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Reaction of *N*-Arylcarbamoyl-1,4-benzoquinone Imines with Sodium Azide

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Abstract—*N*-Arylcarbamoyl-1,4-benzoquinone imines reacted with sodium azide in completely regioselective fashion according to the 1,4-addition pattern with formation of 1-(3-azido-4-hydroxyphenyl)-3-arylureas. The reaction of *N*-arylcarbamoyl-2,6-dichloro-3,5-dimethyl-1,4-benzoquinone imines with sodium azide afforded *N*-arylcarbamoyl-2,6-diazido-3,5-dimethyl-1,4-benzoquinone imines as a result of nucleophilic substitution of the chlorine atoms.

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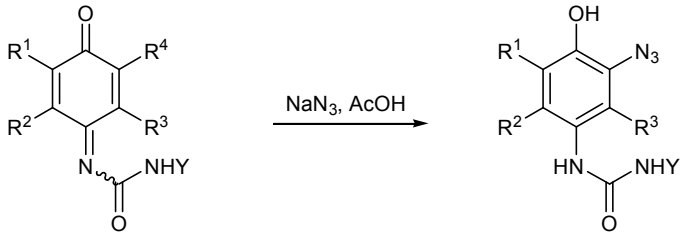
N-Substituted 1,4-benzoquinone imines are known to fairly readily react with sodium arenesulfinates, hydrogen halides, potassium thiocyanate, and sodium azide. Sodium azide is a moderately hard nucleophile occupying an intermediate position between arenesulfinic acids and hydrogen chloride [1]. In reactions with *N*-substituted 1,4-quinone imines having free position *2* and/or *6*, sodium azide behaves similarly to hydrogen chloride, i.e., the reaction follows the 1,4-addition scheme [2–6]. 1,2-Addition products were isolated in reactions of *N*-arenesulfonyl(acyl)-2,3,5,6-tetrachloro- (or 2,6-dichloro-3,5-dimethyl)-1,4-benzoquinone imines [5–6], whereas *N*-arenesulfonyl-2,3,5,6-tetrachloro(or 2,6-dichloro-3,5-dimethyl)-1,4-benzoquinone imines also reacted via nucleophilic substitution of the chlorine atoms in positions *2* and *6* by azido groups [5]. *N*-Arylcarbamoyl-1,4-benzoquinone imines synthesized previously [7] may be expected to give rise to new paths in the reaction with sodium azide, for these substrates are classed, on the one hand, with *N*-substituted 1,4-benzoquinone imines and, on the other, with urea derivatives.

The reactions of *N*-arylcarbamoyl-1,4-benzoquinone imines **I**–**VIII** with sodium azide were carried out in acetic acid using 2 equiv of the nucleophile. As a result, we isolated the corresponding 1,4-addition products, 1-(3-azido-4-hydroxyphenyl)-3-arylureas **IX**–**XV** (Scheme 1). *N*-Arylcarbamoyl-2,6-dimethyl-1,4-benzoquinone imines **VIIIa** and **VIIIb** reacted with sodium azide to give only the reduction products, 1-(4-hydroxy-3,5-dimethylphenyl)-3-arylureas which were reported previously [7]. The quinone imine

Scheme 1.



Ia, **Ib**, **IIa**, **IIb**, **IIIa**, **IIIc**, **IIId**, **IVa**, **IVb** **Va**, **VIa**, **VIIa**, **VIIb**, **VIIIa**, **VIIIb**

IXa, **IXb**, **Xa**, **Xb**, **XIa**, **XIc**, **XId** **XIIa**, **XIIb**, **XIIIa**, **XIVa**, **XVa**, **XVb**

