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

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Abstract—Depending on the conditions and the order of addition of the reactants, reactions of *N*-sulfonyl-1,4-benzoquinone imines with sodium azide afforded *N*-(3-azido-4-hydroxyphenyl)alkane(arene)sulfonamides, *N*-(3-azido-4-oxocyclohexa-2,5-dienylidene)alkane(arene)sulfonamides, and *N*-(3,5-diazido-4-hydroxyphenyl)-alkanesulfonamides. Quantum chemical calculations showed that the reactions begin with addition of azide ion to the quinone imine.

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We previously synthesized new *N*-alkyl(trifluoromethyl)sulfonyl derivatives of 1,4-benzoquinone imine [1] and studied their reactivity toward potassium thiocyanate [1] and sodium arenesulfinates [2]. In the present work we examined reactions of these compounds with sodium azide.

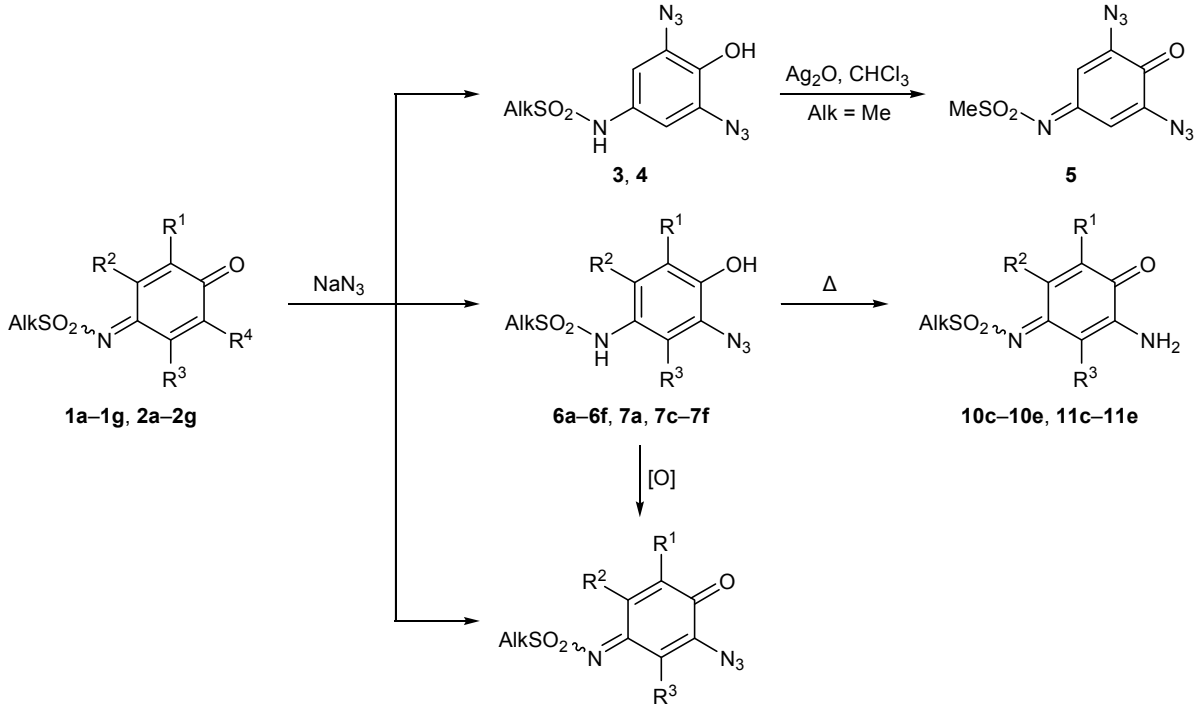
Sodium azide is a moderately hard nucleophile; it occupies an intermediate position between arenesulfinic acids and hydrogen chloride [3]. The addition of sodium azide to *N*-substituted 1,4-quinone imines generally proceeded in a way similar to the addition of HCl, i.e., according to the 1,4-addition path [4–10], while no reaction was observed with 2,6-dimethyl-1,4-benzoquinone imine derivatives; this indicated that no other reaction paths were operative [8].

It was found that the addition products in boiling acetic acid may undergo intramolecular oxidation/reduction with formation of *N*-(3-amino-4-oxocyclohexa-2,5-dienylidene)arenesulfonamides [5, 6, 8, 10], but the mechanism of this process was not studied. Analogous transformations of 1,4-benzo- [11, 12] and 1,4-naphthoquinones [11] were also observed in chloroform in an inert atmosphere.

The reactions of *N*-methyl(trifluoromethyl)sulfonyl-1,4-benzoquinone imines **1a**–**1g** and **2a**–**2g** with sodium azide were carried out under different conditions, namely in acetic acid at room temperature and in a chloroform–acetic acid mixture at room temperature and on cooling under argon with different reactant ratios. The reactions of **1a** and **2a** with sodium azide in acetic acid at room temperature gave only the corresponding 2,6-diazidophenols **3** and **4** regardless of the reactant ratio (1 : 1, 1 : 2, or 1 : 4). The reaction rate increased as the amount of sodium azide increased, but the yields of **3** and **4** did not change (40 and 45%, respectively). The oxidation of sulfonamide **3** with silver oxide in chloroform afforded quinone imine **5** (Scheme 1).

We previously obtained *N*-diazidophenyl sulfonamides only by stepwise addition of two molecules of sodium azide with intermediate oxidation of the primary addition products [8]. Therefore, we presumed that quinone imines **1a** and **2a** react with sodium azide via initial formation of 1,4-addition products **6a** and **7a** which are oxidized during the process to quinone imines **8a** and **9a**; addition of the second sodium azide molecule to **8a** and **9a** yields sulfonamides **3** and **4**. Both initial quinone imine and atmospheric oxygen can act as oxidant. To check this possibility, the reactions of **1a** and **2a** with sodium azide were carried out in a mixture of acetic acid with chloroform at –10°C under argon to avoid oxidation of intermediate compounds **6a** and **7a** with atmospheric oxygen. The

Scheme 1.



