1 mmol of quinone imine **Ia** in 5 ml of anhydrous diethyl ether, and the reaction vessel was tightly capped, shaken, and left to stand at room temperature until the reaction was complete (1–14 days; the mixture turned colorless). The precipitate

was filtered off and recrystallized from petroleum ether (40–65°C). We thus isolated compounds **IIIa**–**IIIe**, **IIIg**, **Ve**–**Vh**, **VIe**–**VIh**, and **VIIe**–**VIIh**.

c. A solution of 1.1 mmol of quinone imine **Xa**–**Xc** in 3 ml of anhydrous methanol was heated for 3.5 h under reflux. When the solution turned colorless, it was cooled to 0°C, and the precipitate was filtered off and recrystallized from benzene to isolate compounds **XIa**–**XIc**.

***N*-(1-Methoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)acetamid (IIIa).** Yield 99%, mp 179–180°C. ^{1}H NMR spectrum, δ, ppm: 1.89 s (6H, Me), 1.97 s (3H, MeCO), 2.99 s (3H, OMe), 6.07 br.s (1H, NH), 6.26 s (2H, 3-H, 5-H). Found, %: N 6.47, 6.40. $C_{11}H_{15}NO_3$. Calculated, %: N 6.69.

The properties of compound **IIIb** were in agreement with published data [2].

***N*-(2,6-Dimethyl-4-oxo-1-propoxycyclohexa-2,5-dien-1-yl)acetamide (IIIc).** Yield 70%, mp 176–177°C. ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, $CH_2C\mathbf{H}_3$), 1.53 d.d (2H, $C\mathbf{H}_2CH_3$, J = 12.3, 6.9 Hz), 1.90 s (6H, 2-Me, 6-Me), 2.00 s (3H, MeCO), 3.03 t (2H, OCH_2), 6.06 s (1H, NH), 6.27 s (2H, 3-H, 5-H). Found, %: N 5.68, 6.15. $C_{13}H_{19}NO_3$. Calculated, %: N 5.90.

***N*-(1-Isopropoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (IIId).** Yield 65%, mp 176–177°C. ^{1}H NMR spectrum, δ, ppm: 1.06 d (6H, $CH\mathbf{Me}_2$, J = 6.0 Hz), 1.94 s (6H, 2-Me, 6-Me), 2.00 s (3H, MeCO), 3.56–3.65 m (1H, OCH), 6.05 s (1H, NH), 6.25 s (2H, 3-H, 5-H). Found, %: N 5.74, 5.81. $C_{13}H_{19}NO_3$. Calculated, %: N 5.90.

***N*-(1-Butoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)acetamide (IIIe).** Yield 82%, mp 170–171°C. ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, $CH_2C\mathbf{H}_3$), 1.29–1.49 m (4H, $C\mathbf{H}_2C\mathbf{H}_2Me$), 1.89 s (6H, 2-Me, 6-Me), 1.99 s (3H, MeCO), 3.06 t (2H, OCH_2), 6.07 s (1H, NH), 6.26 s (2H, 3-H, 5-H). Found, %: N 5.33, 5.95. $C_{14}H_{21}NO_3$. Calculated, %: N 5.57.

***N*-(2,6-Dimethyl-4-oxo-1-pentyloxycyclohexa-2,5-dien-1-yl)acetamide (IIIg).** Yield 65%, mp 121–122°C. ^{1}H NMR spectrum, δ, ppm: 0.87–3.07 m (11H, $C_5H_{11}O$), 1.89 s (6H, 2-Me, 6-Me), 2.00 s (3H, MeCO), 6.00 s (1H, NH), 6.26 s (2H, 3-H, 5-H). Found, %: N 5.02, 5.17. $C_{15}H_{23}NO_3$. Calculated, %: N 5.28.