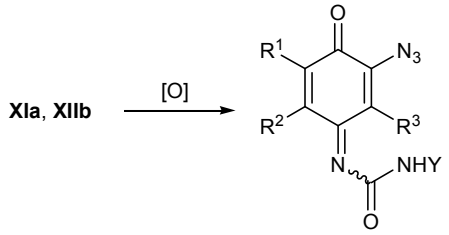
I, $R^1 = R^2 = R^3 = R^4 = H$; **II**, $R^1 = Me$, $R^2 = R^3 = R^4 = H$; **III**, $R^1 = R^2 = Me$, $R^3 = R^4 = H$; **IV**, $R^1 = R^3 = Me$, $R^2 = R^4 = H$; **V**, $R^1 =$ *i*-Pr, $R^3 = Me$, $R^2 = R^4 = H$; **VI**, $R^1 = Me$, $R^3 =$ *i*-Pr, $R^2 = R^4 = H$; **VII**, $R^1 = R^4 = H$, $R^2 = R^3 = Me$; **VIII**, $R^1 = R^4 = Me$, $R^2 = R^3 = H$; **IX**, $R^1 = R^2 = R^3 = H$; **X**, $R^1 = Me$, $R^2 = R^3 = H$; **XI**, $R^1 = R^2 = Me$, $R^3 = H$; **XII**, $R^1 = R^3 = Me$, $R^2 = H$; **XIII**, $R^1 =$ *i*-Pr, $R^2 = H$, $R^3 = Me$; **XIV**, $R^1 = Me$, $R^2 = H$, $R^3 =$ *i*-Pr; **XV**, $R^1 = H$, $R^2 = R^3 = Me$; **XVI**, Y=Ph (**a**), 4-MeC_6H_4 (**b**), 3-MeC_6H_4 (**c**), 3-ClC_6H_4 (**d**).

reduction products were present in the reaction mixtures in almost all cases. Pure 1-(3-azido-4-hydroxyphenyl)-3-arylureas **IX**–**XI** and **XV** were isolated by successive recrystallizations, but we failed to separate product mixtures obtained from 2,5-dialkyl-substituted quinone imines **IV**–**VI**, and the structure of compounds **XII**–**XIV** was determined on the basis of ^{1}H NMR and IR data.

Compounds **Xa** and **Xb** displayed in the ^{1}H NMR spectra two doublets from 2-H (δ 6.85–6.87 ppm) and 6-H (δ 7.19 ppm), and the spectra of **XI**–**XV** contained a singlet at δ 6.60–7.24 ppm from the aromatic proton in the aminophenol fragment. In the IR spectra of the addition products we observed an absorption band at 2110–2180 cm^{-1}, which is typical of stretching vibrations of azido group.

1-(3-Azido-4-hydroxyphenyl)-3-arylureas **XIa** and **XIIb** were oxidized to *N*-arylcarbamoyl-2-azido-1,4-benzoquinone imines **XVI** and **XVII**, respectively, with lead tetraacetate in acetic acid (Scheme 2). Insofar as we failed to isolate compound **XIIb** as individual substance (it contained the corresponding reduced form), its oxidation and subsequent recrystallization gave a product which also contained two compounds, 1-(2-azido-2,5-imethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-(4-methylphenyl)urea (**XVII**) and initial quinone imine **IVb** which could not be separated.

Scheme 2.



XVI, **XVII**

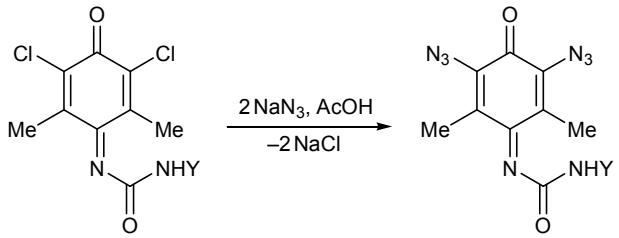
XVI, $R^1 = R^2 = Me$, $R^3 = H$, Y = Ph; **XVII**, $R^1 = R^3 = Me$, $R^2 = H$, Y = 4-MeC_6H_4.

We previously found [5] that *N*-substituted 2-azido-4-aminophenols (1,4-addition products of sodium azide to *N*-substituted 1,4-benzoquinone imines) on heating in acetic acid undergo intramolecular redox transformation with elimination of gaseous nitrogen and formation of *N*-substituted 2-amino-1,4-benzoquinone imines. However, no intramolecular redox reaction typical of *N*-arenesulfonyl derivatives was observed even on prolonged heating of 1-(3-azido-4-hydroxyphenyl)-3-arylureas **IX**–**XV** in boiling acetic acid. Presumably, the redox potential of compounds **IX**–**XV** is higher than that of *N*-arenesulfonyl analogs.

