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Activated Sterically Strained C=N Bond in *N*-Substituted *p*-Quinone Mono- and Diimines: XV.* Synthesis, Structure, and Reactions with Alcohols of *N*-Carbamoyl-1,4-benzoquinone Imines

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Abstract—The reaction of 4-aminophenols with *N*-nitrourea or with sodium cyanate in acetic acid gave the corresponding 4-ureidophenols which were oxidized to *N*-carbamoyl-1,4-benzoquinone imines, substituted *N*-(4-oxocyclohexa-2,5-dien-1-ylidene)ureas. *N*-(2,6-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)urea possessing activated sterically strained C=N bond reacted with alcohols to afford *N*-(1-alkoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dienyl)ureas.

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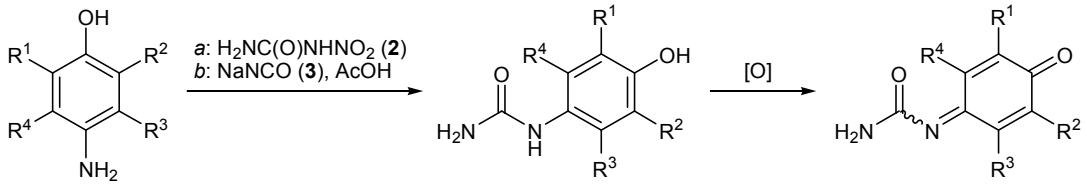
We previously synthesized *N*-aryl(alkyl)aminocarbonyl-1,4-benzoquinone imines [2, 3] and showed that the presence of an NH group in their molecules considerably affects their reactivity [3]. The goal of the present work was to synthesize new N-substituted 1,4-benzoquinone imines containing a carbamoyl group on the nitrogen atom. The most appropriate starting compounds for the synthesis of *N*-carbamoyl-1,4-benzoquinone imines are *N*-(4-hydroxyphenyl)-ureas which can be obtained by reaction of the corresponding aromatic amines with sodium cyanate in acetic acid [4] or by transamination of urea [5–7] or nitrourea [8, 9] with various alkyl(aryl)amines. These reactions are commonly carried out in water [5, 8] or ethanol [9] in the presence of acetic acid or HCl [5].

The most efficient method of synthesis of *N*-(4-hydroxyphenyl)urea (**4a**) was the reaction of 4-aminophenol (**1a**) with nitrourea **2** according to the procedure described in [9] (Scheme 1, *a*). The best way to synthesize 1-(4-hydroxyphenyl)ureas **4b**–**4g** was the reaction of 4-aminophenols **1b**–**1g** with sodium cyanate (**3**) in acetic acid [4] (Scheme 1, *b*), which ensured higher yields and was less laborious. Ureas **4a**–**4g** were readily oxidized with lead(IV) acetate,

Scheme 1.



1a–1g **4a–4g** **5a–5g**

$R^1 = R^2 = R^3 = R^4 = H$ (**a**); R^1 = Me, $R^2 = R^3 = R^4 = H$ (**b**); $R^1 = R^2 = R^3 = H$, R^4 = Me (**c**); $R^1 = R^4$ = Me, $R^2 = R^3 = H$ (**d**); $R^1 = R^3$ = Me, $R^2 = R^4 = H$ (**e**); $R^1 = R^2 = H$, $R^3 = R^4$ = Me (**f**); $R^1 = R^2$ = Me, $R^3 = R^4 = H$ (**g**).

* For communication XIV, see [1].

manganese(IV) oxide, and silver(I) oxide. However, the oxidation with $Pb(OAc)_4$ and MnO_2 gave yellow noncrystallizable oily substances which were difficult to purify, and the desired quinone imines were detected only by TLC. We succeeded in isolating crystalline quinone imines **5a**–**5g** only when ureas **4a**–**4g** were oxidized with Ag_2O in chloroform (Scheme 1).

The ^{1}H NMR spectra of **4a**–**4g** contained signals from the NH, NH_2, and OH protons at δ 7.20–8.17, 5.56–5.73, and 8.04–9.06 ppm, respectively. Methyl protons in **4b**–**4g** resonated as singlets at δ 2.03–2.09 ppm, and signals from the aromatic protons were located in the region δ 6.42–7.23 ppm. Compounds **5a**–**5g** displayed in the ^{1}H NMR spectra a broadened singlet at δ 5.24–5.89 due to NH_2 protons, methyl proton signals δ 2.05–2.23 ppm, and signals from protons in the quinoid ring at δ 6.52–7.26 ppm. In the ^{1}H NMR spectrum of **5f**, protons on the quinoid ring gave rise to a broadened singlet, indicating fast *Z*,*E* isomerization on the NMR time scale.