***N*-(1-Methoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-phenylacetamide (IVa).** Yield 59%, mp 183–184°C. ^{1}H NMR spectrum, δ, ppm: 1.77 s (6H, 2-Me, 6-Me), 2.93 s (3H, OMe), 3.54 s (2H, CH_2), 5.87 br.s (1H, NH), 6.27 s (2H, 3-H, 5-H), 7.26–7.41 m (5H, Ph). Found, %: N 5.14, 5.23. $C_{17}H_{19}NO_3$. Calculated, %: N 4.91.

***N*-(1-Ethoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-phenylacetamide (IVb).** Yield 51%, mp 204–205°C. ^{1}H NMR spectrum, δ, ppm: 1.09 t (3H, $CH_2C\mathbf{H}_3$), 1.78 s (6H, 2-Me, 6-Me), 3.08 q (2H, OCH_2, J = 7.2 Hz), 3.53 s (2H, CH_2), 5.84 br.s (1H, NH), 6.23 s (2H, 2-H, 6-H), 7.29–7.41 m (5H, Ph). Found, %: N 4.52, 4.86. $C_{18}H_{21}NO_3$. Calculated, %: N 4.68.

***N*-(2,6-Dimethyl-4-oxo-1-propoxycyclohexa-2,5-dien-1-yl)-2-phenylacetamide (IVc).** Yield 48%, mp 179–180°C. ^{1}H NMR spectrum, δ, ppm: 0.84 t (3H, $CH_2C\mathbf{H}_3$), 1.47 d.d (2H, $C\mathbf{H}_2CH_3$, J = 21.0, 6.6 Hz), 1.77 s (6H, 2-Me, 6-Me), 2.97 t (2H, OCH_2), 3.54 s (2H, CH_2), 5.84 br.s (1H, NH), 6.24 s (2H, 3-H, 5-H), 7.29–7.41 m (5H, Ph). Found, %: N 4.41, 4.29. $C_{19}H_{23}NO_3$. Calculated, %: N 4.47.

***N*-(1-Isopropoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-phenylacetamide (IVd).** Yield 52%, mp 191–192°C. ^{1}H NMR spectrum, δ, ppm: 1.01 d (6H, $CH\mathbf{Me}_2$, J = 6.6 Hz), 1.81 s (6H, 2-Me, 6-Me), 3.53 s (2H, CH_2), 3.49–3.57 m (1H, OCH), 5.80 s (1H, NH), 6.22 s (2H, 3-H, 5-H), 7.29–7.41 m (5H, Ph). Found, %: N 4.73, 4.55. $C_{19}H_{23}NO_3$. Calculated, %: N 4.47.

***N*-(1-Methoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-(4-methylphenyl)acetamide (Va).** Yield 89%, mp 214–215°C. ^{1}H NMR spectrum, δ, ppm: 1.77 s (6H, 2-Me, 6-Me), 2.36 s (3H, 4′-Me), 2.93 s (3H, OMe), 3.50 s (2H, CH_2), 5.80 br.s (1H, NH), 6.27 s (2H, 3-H, 5-H), 7.14 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.27 d (2H, 3′-H, 5′-H, J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.81 (2-Me, 6-Me), 21.09 (4′-Me), 43.33 (CH_2), 49.63 (MeO), 83.31 (C^1), 129 (C^3, C^5), 129.9 ($C^{2'}$, $C^{6'}$), 130.74 ($C^{3'}$, $C^{5'}$), 137.36 ($C^{4'}$), 153.04 (C^2, C^6), 168.64 (NC=O), 184.97 (C^4). Found, %: N 4.34, 4.42. $C_{18}H_{21}NO_3$. Calculated, %: N 4.68.

***N*-(1-Ethoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-(4-methylphenyl)acetamide (Vb).** Yield 71%, mp 223–224°C. ^{1}H NMR spectrum, δ, ppm: 1.09 t (3H, $OCH_2\mathbf{Me}$), 1.78 s (6H, 2-Me, 6-Me), 2.36 s (3H, 4′-Me), 3.07 q (2H, OCH_2, J = 6.9 Hz), 3.48 s (2H, CH_2), 5.84 br.s (1H, NH), 6.23 s (2H, 3-H, 5-H), 7.15 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.19 d (2H, 3′-H, 5′-H, J = 8.4 Hz). Found, %: N 4.29, 4.66. $C_{19}H_{23}NO_3$. Calculated, %: N 4.47.