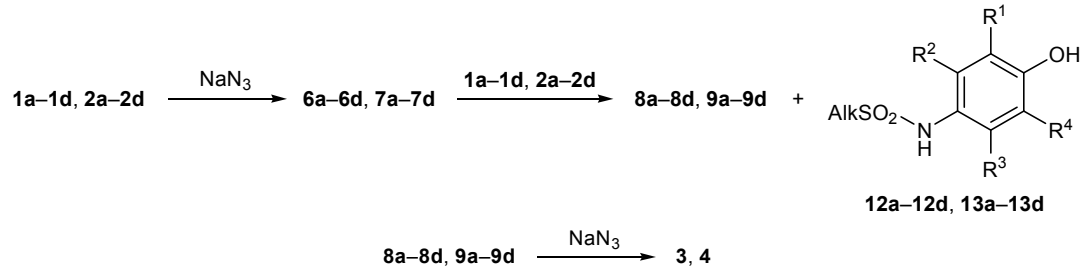
1, **3**, **6**, **8**, **10**, Alk = Me; **2**, **4**, **7**, **9**, **11**, Alk = CF_3; **1**, **2**, $R^1 = R^2 = R^3 = R^4 = H$ (**a**); $R^1 = R^3 = Me$, $R^2 = R^4 = H$ (**b**); $R^1 = i$-Pr, $R^2 = R^4 = H$, $R^3 = Me$ (**c**); $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = i$-Pr (**d**); $R^1 = R^2 = Me$, $R^3 = R^4 = H$ (**e**); $R^1 = R^4 = H$, $R^2 = R^3 = Me$ (**f**); $R^1 = R^4 = Me$, $R^2 = R^3 = H$ (**g**); **6**–**11**, $R^2 = H$, $R^1 = R^3 = H$ (**a**), Me (**b**); $R^1 = i$-Pr, $R^3 = Me$ (**c**); $R^1 = Me$, $R^3 = i$-Pr (**d**); $R^1 = R^2 = Me$, $R^3 = H$ (**e**); $R^1 = H$, $R^2 = R^3 = Me$ (**f**).

resulting mixtures were analyzed by ^1H NMR. The ^1H NMR spectra contained signals assignable to sulfonamides **12a** and **13a** and compounds **3** and **4** at a ratio of 1:1 (Scheme 2). In the ^{19}F NMR spectrum of a mixture of **4** and **13a** we observed two signals at δ_F –76.04 and –76.75 ppm. These findings indicated with certainty that initial quinonimines **1a** and **2a** act as oxidants in the intermediate step. This is also supported by the yields of **3** and **4** (40–45%).

The reactions of **1a** and **2a** with sodium azide were carried out by adding a solution of sodium azide to a solution of **1a** or **2a**; therefore, quinone imines **1a** and **2a** were present in excess in the reaction mixture and were able to oxidize sulfonamides **6a** and **7a**. In order to suppress the redox reaction, the order of addition of the reactants was changed, and a solution of **1a** or **2a** was slowly added dropwise to a solution of sodium azide in acetic acid, so that constant excess of sodium azide was maintained in the reaction mixture. As a result, we isolated sulfonamides **6a** and **7a**.

According to our previous data [1, 2], in no case the addition product formed in reactions of quinone

Scheme 2.



12, Alk = Me; **13**, Alk = CF_3; $R^1 = R^2 = R^3 = R^4 = H$ (**a**); $R^1 = R^3 = Me$, $R^2 = R^4 = H$ (**b**); $R^1 = i$-Pr, $R^2 = R^4 = H$, $R^3 = Me$ (**c**); $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = i$-Pr (**d**).

imines **1** and **2** with potassium thiocyanate and sodium sulfinates was oxidized with the initial quinone imine [1, 2]. A probable reason is that the electron-withdrawing sulfonyl and isothiocyanato groups hinder oxidation of the addition products by increasing the redox potential of the corresponding quinone imines [13]. The azido group exerts a positive or weakly negative mesomeric effect (σ_m = 0.37, σ_p = –0.08) due to p–π or π–π conjugation with the aromatic ring, respectively [14]. Therefore, the redox potential of quinone imines **8a** and **9a** is lower than that of initial quinone imines **1a** and **2a**, and the latter are capable of oxidizing **6a** and **7a**.

In the reaction of **1b** with sodium azide we obtained a mixture of sulfonamide **6b** and quinone imine **8b**, whereas only quinone imine **9b** was isolated in the reaction of sodium azide with quinone imine **2b** (Scheme 1). Compound **9b** was formed in 30 min after the reaction started. The reaction mixture darkened on further stirring, and the isolated product was 6-azido-2,5-dimethyl-1,4-benzoquinone which was formed as a result of hydrolysis. By reactions of **1c**, **1d**, **2c**, and **2d** with sodium azide we obtained mixtures **6c**/**8c**, **6d**/**8d**, **7c**/**9c**, and **7d**/**9d**, respectively (Scheme 1). We succeeded in separating these mixtures by repeated recrystallization from aqueous acetic acid or hexane–benzene (2:1) or by column chromatography on silica gel with benzene as eluent. Compounds **8b**–**8d**, **9c**, and **9d** were also synthesized independently by oxidation of **6b**–**6d**, **7c**, and **7d**, respectively, with freshly prepared silver oxide in chloroform or methylene chloride.

The reactions of **1b**–**1d** and **2b**–**2d** with sodium azide under argon resulted in the formation of mixtures of products. Apart from already isolated compounds **6b**–**6d**, **8b**–**8d** and **7b**–**7d**, **9b**–**9d**, these mixtures contained *N*-(2,5-dialkyl-4-hydroxyphenyl) sulfonamides **12b**–**12d** and **13b**–**13d**. These data suggest intermediate oxidation of **6b**–**6d** and **7b**–**7d** with initial quinone imines **1b**–**1d** and **2b**–**2d** to **8b**–**8d** and **9b**–**9d** (Scheme 2).

Heating of **6c**, **6d**, **7c**, and **7d** in both acetic acid and benzene afforded intramolecular oxidation/reduction products, quinone imines **10c**, **10d**, **11c**, and **11d** (Scheme 1), which is consistent with the data of [8].