N-Substituted 1,4-benzoquinone imines with substituents in both *ortho* positions with respect to the imino carbon atom are known to readily undergo nucleophilic addition to the C=N bond [10–13]. It was presumed that activation of the C=N bond is related to steric strain in the C=N–X fragment due to the presence of *ortho* substituents. We introduced the term "activated sterically strained C=N bond" and found that such C=N bond is present in *N*-arenesulfonyl-1,4-benzoquinone imines provided that the C=N–X bond angle is larger than 130° [14, 15]. The C=N bond in *N*-acyl analogs becomes sterically strained and activated when the C=N–X bond angle increases or the C=N bond is twisted and the quinoid ring loses its planar structure, which may be estimated by the CCNC torsion angle and deviations of the C^1–C^6 atoms from the quinoid ring plane [1].

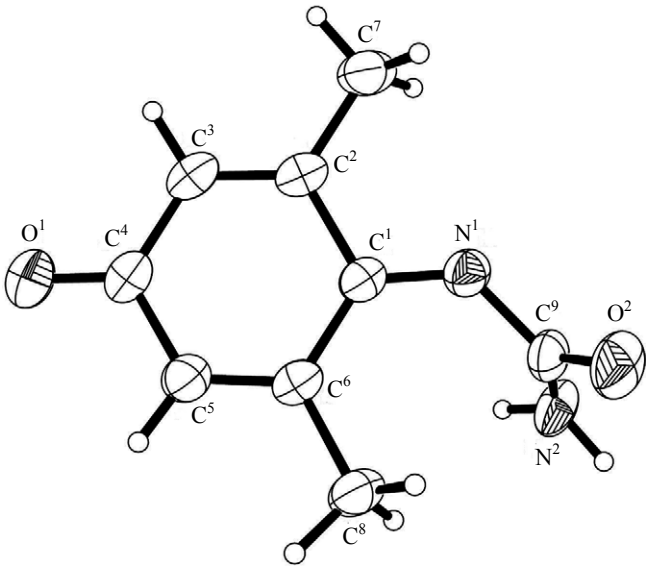
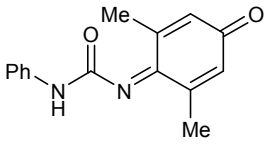


Fig. 1. Structure of the molecule of *N*-(2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)urea (**5f**) according to the X-ray diffraction data.

The structure of quinone imine **5f** was determined by X-ray analysis (Fig. 1). The $C^1N^1C^9$ bond angle in molecule **5f** is 129.3(1)°, which is considerably larger than the average value for many quinone imines (124°) [16] but slightly smaller than 130°. The corresponding angle in the molecule of previously reported *N*-phenylcarbamoyl derivative **5h** is 126.2(4)° (hereinafter, the X-ray diffraction data for **5h** taken from [2] are used).



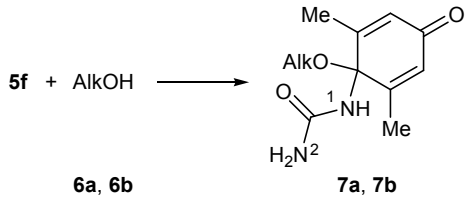
5h

The torsion angle $C^2C^1N^1C^9$ in **5f** is –0.96° against –2.77° in **5h**, and the C^1–C^6 fragment in **5f** and **5h** may be regarded as planar with an accuracy of 0.04 and 0.02 Å, respectively, which is typical of quinone imines having no *ortho* substituents with respect to the imino group [1]. The quinoid ring in **5f** is less planar due to *cis* deformation implying that the C^2, C^3, C^5, and C^6 atoms lie in one plane within 0.01 Å while the C^1 and C^4 atoms deviate from that plane by –0.107(2) and –0.061(2), and O^1 and N^1, by –0.147(3) and –0.320(4) Å, respectively. The dihedral angle between the C^1–C^6 plane and the urea fragment ($N^1O^2N^2C^9$) is 76.92(5)° in **5f** and 87.0(1)° in **5h**. The steric strain in the C=N–C fragment of **5f** and **5h** can also be judged by the presence of short intramolecular contacts $C^9 \cdots C^8$ {2.91 (**5f**) and 2.86 Å (**5h**); the sum of the van der Waals radii is 3.42 Å [17]} and $C^9 \cdots H^{8C}$ {2.69 (**5f**) and 2.56 Å (**5h**); the sum of the van der Waals radii is 2.87 Å [17]}.