***N*-(2,6-Dimethyl-4-oxo-1-propoxycyclohexa-2,5-dien-1-yl)-2-(4-methylphenyl)acetamide (Vc).** Yield

62%, mp 185–186°C. ^{1}H NMR spectrum, δ, ppm: 0.85 t (3H, $CH_2C\mathbf{H}_3$), 1.47 d.d (2H, $C\mathbf{H}_2CH_3$, J = 21.3, 6.9 Hz) , 1.78 s (6H, 2-Me, 6-Me), 2.35 s (3H, 4′-Me), 2.97 t (2H, OCH_2), 3.49 s (2H, CH_2), 5.90 br.s (1H, NH), 6.23 s (2H, 3-H, 5-H), 7.14 d (2H, 2′-H, 6′-H, J = 9.3 Hz), 7.18 d (2H, 3′-H, 5′-H, J = 7.8 Hz). Found, %: N 4.53, 4.37. $C_{20}H_{25}NO_3$. Calculated, %: N 4.28.

***N*-(1-Isopropoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-(4-methylphenyl)acetamide (Vd).** Yield 75%, mp 229–230°C. ^{1}H NMR spectrum, δ, ppm: 1.01 d (6H, $CH\mathbf{Me}_2$, J = 6 Hz), 1.82 s (6H, 2-Me, 6-Me), 2.36 s (3H, 4′-Me), 3.48 s (2H, CH_2), 3.51–3.59 m (1H, OCH), 5.86 s (1H, NH), 6.22 s (2H, 3-H, 5-H), 7.15 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.18 d (2H, 3′-H, 5′-H, J = 8.4 Hz). Found, %: N 4.04, 4.46. $C_{20}H_{25}NO_3$. Calculated, %: N 4.28.

***N*-(1-Butoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-(4-methylphenyl)acetamide (Ve).** Yield 80%, mp 192–193°C. ^{1}H NMR spectrum, δ, ppm: 1.06 t (3H, $CH_2C\mathbf{H}_3$), 1.23–1.43 m (2H, $C\mathbf{H}_2Me$), 1.43–1.47 m (2H, $OCH_2C\mathbf{H}_2$), 1.82 s (6H, 2-Me, 6-Me), 2.36 s (3H, 4′-Me), 3.19 t (2H, OCH_2), 3.48 s (2H, CH_2), 5.87 s (1H, NH), 6.21 br.s (2H, 3-H, 5-H), 7.16 d (2H, 2′-H, 6′-H, J = 8 Hz), 7.18 d (2H, 3′-H, 5′-H, J = 8 Hz). Found, %: N 3.82, 4.38. $C_{21}H_{27}NO_3$. Calculated, %: N 4.10.

***N*-(1-Isobutoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-(4-methylphenyl)acetamide (Vf).** Yield 47%, mp 187–188°C. ^{1}H NMR spectrum, δ, ppm: 0.84 d (6H, $CH\mathbf{Me}_2$, J = 6.8 Hz), 1.65–1.75 m (1H, $C\mathbf{H}Me_2$), 1.77 s (6H, 2-Me, 6-Me), 2.36 s (3H, 4′-Me), 2.78 d (2H, OCH_2), J = 6.4 Hz), 5.91 br.s (1H, NH), 6.23 s (2H, 3-H, 5-H), 7.16 d (2H, 2′-H, 6′-H, J = 8 Hz), 7.18 d (2H, 3′-H, 5′-H, J = 8 Hz). Found, %: N 4.33, 4.41. $C_{21}H_{27}NO_3$. Calculated, %: N 4.10.