Quinone imines **1e**, **1f**, **2e**, and **2f** reacted with sodium azide to give only sulfonamides **6e**, **6f**, **7e**, and **7f**. Compounds **6e** and **7e** on heating in polar and nonpolar organic solvents, as well as under irradiation, underwent intramolecular oxidation/reduction with elimination of nitrogen and formation of amino derivatives **10e** and **11e** (Scheme 1). The transformation of **6e** was complete in a few second, whereas 2–3 days were required for the transformation of **7e**. Numerous attempts to isolate quinone imine **10e** in the pure state were unsuccessful, and it was identified by ^{1}H NMR in a mixture with **6e**.

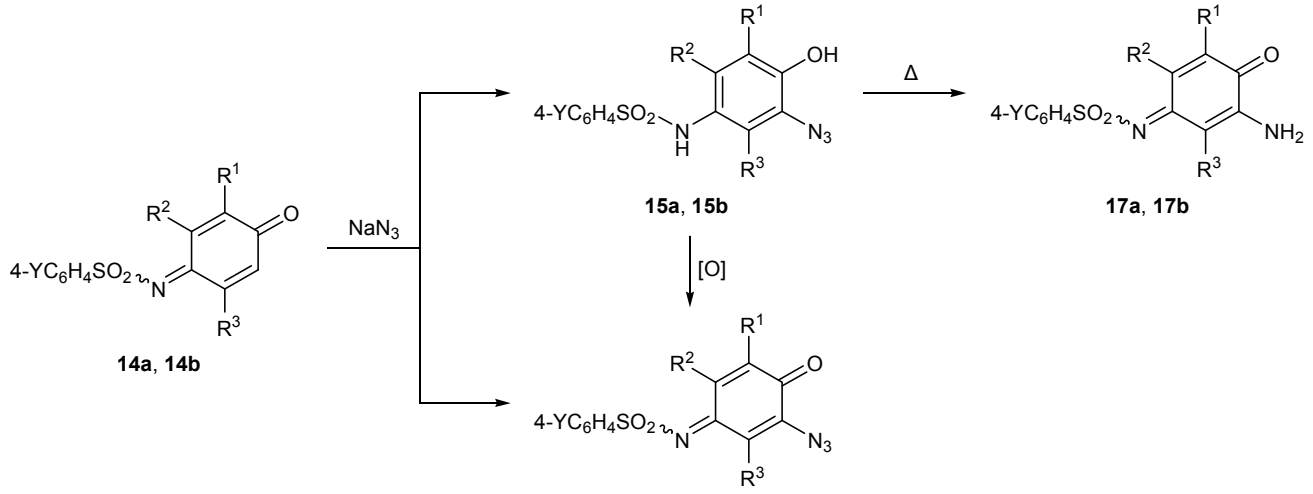
Quinone imines **1g** and **2g** with methyl groups in the *ortho* positions with respect to the carbonyl group reacted with sodium azide to produce mixtures of hydrolysis and reduction products, which confirmed our previous conclusion implying completely regioselective 1,4-addition of azide ion [8].

The structure of all isolated compounds was confirmed by their IR, ^{1}H and ^{19}F NMR spectra, and elemental analyses. Protons in the $MeSO_2$ group resonated in the ^{1}H NMR spectra at δ 2.88–2.96 (**6b**–**6f**), 3.21–3.29 (**8b**–**8f**), and 3.01–3.20 ppm (**10c**–**10e**). The NH_2 signal appeared in the spectra of **10c**–**10e** and **11c**–**11e** as a broadened singlet at δ 5.06–5.98 ppm. The ^{19}F NMR spectra of **7b**–**7f**, **9b**–**9e**, and **11c**–**11e** contained a singlet due to trifluoromethyl group in the regions δ_F –76.04 to –76.85, –79.12 to –79.22, and –79.76 to –81.18 ppm, respectively. Compounds **3**–**9** displayed in the IR spectrum an absorption band at 2110–2180 cm^{-1} corresponding to stretching vibrations of the azido group, and NH stretching band was observed at 3420–3465 cm^{-1} in the IR spectra of **10c**–**10e** and **11c**–**11e**.

In order to compare the reactivities of *N*-arylsulfonyl and *N*-methyl(trifluoromethyl)sulfonyl derivatives, we also studied for the first time reactions of NaN_3 with compounds **14a** and **14b** (Scheme 3). Like quinone imines **1b**, **1e**, **2b**, and **2e**, compound **14a** reacted with sodium azide to give a mixture of azides **15a** and **16a**. From quinone imine **14b** we obtained sulfonamide **15b** which was stable on storage; compound **15b** was readily oxidized to **16b** with sodium dichromate in acetic acid. Thus, replacement of the methyl (trifluoromethyl) group on the sulfur atom by aryl did not affect the reaction course to an appreciable extent.

Our results showed that the first reaction step is 1,4-addition of the nucleophile. Depending on the redox potential of the quinone imine and reaction conditions, next follow oxidation of the addition product with the initial quinone imine and addition of the second nucleophile molecule. However, on the basis of the experimental data it was impossible to determine whether the 1,4-addition step begins with protonation of the nitrogen atom or addition of azide ion. The

Scheme 3.