The above data suggest some steric strain in the C=N–X fragment of molecule **5f**; therefore, addition of alcohols to the C=N bond of **5f** may be expected. In fact, as with other *N*-substituted 1,4-benzoquinone imines [1, 2, 10–15], alcohol addition products to the C=N bond (compounds **7a** and **7b**) were obtained only from *N*-carbamoyl derivative **5f** containing methyl groups in both *ortho* positions with respect to the imino carbon atom (Scheme 2). In the ^{1}H NMR spectra of **7a** and **7b** we observed a singlet at δ 1.82–1.84 ppm due to methyl groups in positions *2* and *6*, a broadened

singlet at δ 6.10–6.13 ppm due to 3-H and 5-H, and a broadened singlet from the NH proton at δ 6.76–6.78 ppm; compound **7a** also showed a singlet at δ 2.89 ppm from the methoxy group.

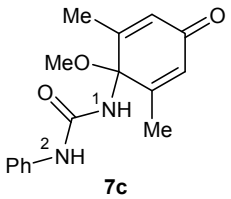
Scheme 2.



6a, **6b** **7a**, **7b**

Alk = Me (**a**), Et (**b**).

As we showed previously [3], analogous reactions of *N*-arylcarbamoyl-1,4-benzoquinone imines with alcohols afforded not only the corresponding 1,2-adducts but also cyclization products of the latter, 7a-alkoxy-3-aryl-3a,7-dimethyl-3a,7a-dihydro-1*H*-benzimidazole-2,5(3*H*,4*H*)-diones. However, we failed to obtain analogous cyclization products from compounds **7a** and **7b**. In order to rationalize this difference we performed quantum chemical calculations of geometric parameters of compound **7a** and 1,2-addition product **7c** reported in [3].



7c

The most favorable conformations of molecules **7a** and **7c** are characterized by spatial proximity of the N^2H_2 (N^2H) group and $C^2=C^3$ double bond (Fig. 2): the distance $N^2 \cdots C^2$ is 3.340 in **7a** and 3.068 Å in **7c**. This conformation is favorable for donor–acceptor interaction between the $\pi(C^2=C^3)$ and $\sigma^*(N^2–H)$ orbitals, which may be responsible for the subsequent cyclization. The energy of this interaction in molecule **7c** is 15.36 kJ/mol against 2.99 kJ/mol in **7a**. The lower energy for **7a** is related to the larger energy gap between the corresponding orbitals due to considerably higher energy of the $\sigma^*(N^2–H)$ orbital of **7a**. The $\sigma^*(N^2–H)$ energy of **7c** is reduced due to the presence of a phenyl substituent on the N^2 atom.

These results suggest that the cyclization of the alcohol addition products to the C=N bond of *N*-carbamoyl-1,4-benzoquinone imines should be favored by introduction of an aryl substituent into the CON^2H group to reduce the $\sigma^*(N^2–H)$ energy.

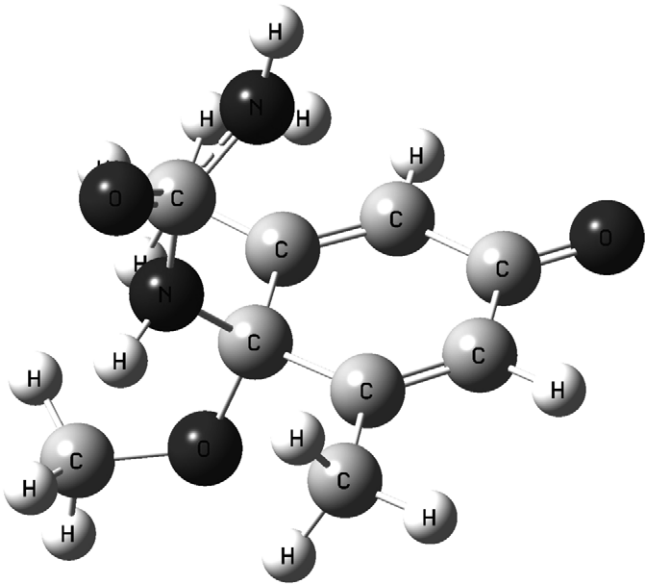


Fig. 2. Structure of the molecule of *N*-(1-methoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)urea (**7a**) according to quantum chemical calculations.