According to published data, *N*-arenesulfonyl-2,6-dichloro-3,5-dimethyl(or 2,3,5,6-tetrachloro)-1,4-benzoquinone imines possessing an activated sterically strained C=N bond can react with sodium azide along two pathways. The reaction at room temperature follows the 1,2-addition pattern, and subsequent $C^2 \rightarrow C^4$ migration of the azido group is possible with simultaneous replacement of the halogen atom in position *2* of the quinoid fragment by azido group. When the reaction is carried out at elevated temperature, both halogen atoms in positions *2* and *6* are replaced by azido groups [5].

In continuation of our studies on the reactivity of 1,4-benzoquinone imines with sterically shielded nitrogen atom and activated sterically strained C=N bond [5, 8], *N*-arylcarbamoyl-2,6-dichloro-3,5-dimethyl-1,4-benzoquinone imines **XVIIIa** and **XVIIIb** were reacted with sodium azide at a reactant ratio of 1:2 in acetic acid at room temperature. These reactions afforded *N*-arylcarbamoyl-2,6-diazido-3,5-dimethyl-1,4-benzoquinone imines **XIXa** and **XIXb** (Scheme 3). The ^{1}H NMR spectra of quinone imines **XIXa** and **XIXb** contained a singlet from protons in the two methyl groups, which indicated their equivalence. In the IR spectrum of **XIXa** and **XIXb**, characteristic absorption band due to stretching vibrations of the azido group was located at 2110–2180 cm^{-1}. The elemental analyses and Beilstein test showed the absence of halogen in molecules **XIXa** and **XIXb**. The product structure suggests that nucleophilic substitution of chlorine in positions *2* and *6* of the quinoid fragment in *N*-arylcarbamoyl-2,6-dichloro-3,5-dimethyl-1,4-benzoquinone imines by azido groups is preferred over 1,2-addition.

Scheme 3.



XVIIIa, **XVIIIb** **XIXa**, **XIXb**

Y= Ph (**a**), 4-MeC_6H_4 (**b**).

In summary, we have found that *N*-arylcarbamoyl-1,4-benzoquinone imines having at least one free *ortho* position with respect to the carbonyl carbon atom react

with sodium azide exclusively according to the 1,4-addition pattern to produce 1-(3-azido-4-hydroxyphenyl)-3-arylureas which do not undergo intramolecular oxidation–reduction. The reaction of *N*-arylcarbamoyl-2,6-dichloro-3,5-dimethyl-1,4-benzoquinone imines with sodium azide follows only nucleophilic substitution mechanism with formation of *N*-arylcarbamoyl-2,6-diazido-3,5-dimethyl-1,4-benzoquinone imines, which may be due to lower reactivity of the activated sterically strained C=N bond in *N*-arylcarbamoyl derivatives **XVIII** as compared to *N*-arenesulfonyl analogs.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-300 instrument (300 MHz) using tetramethylsilane as internal reference. Quinone imines **I**–**VIII** and **XVIII** were synthesized according to the procedures described in [7, 9].

1-(4-Methylphenyl)-3-(4-oxocyclohexa-2,5-dien-1-ylidene)urea (Ib). Yield 66%, mp 115–117°C (from AcOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.33 s (3H, 4-**Me**C_6H_4), 6.55–6.57 d.d (1H, 3-H, J = 10.2 Hz), 6.65–6.69 d.d (1H, 5-H, J = 10.2 Hz), 7.07–7.11 d.d (1H, 2-H, J = 2.4 Hz), 7.15 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.36 br.s (1H, NH), 7.41–7.44 d.d (1H, 6-H), 7.43 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: N 11.35, 11. 59. $C_{13}H_{11}N_2O_2$. Calculated, %: N 11.66.

1-(3-Methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-(4-methylphenyl)urea (IIb). Yield 61%, mp 134–135°C (from AcOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *Z* isomer: 2.04 d (3H, 2-Me, J = 0.9 Hz), 2.34 s (3H, 4-**Me**C_6H_4), 6.69 d (1H, 5-H, J = 9.9 Hz), 7.03–7.07 d.d (1H, 2-H, J = 2.1, 9.9 Hz), 7.17 d (2H, *m*-H, J = 8.1 Hz), 7.19 br.s (1H, 6-H), 7.22 br.s (1H, NH), 7.45 d (2H, *o*-H, J = 8.1 Hz); *E* isomer: 2.09 d (3H, 2-Me, J = 0.9 Hz), 2.34 s (3H, 4-**Me**C_6H_4), 6.57 d (1H, 5-H, J = 9.9 Hz), 6.93 br.s (1H, 2-H), 7.17 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.24 br.s (1H, NH), 7.38–7.42 d.d (1H, 6-H, J = 2.1, 9.9 Hz), 7.45 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: N 11.25, 11.45. $C_{14}H_{13}N_2O_2$. Calculated, %: N 11.66.