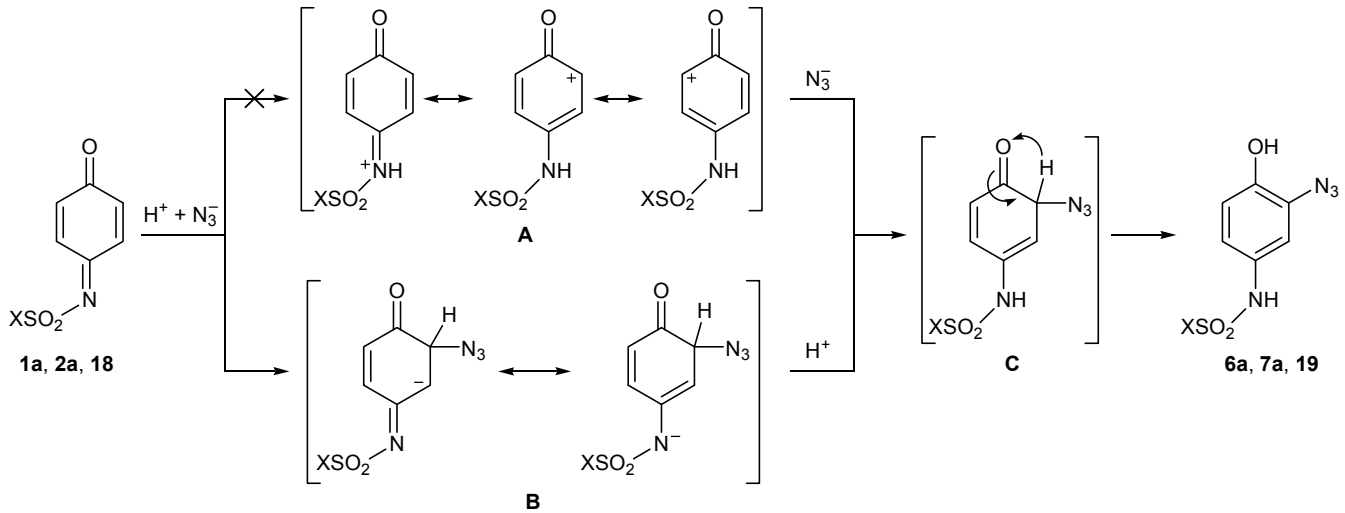


Y = R^2 = H, R^1 = R^3 = Me (**a**); Y = R^1 = R^2 = Me, R^3 = H (**b**).

mechanism proposed in [11] for the reaction of 1,4-naphthoquinone with sodium azide involved initial addition of azide ion to the quinone and subsequent aromatization of the ring. On the other hand, we previously found [15] that nucleophilic addition reactions of *N*-substituted 1,4-benzoquinone imines, in particular hydrohalogenation reactions, are initiated by protonation of the nitrogen atom with subsequent addition of halide ion (nucleophile).

We made an attempt to shed light on this problem by resorting to quantum chemical calculations. The geometric parameters of initial quinone imines **1a**, **2a**, and **18** (having no substituents in the quinoid ring) and possible transition states **A**–**C** (Scheme 4) were optimized at the DFT B3LYP/6-31+G(*d*) level of theory. Here, transition state **C** is common for both reaction paths. The calculations showed that the change in the energy of the system in going to transition state **A** [–1342.602714 (**1a**), –1640.298900 (**2a**), –1534.355226 a.u. (**18**)] is considerably larger than that corresponding to the formation of transition state **B** [–1342.846841 (**1a**), –1640.590947 (**2a**), –1534.596125 a.u. (**18**)]. The energy difference between transition states **A** and **B** is 640.96 (**1a**), 766.77 (**2a**), and 632.48 kJ/mol (**18**), and the energy of the system upon formation of transition state **C** [–1342.812051 (**1a**), –1640.525521 (**2a**), –1534.554440 a.u. (**18**)] is considerably lower than the

Scheme 4.



1a, **6a**, X = Me; **2a**, **7a**, X = CF_3; **18**, **19**, X = Ph.

energy for transition state **A** [the energy difference between **A** and **C** is 549.61 (**1a**), 595.00 (**2a**), and 523.04 kJ/mol (**18**)] and somewhat higher than for transition state **B** [the energy difference between **B** and **C** is 91.34 (**1a**), 171.78 (**2a**), and 109.44 kJ/mol (**18**)]. These data suggest that the reactions of quinone imines with sodium azide involve initial addition of azide ion with formation of transition state **B**, which is followed by protonation of the nitrogen atom to form transition state **C**, and intramolecular proton transfer in the latter yields final product **6a**, **7a**, or **19** (Scheme 4).

As shown above, heating of sulfonamides **6c**–**6e**, **7c**–**7e**, **15a**, and **15b** in boiling acetic acid or benzene leads to the formation of quinone imines **10c**–**10e**, **11c**–**11e**, **17a**, and **17b** as a result of intramolecular oxidation/reduction. Couladouros et al. [11] proposed a mechanism for the formation of 2-azidonaphthalene-1,4-diol from sodium azide and 1,4-naphthoquinone with participation of acetic acid proton. It was also noted that intramolecular oxidation/reduction of analogous adduct derived from NaN_3 and 1,4-benzoquinone follows a similar scheme, though the reaction was carried out in an aprotic solvent under argon [11, 12].

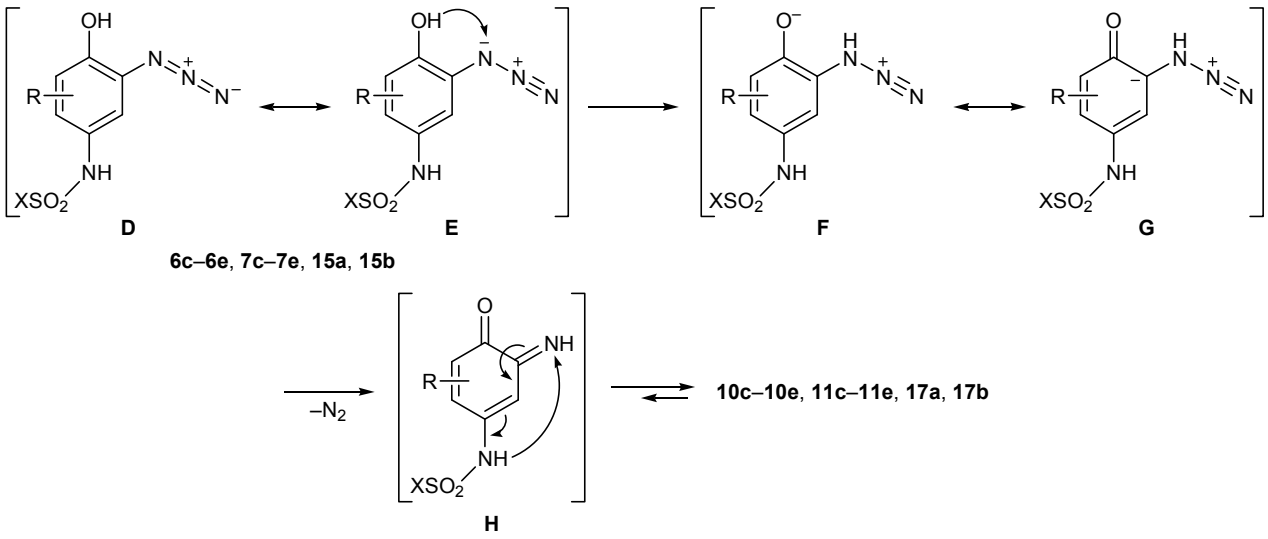
Taking into account that intramolecular oxidation/reduction of **6c**–**6e**, **7c**–**7e**, **15a**, and **15b** occurred in both acetic acid and aprotic solvent, we proposed a reaction mechanism shown in Scheme 5. Compounds **6c**–**6e**, **7c**–**7e**, **15a**, and **15b** may be represented by canonical structures **D** and **E**. Proton transfer from the hydroxy group to the negatively charged nitrogen atom of the azido group in **E** gives intermediate resonance structures **F** and **G** which lose nitrogen molecule with formation of *o*-quinone imine **H**, and prototropic tautomerization of the latter yields final *p*-quinone imine **10c**–**10e**, **11c**–**11e**, **17a**, or **17b**.