EXPERIMENTAL

The ^1H NMR spectra were measured on a Varian VXR-300 spectrometer at 300 MHz relative to TMS. The IR spectra were recorded in KBr on a UR-20 spectrometer. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates; samples were applied from solutions in chloroform, benzene–hexane (10:1) was used as eluent, and spots were visualized under UV light.

Quantum chemical calculations were performed using Gaussian 03 software package [18]. The molecular structures were optimized for the gas phase at the DFT level with B3LYP functional [19–24] and standard 6-31+G(*d*) basis set [25, 26]. Conjugative and hyperconjugative interactions were included by the natural bond orbital (NBO) analysis [27] using NBO 5.0 software [28].

The X-ray diffraction data for compound **5f** were obtained from a 0.45×0.25×0.15-mm single crystal on an Oxford Diffraction diffractometer (MoK_α radiation, λ 0.71073 Å, graphite monochromator, Sapphire 3 CCD detector). The structure was solved and refined using SHELX-97 software package [29]. Monoclinic crystal system, space group $P2_1/c$; $C_9H_{10}N_2O_2$, *M* 178.19 g/mol; unit cell parameters [293(2) K]: a = 4.6965(2), b = 12.2440(5), c = 15.6104(6) Å; β = 96.517(4)°; V = 891.86(6) $Å^3$; Z = 4; d_{calc} = 1.327 g×cm^{-3}; $F(000)$ = 376; μ = 0.096 mm^{-1}; transmission

coefficients T_{min}/T_{max} 0.9581/0.9858; $-5 \le h \le 5$, $-15 \le k \le 15$, $-19 \le l \le 19$; ω-scanning, $3.04 \le \theta \le 25.99°$. Total of 11961 reflection intensities were measured, 1724 of which were independent (R_{int} = 0.0228), and 1407 reflections were characterized by $I_{hkl} > 2\sigma(I)$; completeness 98.5%. Hydrogen atoms were localized by difference syntheses, and their positions were refined according to the riding model, except for the NH hydrogen atoms which were refined in isotropic approximation with fixed thermal parameters. The full matrix refinement against F^2 was terminated at R_F = 0.0344, wR^2 = 0.0972 [reflections with $I > 2\sigma(I)$]; R_F = 0.0441, wR^2 = 0.1040 (all independent reflections); goodness of fit 0.995; $\Delta\rho_{min}/\Delta\rho_{max}$ –0.118/0.134 $\bar{e}$/Å^3. The coordinate of atoms and complete tables of bond lengths and bond angles for compound **5f** were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 1025982).

N*-(4-Hydroxyphenyl)ureas 4a–4g (general procedure*).** *a*. *N*-Nitrourea [30], 1.53 g (14.6 mmol), was added to a mixture of 12 mmol of aminophenol **1a**–**1g** and 15–20 mL of water. The mixture was heated for 45–60 min on a water bath in a flask equipped with a reflux condenser which was connected to a bubble counter. When gas no longer evolved, the precipitate was filtered off and recrystallized from water.

b. A solution of 1 g (15.4 mmol) of sodium cyanate (**3**) in 10 mL of water was added under stirring at 20°C to a solution of 7.7 mmol of aminophenol **1a**–**1g** in a mixture of 5 mL of glacial acetic acid and 10 mL of water. The first part of NaOCN solution, 3–4 mL, was added until a solid separated, and the remaining part was added under vigorous stirring. The mixture was then stirred for 10–15 min and left to stand for 2–3 h at room temperature. The precipitate was filtered off, washed with water, and dried in air.

***N*-(4-Hydroxyphenyl)urea (4a).** Yield 50%, mp 171–173°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.63 d (2H, 2-H, 6-H, J = 9 Hz), 7.15 d (2H, 3-H, 5-H, J = 9 Hz), 5.68 br.s (2H, NH_2), 8.17 s (1H, NH), 8.96 br.s (1H, OH). Found, %: N 17.32, 18.10. $C_7H_8N_2O_2$. Calculated, %: N 18.41.