***N*-(2,6-Dimethyl-4-oxo-1-pentyloxycyclohexa-2,5-dien-1-yl)-2-(4-methylphenyl)acetamide (Vg).** Yield 18%, mp 174–175°C. ^{1}H NMR spectrum, δ, ppm: 0.88–1.67 m (10H, $C_5H_{11}O$), 1.78 s (6H, 2-Me, 6-Me), 2.36 s (3H, 4′-Me), 3.01 t (1H, OCH_2), 3.49 s (1H, CH_2), 5.88 br.s (1H, NH), 6.23 s (2H, 3-H, 5-H), 7.16 d (2H, 2′-H, 6′-H, J = 8 Hz), 7.18 d (2H, 3′-H, 5′-H, J = 8 Hz). Found, %: N 3.74, 3.82. $C_{22}H_{29}NO_3$. Calculated, %: N 3.94.

***N*-(1-Cyclohexyloxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-(4-methylphenyl)acetamide (Vh).** Yield 35%, mp 210–211°C. ^{1}H NMR spectrum, δ, ppm: 1.20–1.61 m (10H, $C_6H_{11}O$), 1.82 s (6H, 2-Me, 6-Me), 2.36 s (3H, 4′-Me), 3.17–3.22 m (1H, OCH), 3.48 s (2H, CH_2), 5.87 s (1H, NH), 6.21 br.s (2H, 3-H, 5-H), 7.16 d (2H, 2′-H, 6′-H, J = 8 Hz), 7.18 d (2H, 3′-H, 5′-H, J = 8 Hz). Found, %: N 3.65, 4.08. $C_{23}H_{29}NO_3$. Calculated, %: N 3.81.

***N*-(1-Methoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-phenoxyacetamide (VIa).** Yield 68%, mp 114–115°C. ^{1}H NMR spectrum, δ, ppm: 1.86 s (6H, 2-Me, 6-Me), 3.03 s (3H, OMe), 4.46 s (2H, OCH_2), 6.32 s (2H, 3-H, 5-H), 6.95 br.s (1H, NH), 6.94–7.37 m (5H, Ph). Found, %: N 4.54, 4.41. $C_{17}H_{19}NO_4$. Calculated, %: N 4.65.

***N*-(1-Ethoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-phenoxyacetamide (VIb).** Yield 70%, mp 155–156°C. ^{1}H NMR spectrum, δ, ppm: 1.19 t (3H, $CH_2\mathbf{Me}$), 1.87 s (6H, 2-Me, 6-Me), 3.16 q (2H, OCH_2, J = 6.6 Hz), 4.56 s (2H, $PhOC\mathbf{H}_2$), 6.29 s (2H, 3-H, 5-H), 6.96–7.38 m (5H, Ph). Found, %: N 4.68, 4.75. $C_{18}H_{21}NO_4$. Calculated, %: N 4.44.

***N*-(2,6-Dimethyl-4-oxo-1-propoxycyclohexa-2,5-dien-1-yl)-2-phenoxyacetamide (VIc).** Yield 60%, mp 130–131°C. ^{1}H NMR spectrum, δ, ppm: 0.92 t (3H, $CH_2C\mathbf{H}_3$), 1.57 d.d (2H, $C\mathbf{H}_2CH_3$, J = 21.2, 7.2 Hz), 1.87 s (6H, 2-Me, 6-Me), 3.05 t (2H, OCH_2), 4.64 s (2H, $PhOC\mathbf{H}_2$), 6.29 s (2H, 3-H, 5-H), 6.97 br.s (1H, NH), 7.00–7.38 m (5H, Ph). Found, %: N 4.13, 3.95. $C_{19}H_{23}NO_4$. Calculated, %: N 4.25.