It is known that *ortho*- and *para*-quinoid structures can be converted into each other; however, the *para*-quinoid structure is energetically more favorable than *ortho*-quinoid, which follows from their redox potentials [16, 17]. For example, the redox potential of 1,4-benzoquinone is E_o = 0.699 V against 0.792 V for 1,2-benzoquinone [16]. Presumably, compounds **10c**–**10e**, **11c**–**11e**, **17a**, or **17b** in solution give rise to a small amount of *ortho*-quinoid structure **H**. This follows from the color change of a solution of *N*-[3-(benzenesulfonyl)-4-oxocyclohexa-2,5-dienylidene]benzenesulfonamide after addition of an alkali solution. This compound changes its color due to formation of mesomeric ion, and this property underlies the use of analogous quinone imines as acid–base indicators [18].

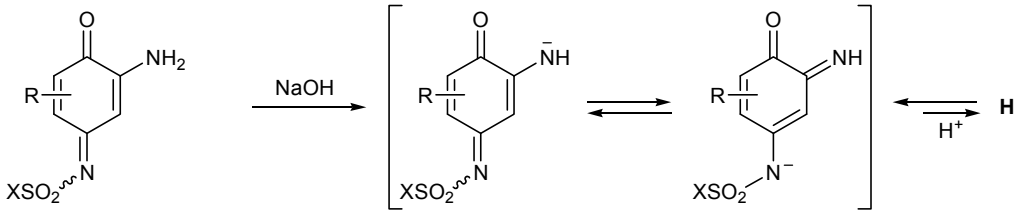
In fact, addition of alkali to a solution of **10c**–**10e**, **11c**–**11e**, **17a**, or **17b** in alcohol changed the color from pink or violet to deep dark blue. This confirms the presence in their solutions of mesomeric ion **I** as intermediate species in the tautomeric transformation of *para*- (**10c**–**10e**, **11c**–**e, 17a**, **b**) and *ortho*-quinoid structures (**H**) (Scheme 6) and provides an additional support to the mechanism of intramolecular oxidation/reduction involving structure **H** (Scheme 5).

In summary, we have studied the reactivity of *N*-sulfonyl-1,4-benzoquinone imines toward sodium azide. 2,5-Dialkyl-substituted *N*-(3-amino-4-oxocyclohexa-2,5-dienylidene) sulfonamides and *N*-(3,5-diazido-4-hydroxyphenyl)alkanesulfonamides have been isolated as the reaction products for the first time. This

Scheme 5.



Scheme 6.



10c–10e, **11c–11e**, **17a**, **17b** **I**

may be rationalized by the ability of the corresponding monoazido-substituted sulfonamides to readily undergo oxidation with the initial quinone imine and take up the second HN_3 molecule provided that the *ortho* position with respect to the carbonyl group is free. The product composition and structure depend on the reaction conditions and order of addition of the reactants. A probable reaction mechanism has been proposed on the basis of the experimental data and quantum chemical calculations.

EXPERIMENTAL

The IR spectra were recorded on a Bruker Vertex-70 spectrometer from samples pressed with KBr (**3**, **4**, **6a–6f**, **7a**, **7c–7f**, **12c**, **12d**, **13c**, **13d**, **15a**, **15b**) or dissolved in chloroform (**1c**, **1d**, **2c**, **2d**, **5**, **8b–8f**, **9b–9e**, **10c–10e**, **11c–11e**, **16a**, **16b**, **17a**, **17b**). The ^{1}H NMR spectra were recorded on a Varian VXR-300 instrument at 300 MHz using tetramethylsilane as standard. The ^{19}F NMR spectra were measured on a Varian Gemini-200 spectrometer at 188.14 MHz relative to trichloro(fluoro)methane. The purity of the initial quinone imines and isolated compounds was checked by TLC on Silufol UV-254 plates; samples were applied from solutions in chloroform, acetone, or THF; plates were eluted with ethanol–chloroform (1 : 10), benzene–hexane (10 : 1), or hexane–ethyl acetate (1 : 2); spots were visualized under UV light.

Quantum-chemical calculations were performed using Firefly QC software [19] which is based in part on the GAMESS code [20]. Transition states were localized by standard structure optimization procedure.

Compounds **1c**, **1d**, **2c**, and **2d** were synthesized according to the procedures described in [1]. Compounds **1a**, **1b**, **1e–1g**, **2a**, **2b**, **2e–2g**, **12a**, **12b**, **13a**, **13b** [1], **14a** [21], and **14b** [22] were reported previously.

***N*-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (1c).** Yield 90%, mp 79–81°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.15 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.12 s (2-Me), 2.97–3.09 m (1H, C**H**Me$_2$), 3.29 s (3H, CH_3SO_2), 6.55 q (1H, 3-H), 7.65 s (1H, 6-H). Found, %: N 5.70, 5.75; S 13.28, 13.33. $C_{11}H_{15}NO_3S$. Calculated, %: N 5.80; S 13.29.

***N*-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (1d).** Yield 92%, mp 88–89°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.17 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.08 d (5-Me, J = 1.8 Hz), 3.13–3.23 m (1H, C**H**Me$_2$), 3.30 s (3H, CH_3SO_2), 6.52 s (1H, 3-H), 7.73 q (1H, 6-H). Found, %: N 5.80, 5.88; S 13.25, 13.37. $C_{11}H_{15}NO_3S$. Calculated, %: N 5.80; S 13.29.