1-(2,3-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-(3-methylphenyl)urea (IIIc). Yield 47%, mp 154–155°C (from AcOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.04 s (3H, 2-Me), 2.17 s (3H, 3-Me), 2.36 s (3H, 3-**Me**C_6H_4), 6.51 d (1H, 5-H, J = 10.2 Hz), 6.96 d (1H, 6′-H, J = 7.5 Hz), 7.16 br.s (1H, NH), 7.20–7.25 t (1H, 5′-H), 7.22 d (1H, 6-H), 7.31 d (1H, 4′-H), 7.41 br.s (1H, 2′-H). Found, %: N 10.48, 10.65. $C_{16}H_{16}N_2O_2$. Calculated, %: N 10.44.

1-(3-Chlorophenyl)-3-(2,3-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)urea (IIId). Yield 54%, mp 162–164°C (from AcOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.05 s (3H, 2-Me), 2.16 s (3H, 3-Me), 6.52 d (1H, 5-H, J = 10.2 Hz), 7.12 d (1H, 6′-H, J = 8.1 Hz), 7.21 d (1H, 6-H), 7.24–7.29 t (1H, 5′-H), 7.31 d (1H, 4′-H), 7.36 br.s (1H, 2′-H), 7.68 br.s (1H, NH). Found, %: N 9.78, 9.90. $C_{15}H_{13}ClN_2O_2$. Calculated, %: N 9.70.

1-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-(4-methylphenyl)urea (IVb). Yield 63%, mp 177–179°C (from AcOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.99 br.s (3H, 2-Me), 2.18 br.s (3H, 5-Me), 2.34 s (3H, 4-**Me**C_6H_4), 6.54 br.s (1H, 3-H), 7.00 br.s (1H, NH), 7.10 br.s (1H, 6-H), 7.17 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.45 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: N 10.48, 10.51. $C_{15}H_{15}N_2O_2$. Calculated, %: N 10.97.

Reaction of 1,4-benzoquinone imines I–VIII and XVIII with sodium azide (*general procedure*). Sodium azide, 0.01 mol (0.02 mol in the reactions with **XVIII**) was added to a solution of 0.005 mol of the corresponding quinone imine in 10 mL of acetic acid. The precipitate was filtered off, washed with water, and dried. Compounds **XI** and **XII** were recrystallized from ethyl acetate, and **IX**, **X**, **XIII**, and **XIV**, from ethyl acetate–heptane (7:3).

1-(3-Azido-4-hydroxyphenyl)-3-phenylurea (IXa). Yield 67%, mp 110–112°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.68 d (1H, 6-H, J = 8.7 Hz), 7.03 br.s (1H, 2-H), 7.22 d.d (1H, 5-H, J = 1.8, 8.7 Hz), 6.97–7.51 m (5H, Ph), 8.33 s (1H, N^{1}H), 8.53 s (1H, N^{3}H), 9.08 s (1H, OH). Found, %: N 25.03, 26.11. $C_{13}H_{11}N_5O_2$. Calculated, %: N 26.01.

1-(3-Azido-4-hydroxyphenyl)-3-(4-methylphenyl)urea (IXb). Yield 80%, mp 105–107°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.23 s (3H, 4-**Me**C_6H_4), 6.67 d (1H, 6-H, J = 8.7 Hz), 7.06 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.07 br.s (1H, 2-H), 7.20 d.d (1H, 5-H, J = 1.8, 8.7 Hz), 7.31 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 8.31 s (1H, N^{1}H), 8.46 s (1H, N^{3}H), 9.06 br.s (1H, OH). Found, %: N 24.64, 24.79. $C_{14}H_{13}N_5O_2$. Calculated, %: N 24.72.