***N*-(4-Hydroxy-3-methylphenyl)urea (4b).** Yield 78%, mp 194–195°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.07 s (3H, 3-Me), 5.67 br.s (2H, NH_2), 6.63 d (1H, 5-H, J = 9 Hz), 6.97 d.d (1H, 6-H, J = 1.8, 9.0 Hz), 7.06 d (1H, 2-H, J = 1.8 Hz), 8.11 s (1H, NH), 8.83 br.s (1H, OH). Found, %: N 17.25, 15.86. $C_8H_{10}N_2O_2$. Calculated, %: N 16.86.

***N*-(4-Hydroxy-2-methylphenyl)urea (4c).** Yield 81%, mp 223–225°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (3H, 2-Me), 5.73 br.s (2H, NH_2), 6.51 d.d (1H, 5-H, J = 1.8, 9 Hz), 6.56 d (1H, 3-H, J = 1.8 Hz), 7.23 d (1H, 6-H, J = 9 Hz), 7,47 s (1H, NH), 8.97 br.s (1H, OH). Found, %: N 17.29, 16.27. $C_8H_{10}N_2O_2$. Calculated, %: N 16.86.

***N*-(4-Hydroxy-2,3-dimethylphenyl)urea (4d).** Yield 78%, mp 182–183°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.03 s (3H, 2-Me), 2.04 s (3H, 3-Me), 5.62 br.s (2H, NH_2), 6.55 d (1H, 5-H, J = 9 Hz), 6.94 d (1H, 6-H, J = 9 Hz), 7.47 s (1H, NH), 8.98 br.s (1H, OH). Found, %: N 15.12, 15.23. $C_9H_{12}N_2O_2$. Calculated, %: N 15.55.

***N*-(4-Hydroxy-2,5-dimethylphenyl)urea (4e).** Yield 85%, mp 223–224°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.03 s (3H, 2-Me), 2.05 s (3H, 5-Me), 5.68 br.s (2H, NH_2), 6.54 d (1H, 3-H, J = 9 Hz), 7.13 d (1H, 6-H, J = 9 Hz), 7.39 s (1H, NH), 8.83 br.s (1H, OH). Found, %: N 15.43, 15.12. $C_9H_{12}N_2O_2$. Calculated, %: N 15.55.

***N*-(4-Hydroxy-2,6-dimethylphenyl)urea (4f).** Yield 71%, mp 245–247°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.06 s (6H, 2-Me, 6-Me), 5.56 br.s (2H, NH_2), 6.42 s (2H, 3-H, 5-H), 7.20 s (1H, NH), 9.06 br.s (1H, OH). Found, %: N 14.84, 15.27. $C_9H_{12}N_2O_2$. Calculated, %: N 15.55.

***N*-(4-Hydroxy-3,5-dimethylphenyl)urea (4g).** Yield 64%, mp 190–191°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (6H, 3-Me, 5-Me), 5.64 s (2H, NH_2), 6.90 s (2H, 2-H, 6-H), 7.76 s (1H, NH), 8.04 s (1H, OH). Found, %: N 16.47, 16.08. $C_9H_{12}N_2O_2$. Calculated, %: N 15.55.

N*-Carbamoyl-1,4-benzoquinone imines 5a–5g (general procedure*).** Silver oxide, 1.54 g (6.8 mmol), was added to a mixture of 6.2 mmol of *N*-(4-hydroxyphenyl)urea **4a**–**4g** and 30–35 mL of chloroform, and the mixture was stirred for 1.5 h (**4a**, **4g**) or 2–3 h (**4b**–**4e**). The mixture was then filtered, the filtrate was evaporated, and the yellow solid was recrystallized from benzene.

***N*-(4-Oxocyclohexa-2,5-dien-1-ylidene)urea (5a).** Yield 40%, mp 90–91°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.41 br.s (1H, NH_2), 5.83 br.s (1H, NH_2), 6.61 d.d (1H, 6-H, J = 2.4, 12.9 Hz), 6,70 d.d (1H, 2-H, J = 2.4, 12.9 Hz), 7.10 d.d (1H, 5-H, J = 2.4, 12.9 Hz), 7.26 d.d (1H, 3-H, J = 2.4, 12.9 Hz). Found, %: N 17.86, 17.69. $C_7H_6N_2O_2$. Calculated, %: N 18.66.