***N*-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (2c).** Yield 87%, mp 34–36°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.14 d (2-Me, J = 1.8 Hz), 3.00–3.17 m (1H, C**H**Me$_2$), 6.62 q (1H, 3-H), 7.36 d (1H, 6-H, J = 1.2 Hz). ^{19}F NMR spectrum ($CFCl_3$): δ_F –79.08 ppm, s. Found, %: N 4.68, 4.72; S 10.80, 10.88. $C_{11}H_{12}F_3NO_3S$. Calculated, %: N 4.74; S 10.86.

***N*-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (2d).** Yield 95%, mp 56–57°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.19 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.13 d (5-Me, J = 1.8 Hz), 3.04–3.17 m (1H, C**H**Me$_2$), 6.59 d (1H, 2-H, J = 1.2 Hz), 7.47 q (1H, 5-H). ^{19}F NMR spectrum ($CFCl_3$): δ_F –79.15 ppm, s. Found, %: N 4.65, 4.70; S 10.82, 10.90. $C_{11}H_{12}F_3NO_3S$. Calculated, %: N 4.74; S 10.86.

Reaction of quinone imines 1a–1g, 2a–2g, 14a, and 14 b with sodium azide (*general procedures*). *a*. Sodium azide, 4 mmol, was added in one portion to a solution of 2 mmol of quinone imine **1a–1g**, **14a**, or **14b** in 20 mL of glacial acetic acid. The solution turned red and then became colorless. When the mixture bleached, it was poured onto ice, and the precipitate was filtered off, washed with water, and recrystallized from acetic acid or benzene–hexane (1 : 2) or purified by column chromatography on silica gel.

b. A solution of 4 mmol of sodium azide in 10 mL of glacial acetic acid was added dropwise to a solution of 2 mmol of quinone imine **1a**–**1g** or **2a**–**2g** in 10 mL of chloroform or methylene chloride at room temperature or on cooling to –10°C, and the mixture was purged with argon. The mixture turned red and then bleached. When the reaction was complete, the mixture was evaporated under reduced pressure, and the residue was poured onto ice. The precipitate was filtered off, washed with water, and purified by recrystallization from acetic acid or benzene–hexane (1:2) or by column chromatography on silica gel.

c. A solution of 2 mmol of quinone imine **1a** or **2a** was added dropwise under vigorous stirring over a period of 30 min to a solution of 4 mmol of sodium azide in 10 mL of glacial acetic acid maintained at room temperature. The solution immediately turned colorless and was stirred for 1 h and evaporated under reduced pressure. The residue was poured onto ice, the precipitate was extracted with diethyl ether, the extract was dried over magnesium sulfate and evaporated, and the residue was recrystallized from benzene–hexane (1:2).

***N*-(3,5-Diazido-4-hydroxyphenyl)methanesulfonamide (3).** Yield 43%, mp 134–136°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.94 s (3H, CH_3SO_2), 6.69 s (2H, 2-H, 6-H), 9.20 br.s (1H, NH), 9.61 br.s (1H, OH). Found, %: N 36.25, 36.30; S 11.85, 11.93. $C_7H_7N_7O_3S$. Calculated, %: N 36.42; S 11.91.

***N*-(3,5-Diazido-4-hydroxyphenyl)trifluoromethanesulfonamide (4).** Yield 45%, mp 119–121°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.72 s (2H, 2-H, 6-H), 8.96 br.s (1H, NH), 10.15 br.s (1H, OH). ^{19}F NMR spectrum ($CFCl_3$): δ_F –75.63 ppm, s. Found, %: N 30.25, 30.40; S 9.85, 9.93. $C_7H_4F_3N_7O_3S$. Calculated, %: N 30.34; S 9.92.

***N*-(3,5-Diazido-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (5).** Yield 90%, mp 113–114°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.21 s (3H, $MeSO_2$), 6.41 s (1H, 3-H), 7.32 s (1H, 5-H). Found, %: N 36.55, 36.70; S 11.95, 12.15. $C_7H_5N_7O_3S$. Calculated, %: N 36.69; S 12.00.

***N*-(3-Azido-4-hydroxyphenyl)methanesulfonamide (6a).** Yield 75%, mp 130–132°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.88 s (3H, CH_3SO_2), 6.79 d (1H, 2-H, J = 1.8 Hz), 6.83 d (1H, 5-H, J = 6.9 Hz), 6.88 d.d (1H, 6-H), 9.34 s (1H, NH), 10.04 s (1H, OH). Found, %: N 24.15, 24.25; S 13.98, 14.12. $C_7H_8N_4O_3S$. Calculated, %: N 24.55; S 14.05.

***N*-(3-Azido-4-hydroxy-2,5-dimethylphenyl)methanesulfonamide (6b).** Yield 69%, mp 105–107°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.13 s (3H, 2-Me), 2.17 s (3H, 5-Me), 2.90 s (3H, CH_3SO_2), 6.85 s (1H, 6-H), 8.88 s (1H, NH), 9.35 s (1H, OH). Found, %: N 21.75, 21.80; S 12.42, 12.49. $C_9H_{12}N_4O_3S$. Calculated, %: N 21.86; S 12.51.

***N*-(3-Azido-4-hydroxy-5-isopropyl-2-methylphenyl)methanesulfonamide (6c).** Yield 21%, mp 115–117°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.14 d (6H, CH**Me**$_2$, J = 6 Hz), 2.15 s (2-Me), 2.90 s (3H, CH_3SO_2), 3.19–3.30 m (1H, C**H**Me$_2$), 6.89 s (1H, 6-H), 8.89 s (1H, NH), 9.26 s (1H, OH). Found, %: N 19.67, 19.72; S 11.29, 11.35. $C_{11}H_{16}N_4O_3S$. Calculated, %: N 19.70; S 11.28.