1-(3-Azido-4-hydroxy-5-methylphenyl)-3-phenylurea (Xa). Yield 90%, mp 134–135°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.14 s (3H, 5-Me), 6.87 d (1H, 2-H, J = 1.8 Hz), 7.19 d (1H, 6-H, J = 1.8 Hz), 6.93–7.45 m (5H, Ph), 8.49 s (1H, N^{1}H),

8.60 s (1H, N^3H), 8.66 br.s (1H, OH). Found, %: N 24.59, 24.67. $C_{14}H_{13}N_5O_2$. Calculated, %: N 24.72.

1-(3-Azido-4-hydroxy-5-methylphenyl)-3-(4-methylphenyl)urea (Xb). Yield 81%, mp 129–130°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.14 s (3H, 5-Me), 2.24 s (3H, 4-**Me**C_6H_4), 6.85 d (1H, 2-H, J = 2.1 Hz), 7.07 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.19 d (1H, 6-H, J = 2.1 Hz), 7.32 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 8.42 s (1H, N^1H), 8.47 s (1H, N^3H), 8.65 br.s (1H, OH). Found, %: N 23.61, 23.85. $C_{15}H_{15}N_5O_2$. Calculated, %: N 23.56.

1-(5-Azido-4-hydroxy-2,3-dimethylphenyl)-3-phenylurea (XIa). Yield 76%, mp 142–144°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (3H, 3-Me), 2.12 s (3H, 2-Me), 7.23 s (1H, 6-H), 6.91–7.46 m (5H, Ph), 7.96 s (1H, N^1H), 8.93 s (1H, N^3H), 9.35 br.s (1H, OH). Found, %: N 23.45, 23.59. $C_{15}H_{15}N_5O_2$. Calculated, %: N 23.56.

1-(5-Azido-4-hydroxy-2,3-dimethylphenyl)-3-(3-methylphenyl)urea (XIc). Yield 75%, mp 167–169°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (3H, 3-Me), 2.26 s (3H, 3-**Me**C_6H_4), 2.11 s (3H, 2-Me), 6.74–6.76 d.d (1H, 4′-H), 7.10–7.15 t (1H, 6′-H), 7.20–7.22 d.d (1H, 5′-H), 7.22 s (1H, 6-H), 7.30 br.s (1H, 2′-H), 8.04 s (1H, N^1H), 8.96 s (1H, N^3H), 9.99 br.s (1H, OH). Found, %: N 22.38, 22.56. $C_{16}H_{17}N_5O_2$. Calculated, %: N 22.49.

1-(5-Azido-4-hydroxy-2,3-dimethylphenyl)-3-(3-chlorophenyl)urea (XId). Yield 85%, mp 181–182°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.07 s (3H, 3-Me), 2.10 s (3H, 2-Me), 6.89–6.92 d.d (1H, 4′-H), 7.22 s (1H, 6-H), 7.20–7.25 t (1H, 6′-H), 7.34–7.37 d.d (1H, 5′-H), 7.74 q (1H, 2′-H), 8.96 s (1H, N^1H), 9.04 s (1H, N^3H), 10.54 br.s (1H, OH). Found, %: N 21.17, 21.52. $C_{15}H_{14}ClN_5O_2$. Calculated, %: N 21.11.

1-(3-Azido-4-hydroxy-2,5-dimethylphenyl)-3-phenylurea (XIIa). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.06 s (3H, 5-Me), 2.15 s (3H, 2-Me), 7.16 s (1H, 6-H), 6.91–7.44 m (5H, Ph), 7.77 s (1H, N^1H), 8.77 s (1H, N^3H), 9.01 br.s (1H, OH).

1-(3-Azido-4-hydroxy-2,5-dimethylphenyl)-3-(4-methylphenyl)urea (XIIb). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.06 s (3H, 5-Me), 2.16 s (3H, 2-Me), 2.23 s (3H, 4-**Me**C_6H_4), 7.03 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.16 s (1H, 6-H), 7.31 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.72 s (1H, N^1H), 8.66 s (1H, N^3H), 8.99 br.s (1H, OH).