***N*-(1-Isopropoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-phenoxyacetamide (VId).** Yield 75%, mp 156–157°C. ^{1}H NMR spectrum, δ, ppm: 1.07 d (6H, $CH\mathbf{Me}_2$, J = 5.7 Hz), 1.89 s (6H, 2-Me, 6-Me), 3.59–3.63 m (1H, OCH), 4.43 s (2H, $PhOC\mathbf{H}_2$), 6.25 s (2H, 3-H, 5-H), 6.89 s (1H, NH), 6.94–7.36 m (5H, Ph). Found, %: N 4.06, 4.42. $C_{19}H_{23}NO_4$. Calculated, %: N 4.25.

***N*-(1-Butoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-phenoxyacetamide (VIe).** Yield 47%, mp 129–130°C. ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, $CH_2C\mathbf{H}_3$), 1.29–1.41 m (2H, $C\mathbf{H}_2Me$), 1.48–1.57 m (2H, $OCH_2C\mathbf{H}_2$), 1.86 s (6H, 2-Me, 6-Me), 3.08 t (2H, OCH_2), 4.45 s (2H, $PhOC\mathbf{H}_2$), 6.29 s (2H, 3-H, 5-H), 6.99 s (1H, NH), 6.96–7.38 m (5H, Ph). Found, %: N 5.60, 5.55. $C_{14}H_{21}NO_3$. Found, %: N 4.25, 4.10. $C_{20}H_{25}NO_4$. Calculated, %: N 4.08.

***N*-(1-Isobutoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-phenoxyacetamide (VIf).** Yield 38%, mp 159–160°C. ^{1}H NMR spectrum, δ, ppm: 0.9 d (6H, $CH\mathbf{Me}_2$, J = 6.4 Hz), 1.78–1.84 m (1H, $C\mathbf{H}Me_2$), 1.85 s (6H, 2-Me, 6-Me), 2.85 d (2H, OCH_2, J = 6.8 Hz), 4.47 s (2H, $PhOC\mathbf{H}_2$), 6.28 br.s (2H, 3-H, 5-H), 6.93 br.s (1H, NH), 6.97–7.38 m (5H, Ph).

Found, %: N 3.79, 3.95. $C_{20}H_{25}NO_4$. Calculated, %: N 4.08.

***N*-(2,6-Dimethyl-4-oxo-1-pentyloxycyclohexa-2,5-dien-1-yl)-2-phenoxyacetamide (VIg).** Yield 34%, mp 121–122°C. ^{1}H NMR spectrum, δ, ppm: 0.90–1.55 m (9H, $C_5H_{11}O$), 1.86 s (6H, 2-Me, 6-Me), 3.06–3.09 t (2H, OCH_2), 4.46 s (2H, PhOC**H**$_2$), 6.28 br.s (2H, 3-H, 5-H), 6.94 br.s (1H, NH), 6.97–7.37 m (5H, Ph). Found, %: N 4.28, 4.15. $C_{21}H_{27}NO_4$. Calculated, %: N 3.92.

***N*-(1-Cyclohexyloxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-2-phenoxyacetamide (VIh).** Yield 28%, mp 186–187°C. ^{1}H NMR spectrum, δ, ppm: 1.22–1.68 m (10H, $C_6H_{11}O$), 1.91 s (6H, 2-Me, 6-Me), 3.24–3.30 m (1H, OCH), 4.46 s (2H, PhOC**H**$_2$), 6.26 br.s (2H, 3-H, 5-H), 6.93 br.s (1H, NH), 6.97–7.38 m (5H, Ph). Found, %: N 4.63, 4.52. $C_{22}H_{27}NO_4$. Calculated, %: N 3.79.

(*E*)-*N*-(1-Methoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-3-phenylprop-2-enamide (VIIa). Yield 74%, mp 195–196°C. ^{1}H NMR spectrum, δ, ppm: 1.93 s (6H, 2-Me, 6-Me), 3.05 s (3H, OMe), 6.32 br.s (1H, NH), 6.35 s (2H, 3-H, 5-H), 6.45 d (1H, 3′-H, J = 15.6 Hz), 7.36–7.50 m (5H, Ph), 7.61 d (1H, 2′-H, J = 15.3 Hz). Found, %: N 5.05, 4.89. $C_{18}H_{19}NO_3$. Calculated, %: N 4.71.