***N*-(3-Methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-urea (5b).** Yield 45%, mp 121–122°C. ^{1}H NMR spec-

trum ($CDCl_3$), δ, ppm: *Z* isomer (60%): 2.05 br.s (3H, 3-Me), 5.41 br.s and 5.89 br.s (1H each, NH_2), 6.67 d (1H, 5-H, *J* = 9.3 Hz), 7.03 d.d (1H, 6-H, *J* = 2.1, 9.3 Hz), 7.05 br.s (1H, 2-H); *E* isomer (40%): 2.07 br.s (3H, 3-Me), 5.41 br.s and 5.89 br.s (1H each, NH_2), 6.58 d (1H, 5-H, *J* = 9.3 Hz), 6.90 br.s (1H, 2-H), 7.20 d.d (1H, 6-H, *J* = 2.1, 9.3 Hz). Found, %: N 17.64, 16.35. $C_8H_8N_2O_2$. Calculated, %: N 17.06.

***N*-(2-Methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-urea (5c).** Yield 42%, mp 137–138°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.18 d (3H, 2-Me, *J* = 1.5 Hz), 5.32 br.s and 5.73 br.s (1H each, NH_2), 6.53 d.d (1H, 5-H, *J* = 2.1, 9.3 Hz), 6.54 br.s (1H, 3-H), 7.18 d (1H, 6-H, *J* = 9.3 Hz). Found, %: N 16.49, 16.71. $C_8H_8N_2O_2$. Calculated, %: N 17.06.

***N*-(2,3-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)urea (5d).** Yield 40%, mp 129–130°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.05 s (3H, 2-Me), 2.16 s (3H, 3-Me), 5.24 br.s and 5.45 br.s (1H each, NH_2), 6.53 d (1H, 5-H, *J* = 9 Hz), 7.13 d (1H, 6-H, *J* = 9 Hz). Found, %: N 15.57, 15.61. $C_9H_{10}N_2O_2$. Calculated, %: N 15.72.

***N*-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)urea (5e).** Yield 55%, mp 159–160°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.01 d (3H, 2-Me, *J* = 1.8 Hz), 2.15 d (3H, 5-Me, *J* = 1.8 Hz), 5.32 br.s and 5.81 br.s (1H each, NH_2), 6.52 s (1H, 3-H), 6.97 s (1H, 6-H). Found, %: N 15.23, 15.42. $C_9H_{10}N_2O_2$. Calculated, %: N 15.72.

***N*-(2,6-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)urea (5f).** Yield 40%, mp 173–174°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.23 s (6H, 2-Me, 6-Me), 5.54 br.s (2H, NH_2), 6.40 br.s (2H, 3-H, 5-H). Found, %: N 14.87, 14.96. $C_9H_{10}N_2O_2$. Calculated, %: N 15.72.

***N*-(3,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)urea (5g).** Yield 45%, mp 139–140°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.05 s (6H, 3-Me, 5-Me), 5.37 br.s and 5.78 br.s (1H each, NH_2), 6.83 br.s (1H, 6-H), 7.01 br.s (1H, 2-H). Found, %: N 15.58, 16.37. $C_9H_{10}N_2O_2$. Calculated, %: N 15.72.

Reaction of quinone imine 5f with alcohols 6a and 6b (*general procedure*). A solution of 2 mmol of quinone imine **5f** in 8 mL of anhydrous methanol (**6a**) or ethanol (**6b**) was heated under reflux with protection from atmospheric moisture until the mixture turned colorless. The reaction completion was checked by TLC. The mixture was cooled, and the precipitate was filtered off and washed with the corresponding alcohol.

***N*-(1-Methoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)urea (7a).** Yield 43%, mp 185–186°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.82 br.s (6H, 2-Me, 6-Me), 2.89 br.s (3H, MeO), 5.62 br.s (2H, NH_2), 6.13 br.s (2H, 3-H, 5-H), 6.76 br.s (1H, NH). Found, %: N 14.86, 15.04. $C_8H_{10}N_2O_3$. Calculated, %: N 15.39.

***N*-(1-Ethoxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)urea (7b).** Yield 55%, mp 156–157°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.07–1.11 t (3H, $CH_2C\mathbf{H}_3$), 1.84 br.s (6H, 2-Me, 6-Me), 3.01–3.05 d.d (2H, $C\mathbf{H}_2CH_3$), 5.58 br.s (2H, NH_2), 6.10 br.s (2H, 3-H, 5-H), 6.78 br.s (1H, NH). Found, %: N 12.05, 12.34. $C_{11}H_{16}N_2O_3$. Calculated, %: N 12.49.

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