1-(3-Azido-4-hydroxy-5-isopropyl-2-methylphenyl)-3-phenylurea (XIIIa). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.13 d [6H, CH(C**H**$_3$)$_2$], 2.07 s (3H, 2-Me), 3.19–3.28 m [1H, C**H**(CH$_3$)$_2$], 7.22 s (1H, 6-H), 6.91–7.44 m (5H, Ph), 7.82 s (1H, N^1H), 8.79 s (1H, N^3H), 8.91 br.s (1H, OH).

1-(3-Azido-4-hydroxy-2-isopropyl-5-methylphenyl)-3-phenylurea (XIVa). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.25 d [6H, CH(C**H**$_3$)$_2$], 2.06 s (3H, 5-Me), 3.19–3.28 m [1H, C**H**(CH$_3$)$_2$], 7.24 s (1H, 6-H), 6.88–7.47 m (5H, Ph), 7.64 s (1H, N^1H), 8.70 s (1H, N^3H), 9.67 br.s (1H, OH).

1-(3-Azido-4-hydroxy-2,6-dimethylphenyl)-3-phenylurea (XVa). Yield 86%, mp 136–137°C (from EtOAc). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.04 s (3H, 6-Me), 2.09 s (3H, 2-Me), 6.61 s (1H, 5-H), 6.89–7.43 m (5H, Ph), 7.53 s (1H, N^1H), 8.70 br.s (1H, N^3H), 10.12 br.s (1H, OH). Found, %: N 23.64, 23.87. $C_{15}H_{15}N_5O_2$. Calculated, %: N 23.56.

1-(3-Azido-4-hydroxy-2,6-dimethylphenyl)-3-(4-methylphenyl)urea (XVb). Yield 84%, mp 110–113°C (from EtOAc). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.04 s (3H, 6-Me), 2.08 s (3H, 2-Me), 2.23 s (3H, 3-**Me**C_6H_4), 6.60 s (1H, 5-H), 7.03 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.31 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.65 s (1H, N^1H), 8.73 br.s (1H, N^3H), 11.02 br.s (1H, OH). Found, %: N 22.41, 22.72. $C_{16}H_{17}N_5O_2$. Calculated, %: N 22.49.

1-(3,5-Diazido-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-phenylurea (XIXa). Yield 35%, mp 141–142°C (from EtOAc). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.12 s (6H, 2-Me, 6-Me), 7.07 br.s (1H, NH), 7.12–7.49 m (5H, Ph). Found, %: N 33.35, 33.67. $C_{15}H_{12}N_8O_2$. Calculated, %: N 33.32.

1-(3,5-Diazido-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-(4-methylphenyl)urea (XIXb). Yield 20%, mp 140–141°C (from EtOAc). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.12 s (6H, 2-Me, 6-Me), 2.33 s (3H, 4-**Me**C_6H_4), 6.91 br.s (1H, NH), 7.15 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.36 d (2H, 3′-H, 5′-H, J = 8.1 Hz). Found, %: N 32.11, 32.37. $C_{16}H_{14}N_8O_2$. Calculated, %: N 31.98.

Oxidation of compounds XIa and XIIb (*general procedure*). A suspension of 0.01 mol of compound **XIa** or **XIIb** in 2–3 mL of glacial acetic acid was cooled in an ice bath, 0.011 mol of lead tetraacetate was added, and the mixture was stirred for 30 min until bright orange crystalline material was formed. A few drops of ethylene glycol were added, the mixture was stirred for 5 min, and the precipitate was filtered off and recrystallized from benzene.

1-(5-Azido-2,3-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-phenylurea (XVI). Yield 56%, mp 115–

116°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.09 s (3H, 2-Me), 2.20 s (3H, 3-Me), 6.72 s (1H, 5-H), 7.04 br.s (1H, NH), 7.13–7.54 m (5H, Ph). Found, %: N 23.53, 23.88. $C_{15}H_{13}N_5O_2$. Calculated, %: N 23.72.

1-(3-Azido-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-(4-methylphenyl)urea (XVII). Yield 28%, mp 124–126°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.03 d (3H, 2-Me), 2.10 s (3H, 5-Me), 2.34 s (3H, 4-**Me**C_6H_4), 6.99 br.s (1H, NH), 7.12 s (1H, 3-H), 7.17 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.44 d (2H, 3′-H, 5′-H, J = 8.1 Hz). Found, %: N 22.31, 22.72. $C_{16}H_{15}N_5O_2$. Calculated, %: N 22.64.

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