(*E*)-*N*-(1-Ethoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-3-phenylprop-2-enamide (VIIb). Yield 80%, mp 199–200°C. ^{1}H NMR spectrum, δ, ppm: 1.19 t (3H, CH_2**Me**), 1.93 s (6H, 2-Me, 6-Me), 3.18 q (2H, OCH_2, J = 6.9 Hz), 6.21 s (1H, NH), 6.32 s (2H, 3-H, 5-H), 6.42 d (1H, 3′-H, J = 15.9 Hz), 7.38–7.49 m (5H, Ph), 7.61 d (1H, 2′-H, J = 15.9 Hz). Found, %: N 4.23, 4.67. $C_{19}H_{21}NO_3$. Calculated, %: N 4.50.

(*E*)-*N*-(2,6-Dimethyl-4-oxo-1-propoxycyclohexa-2,5-dien-1-yl)-3-phenylprop-2-enamide (VIIc). Yield 98%, mp 209–210°C. ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, CH_2C**H**$_3$), 1.58 d.d (2H, C**H**$_2CH_3$, J = 20.7, 7.2 Hz), 1.93 s (6H, 2-Me, 6-Me), 3.08 t (OCH_2), 6.19 br.s (1H, NH), 6.32 s (2H, 3-H, 5-H), 6.43 d (1H, 3′-H, J = 15.6 Hz), 7.38–7.50 m (5H, Ph), 7.63 d (1H, 2′-H, J = 15.6 Hz). Found, %: N 4.55, 4.48. $C_{20}H_{23}NO_3$. Calculated, %: N 4.30.

(*E*)-*N*-(1-Isopropoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-3-phenylprop-2-enamide (VIId). Yield 41%, mp 219–220°C. ^{1}H NMR spectrum, δ, ppm: 1.09 d (6H, CH**Me**$_2$, J = 6.3 Hz), 1.97 s (6H, 2-Me, 6-Me), 3.60–3.73 m (1H, OCH), 6.11 br.s (1H, NH), 6.30 s (2H, 3-H, 5-H), 6.43 d (1H, 3′-H, J = 15.6 Hz), 7.38–7.50 m (5H, Ph), 7.60 d (1H, 2′-H, J = 15.9 Hz). Found, %: N 4.14, 4.05. $C_{20}H_{23}NO_3$. Calculated, %: N 4.30.

(*E*)-*N*-(1-Butoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-3-phenylprop-2-enamide (VIIe). Yield 39%, mp 197–198°C. ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, (CH_2C**H**$_3$), 1.29–1.41 m (2H, C**H**$_2CH_3$), 1.48–1.57 m (2H, OCH_2C**H**$_2$), 1.97 s (6H, 2-Me, 6-Me), 3.08 t (2H, OCH_2), 6.11 br.s (1H, NH), 6.30 s (2H, 3-H, 5-H), 6.43 d (1H, 3′-H, J = 15.6 Hz), 7.38–7.50 m (5H, Ph), 7.60 d (1H, 2′-H, J = 15.9 Hz). Found, %: N 4.38, 4.25. $C_{21}H_{25}NO_3$. Calculated, %: N 4.13.

(*E*)-*N*-(1-Isobutoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-3-phenylprop-2-enamide (VIIf). Yield 26%, mp 216–217°C. ^{1}H NMR spectrum, δ, ppm: 0.92 d (6H, CH**Me**$_2$, J = 6.9 Hz), 1.77–1.85 m (1H, C**H**Me_2), 1.92 s (6H, 2-Me, 6-Me), 2.88 d (2H, OCH_2, J = 6.0 Hz), 6.15 br.s (1H, NH), 6.32 s (2H, 3-H, 5-H), 6.45 d (1H, 3′-H, J = 15.3 Hz), 7.38–7.50 m (5H, Ph), 7.63 d (1H, 2′-H, J = 15.9 Hz). Found, %: N 3.85, 4.10. $C_{21}H_{25}NO_3$. Calculated, %: N 4.13.