***N*-(3-Azido-4-hydroxy-2-isopropyl-5-methylphenyl)methanesulfonamide (6d).** Yield 32%, mp 144–145°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.27 d (6H, CH**Me**$_2$, J = 3.6 Hz), 2.17 s (5-Me), 2.93 s (3H, CH_3SO_2), 3.45–3.57 m (1H, CH**Me**$_2$), 6.86 s (1H, 6-H), 8.87 s (1H, NH), 9.39 s (1H, OH). Found, %: N 19.64, 19.68; S 11.24, 11.30. $C_{11}H_{16}N_4O_3S$. Calculated, %: N 19.70; S 11.28.

***N*-(5-Azido-4-hydroxy-2,3-dimethylphenyl)methanesulfonamide (6e).** Yield 71%, mp 155–157°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.04 s (3H, 3-Me), 2.15 s (3H, 2-Me), 2.95 s (3H, CH_3SO_2), 6.72 s (1H, 6-H), 8.57 s (1H, NH), 8.82 s (1H, OH). Found, %: N 21.83, 21.90; S 12.48, 12.53. $C_9H_{12}N_4O_3S$. Calculated, %: N 21.86; S 12.51.

***N*-(3-Azido-4-hydroxy-2,6-dimethylphenyl)methanesulfonamide (6f).** Yield 58%, mp 139–140°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.16 s (3H, 6-Me), 2.22 s (3H, 2-Me), 2.96 s (3H, C**H**$_3$SO$_2$), 6.61 s (1H, 5-H), 8.72 s (1H, NH), 9.29 s (1H, OH). Found, %: N 21.81, 21.85; S 12.50, 12.54. $C_9H_{12}N_4O_3S$. Calculated, %: N 21.86; S 12.51.

***N*-(3-Azido-4-hydroxyphenyl)trifluoromethanesulfonamide (7a).** Yield 87%, mp 110–112°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.77 s (1H, 5-H), 6.90 s (2H, 2-H, 6-H), 10.43 s (1H, NH), 11.59 br.s (1H, OH). ^{19}F NMR spectrum ($CFCl_3$): δ_F –75.56 ppm, s. Found, %: N 19.75, 19.80; S 11.30, 11.33. $C_7H_5F_3N_4O_3S$. Calculated, %: N 19.85; S 11.36.

***N*-(3-Azido-4-hydroxy-5-isopropyl-2-methylphenyl)trifluoromethanesulfonamide (7c).** Yield 29%, mp 123–124°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.21 d (6H, CH**Me**$_2$, J = 6.6 Hz), 2.38 s (3H, 2-Me), 3.11–3.22 m (1H, C**H**Me$_2$), 5.75 s (1H, NH), 6.53 s (1H, OH), 6.99 s (1H, 6-H). ^{19}F NMR spectrum

($CFCl_3$): δ_F –76.04 ppm, s. Found, %: N 16.50, 16.55; S 9.40, 9.47. $C_{11}H_{13}F_3N_4O_3S$. Calculated, %: N 16.56; S 9.48.

***N*-(3-Azido-4-hydroxy-2-isopropyl-5-methylphenyl)trifluoromethanesulfonamide (7d).** Yield 39%, mp 118–120°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.37 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.22 s (3H, 5-Me), 3.29–3.43 m (1H, C**H**Me$_2$), 6.72 s (1H, NH), 6.93 s (1H, 6-H), 7.06 s (1H, OH). ^{19}F NMR spectrum ($CFCl_3$): δ_F –76.29 ppm, s. Found, %: N 16.45, 16.51; S 9.44, 9.49. $C_{11}H_{13}F_3N_4O_3S$. Calculated, %: N 16.56; S 9.48.

***N*-(5-Azido-4-hydroxy-2,3-dimethylphenyl)trifluoromethanesulfonamide (7e).** Yield 57%, mp 120–122°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.20 s (3H, 3-Me), 2.26 s (3H, 2-Me), 5.50 s (1H, NH), 6.48 s (1H, OH), 6.95 s (1H, 6-H). ^{19}F NMR spectrum ($CFCl_3$): δ_F –76.42 ppm, s. Found, %: N 18.00, 18.10; S 10.28, 10.36. $C_9H_9F_3N_4O_3S$. Calculated, %: N 18.06; S 10.34.

***N*-(3-Azido-4-hydroxy-2,6-dimethylphenyl)trifluoromethanesulfonamide (7f).** Yield 29%, mp 125–127°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.33 s (3H, 2-Me), 2.37 s (3H, 6-Me), 5.49 s (1H, NH), 6.13 s (1H, OH), 6.65 s (1H, 5-H). ^{19}F NMR spectrum ($CFCl_3$): δ_F –76.85 ppm, s. Found, %: N 17.99, 18.01; S 10.30, 10.38. $C_9H_9F_3N_4O_3S$. Calculated, %: N 18.06; S 10.34.

***N*-(3-Azido-4-hydroxy-2,5-dimethylphenyl)benzenesulfonamide (15a).** Yield 42%, mp 178–180°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.87 s (3H, 2-Me), 2.06 s (3H, 5-Me), 6.45 s (1H, 6-H), 7.31–7.60 m (5H, Ph), 9.05 s (1H, NH), 9.25 s (1H, OH). Found, %: N 17.35, 17.55; S 10.02, 10.15. $C_{14}H_{14}N_4O_3S$. Calculated, %: N 17.60; S 10.07.

***N*-(5-Azido-4-hydroxy-2,3-dimethylphenyl)-4-methylbenzenesulfonamide (15b).** Yield 80%, mp 156–158°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.91 s (3H, 3-Me), 2.02 s (3H, 2-Me), 2.37 s (3H, 4′-Me), 6.17 s (1H, 6-H), 7.35–7.50 d.d (4H, C_6H_4, J = 7.8 Hz), 9.00 s (1H, NH), 9.31 s (1H, OH). Found, %: N 16.54, 16.65; S 9.52, 9.63. $C_{15}H_{16}N_4O_3S$. Calculated, %: N 16.86; S 9.65.

***N*-(3-Azido-2,5-dimethyl-4-oxocyclohexa-2,5-dienylidene)benzenesulfonamide (16a).** Yield 65%, mp 105–107°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.94 s (3H, 2-Me), 2.13 d (3H, 5-Me, J = 1.8 Hz), 7.54–8.01 m (5H, Ph), 7.95 q (1H, 6-H). Found, %: N 17.73, 17.78; S 10.05, 10.14. $C_{14}H_{12}N_4O_3S$. Calculated, %: N 17.71; S 10.14.