(*E*)-*N*-(2,6-Dimethyl-4-oxo-1-pentyloxycyclohexa-2,5-dien-1-yl)-3-phenylprop-2-enamide (VIIg). Yield 36%, mp 175–176°C. ^{1}H NMR spectrum, δ, ppm: 0.88–3.13 m (11H, $C_5H_{11}O$), 1.93 s (6H, 2-Me, 6-Me), 6.16 br.s (1H, NH), 6.32 s (2H, 3-H, 5-H), 6.43 d (1H, 3′-H, J = 15.6 Hz), 7.37–7.51 m (5H, Ph), 7.63 d (1H, 2′-H, J = 15.9 Hz). Found, %: N 3.75, 4.23. $C_{22}H_{27}NO_3$. Calculated, %: N 3.96.

(*E*)-*N*-(1-Cyclohexyloxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-3-phenylprop-2-enamide (VIIh). Yield 42%, mp 213–214°C. ^{1}H NMR spectrum, δ, ppm: 1.15–1.69 m (10H, $C_6H_{11}O$), 1.97 s (6H, 2-Me, 6-Me), 3.28–3.34 m (1H, OCH), 6.13 br.s (1H, NH), 6.29 br.s (2H, 3-H, 5-H), 6.43 d (1H, 3′-H, J = 15.6 Hz), 7.37–7.50 m (5H, Ph), 7.63 d (1H, 2′-H, J = 15.9 Hz). Found, %: N 3.64, 3.57. $C_{23}H_{27}NO_3$. Calculated, %: N 3.83.

***N*-(1-Methoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)benzamide (VIIIa).** Yield 70%, mp 150–151°C. ^{1}H NMR spectrum, δ, ppm: 1.94 s (6H, 2-Me, 6-Me), 3.08 s (3H, OMe), 6.36 s (2H, 3-H, 5-H), 6.65 br.s (1H, NH), 7.44–7.81 m (5H, Ph). Found, %: N 4.93, 5.25. $C_{16}H_{17}NO_3$. Calculated, %: N 5.16.

***N*-(1-Ethoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)benzamide (VIIIb).** Yield 56%, mp 189–190°C. ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H,

CH_2**Me**), 1.95 s (6H, 2-Me, 6-Me), 3.21 q (2H, OCH_2, J = 7.2 Hz), 6.34 s (2H, 3-H, 5-H), 6.62 s (1H, NH), 7.44–7.83 m (5H, Ph). Found, %: N 5.06, 5.39. $C_{16}H_{19}NO_3$. Calculated, %: N 5.12.

***N*-(2,6-Dimethyl-4-oxo-1-propoxycyclohexa-2,5-dien-1-yl)benzamide (VIIIc).** Yield 32%, mp 177–178°C. ^{1}H NMR spectrum, δ, ppm: 0.94 t (3H, CH_2**Me**), 1.58 d.d (2H, C**H**$_2$Me, J = 21, 6.9 Hz), 1.94 s (6H, 2-Me, 6-Me), 3.11 t (2H, OCH_2), 6.33 s (2H, 3-H, 5-H), 6.64 br.s (1H, NH), 7.44–7.83 m (5H, Ph). Found, %: N 4.57, 4.72. $C_{17}H_{21}NO_3$. Calculated, %: N 4.87.

N*-(1-Methoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-4-methylbenzamide (IXa).* Yield 91%, mp 143–144°C. ^{1}H NMR spectrum, δ, ppm: 1.93 s (6H, 2-Me, 6-Me), 2.41 s (3H, 4′-Me), 3.07 s (3H, OMe), 6.36 s (2H, 3-H, 5-H), 6.61 br.s (1H, NH), 7.25 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.71 d (2H, 3′-H, 5′-H, J = 8.1 Hz). Found, %: N 5.20, 5.16. $C_{17}H_{19}NO_3$. Calculated, %: N 4.91.

N*-(1-Ethoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-4-methylbenzamide (IXb).* Yield 62%, mp 181–182°C. ^{1}H NMR spectrum, δ, ppm: 1.24 t (3H, CH_2**Me**), 1.94 s (6H, 2-Me, 6-Me), 2.41 s (3H, 4′-Me), 3.21 q (2H, OCH_2, J = 7.2 Hz), 6.33 s (2H, 3-H, 5-H), 6.58 br.s (1H, NH), 7.26 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.71 d (2H, 3′-H, 5′-H, J = 8.7 Hz). Found, %: N 4.32, 4.45. $C_{18}H_{21}NO_3$. Calculated, %: N 4.68.

***N*-(2,6-Dimethyl-4-oxo-1-pentyloxycyclohexa-2,5-dien-1-yl)-4-methylbenzamide (IXg).** Yield 63%, mp 126–127°C. ^{1}H NMR spectrum, δ, ppm: 0.88–3.13 m (11H, $C_5H_{11}O$), 1.93 s (6H, 2-Me, 6-Me), 2.41 s (3H, 4′-Me), 6.33 s (2H, 3-H, 5-H), 6.59 br.s (1H, NH), 7.26 d (2H, 2′-H, 6′-H, J = 6.9 Hz), 7.71 d (2H, 3′-H, 5′-H, J = 7.8 Hz). Found, %: N 4.25, 4.36. $C_{21}H_{27}NO_3$. Calculated, %: N 4.10.

3-Chloro-*N*-(2,5-dichloro-1-methoxy-3,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)-4-methoxybenzamide (XIa). Yield 78%, mp 214–215°C. ^{1}H NMR spectrum, δ, ppm: 2.13 s (3H, 3-Me), 2.17 s (3H, 6-Me), 3.11 s (3H, 1-MeO), 3.96 s (3H, 4′-MeO), 6.56 br.s (1H, NH), 6.97 d (1H, 5′-H, J = 8.4 Hz), 7.69 d.d (1H, 6′-H, ^3J = 8.4, ^4J = 2.4 Hz), 7.79 d (1H, 2′-H, ^4J = 2.4 Hz). Found, %: Cl 26.10, 26.06; N 3.55, 3.64. $C_{17}H_{16}Cl_3NO_4$. Calculated, %: N 3.46; Cl 26.28.

2,6-Dichloro-3,4,5-trimethoxy-*N*-(2,3,5-trichloro-1-methoxy-6-methyl-4-oxocyclohexa-2,5-dien-1-yl)-benzamide (XIb). Yield 74%, mp 242–243°C. ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, 6-Me), 3.13 s (3H, 1-MeO), 3.90 s (6H, 3′-Me, 5′-MeO), 3.95 s (3H, 4′-MeO), 6.36 br.s (1H, NH). Found, %: Cl 34.28, 34.36; N 2.55, 2.64. $C_{18}H_{16}Cl_5NO_6$. Calculated, %: Cl 34.12; N 2.70.

***N*-2-Bromo-(2,3-dibromo-1-methoxy-6-methyl-4-oxocyclohexa-2,5-dien-1-yl)-3,4,5-trimethoxybenzamide (XIc).** Yield 69%, mp 178–180°C. ^{1}H NMR spectrum, δ, ppm: 2.19 s (3H, 6-Me), 3.22 s (3H, 1-MeO), 3.88 s (3H, 3′-MeO), 3.89 s (3H, 4′-MeO), 3.92 s (3H, 5′-MeO), 7.06 br.s (1H, NH), 7.15 s (1H, 6′-H). Found, %: Br 31.42, 31.53; N 2.86, 2.91. $C_{18}H_{19}Br_2NO_6$. Calculated, %: Br 31.64; N 2.77.

** Compounds **IXa** and **IXb** were synthesized by I.L. Marchenko.

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