***N*-(5-Azido-2,3-dimethyl-4-oxocyclohexa-2,5-dienylidene)-4-methylbenzenesulfonamide (16b).** Yield 55%, mp 122–124°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.05 s (3H, 3-Me), 2.07 s (3H, 2-Me), 2.46 s (3H, 4′-Me), 7.54 s (1H, 6-H), 7.35–7.87 d.d (4H, C_6H_4, J = 8.1 Hz). Found, %: N 16.85, 17.00; S 9.61, 9.69. $C_{15}H_{14}N_4O_3S$. Calculated, %: N 16.96; S 9.71.

Oxidation of compounds 3, 6b–6f, 7a, 7c–7e, 15a, and 15b (*general procedures*). *a*. Silver oxide, 0.26 g (1.1 mmol), was added under stirring to a suspension of 1 mmol of compound **3**, **6b**–**6f**, or **7c**–**7e** in 20 mL of anhydrous chloroform or methylene chloride. The mixture was stirred for 24 h, the precipitate of silver was filtered off, the filtrate was evaporated under reduced pressure, and the red–orange precipitate was recrystallized from benzene–hexane or chloroform–hexane.

b. A suspension of 1 mmol of compound **15a** or **15b** in 2 mL of acetic acid was heated under stirring until complete dissolution and was then cooled under continuous stirring to 15–18°C. Sodium dichromate, 0.21 g (1 mmol), was added in one portion, and the mixture was vigorously stirred for 1 h so that the temperature did not exceed 35°C. The mixture was cooled to 15°C, and the precipitate was filtered off and washed with acetic acid and ethanol.

***N*-(3-Azido-2,5-dimethyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (8b).** Yield 53%, mp 131–132°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.02 s (3H, 2-Me), 2.09 s (3H, 3-Me), 3.26 s (3H, CH_3SO_2), 7.71 s (1H, 6-H). Found, %: N 21.95, 21.99; S 12.57, 12.59. $C_9H_{10}N_4O_3S$. Calculated, %: N 22.03; S 12.61.

***N*-(3-Azido-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (8c).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.10 d (6H, CH**Me**$_2$, J = 6.9 Hz), 1.96 s (3H, 2-Me), 2.92–3.05 m (1H, C**H**Me$_2$), 3.21 s (3H, CH_3SO_2), 7.60 s (1H, 6-H).

***N*-(3-Azido-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (8d).** Yield 76%, mp 83–85°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 d (6H, CH**Me**$_2$, J = 7 Hz), 2.04 s (3H, 5-Me), 3.19–3.30 m (1H, C**H**Me$_2$), 3.24 s (3H, CH_3SO_2), 7.69 s (1H, 6-H). Found, %: N 19.79, 19.81; S 11.29, 11.32. $C_{11}H_{14}N_4O_3S$. Calculated, %: N 19.85; S 11.36.

***N*-(5-Azido-2,3-dimethyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (8e).** Yield 77%, mp 112–114°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.10 s (3H, 3-Me), 2.14 s (3H, 2-Me), 3.26 s (3H,

CH_3SO_2), 7.29 s (1H, 6-H). Found, %: N 22.01, 22.07; S 12.59, 12.65. $C_9H_{10}N_4O_3S$. Calculated, %: N 22.03; S 12.61.

***N*-(3-Azido-2,6-dimethyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (8f).** Yield 61%, mp 102–105°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.27 s (3H, 6-Me), 2.30 s (3H, 2-Me), 3.29 s (3H, CH_3SO_2), 6.50 s (1H, 5-H). Found, %: N 21.98, 22.01; S 12.60, 12.66. $C_9H_{10}N_4O_3S$. Calculated, %: N 22.03; S 12.61.

***N*-(3-Azido-2,5-dimethyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (9b).** Yield 35%, mp 115–117°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.05 s (3H, 2-Me), 2.16 d (3H, 5-Me, J = 1.5 Hz), 7.45 q (1H, 6-H). ^{19}F NMR spectrum ($CFCl_3$): δ_F –79.13 ppm, s. Found, %: N 18.10, 18.15; S 10.38, 10.44. $C_9H_7F_3N_4O_3S$. Calculated, %: N 18.18; S 10.40.

***N*-(3-Azido-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (9c).** Yield 71%, mp 85–86°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.18 d (6H, CH**Me**$_2$, J = 6.6 Hz), 2.04 s (3H, 2-Me), 3.01–3.17 m (1H, C**H**Me$_2$), 7.36 s (1H, 6-H). ^{19}F NMR spectrum ($CFCl_3$): δ_F –79.12 ppm, s. Found, %: N 16.55, 16.60; S 9.48, 9.55. $C_{11}H_{11}F_3N_4O_3S$. Calculated, %: N 16.66; S 9.53.

***N*-(3-Azido-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (9d).** Yield 82%, mp 105–107°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.26 d (6H, CH**Me**$_2$, J = 7 Hz), 2.14 s (3H, 5-Me), 3.27–3.46 m (1H, C**H**Me$_2$), 7.43 s (1H, 6-H). ^{19}F NMR spectrum ($CFCl_3$): δ_F –79.22 ppm, s. Found, %: N 16.45, 16.51; S 9.48, 9.55. $C_{11}H_{11}F_3N_4O_3S$. Calculated, %: N 16.66; S 9.53.

***N*-(5-Azido-2,3-dimethyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (9e).** Yield 68%, mp 78–81°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.14 s (3H, 3-Me), 2.16 s (3H, 2-Me), 6.99 s (1H, 6-H). ^{19}F NMR spectrum ($CFCl_3$): δ_F –79.18 ppm, s. Found, %: N 18.11, 18.17; S 10.35, 10.41. $C_9H_7F_3N_4O_3S$. Calculated, %: N 18.18; S 10.40.

Intramolecular oxidation/reduction of compounds 6c–6e, 7c–7e, 15a, and 15b (*general procedure*). Compound **6c**–**6e**, **7c**–**7e**, **15a**, or **15b** was heated for 10–15 min in boiling glacial acetic acid, and the solution turned dark red or violet. The mixture was cooled and diluted with water, and the dark precipitate was recrystallized from benzene–hexane.

***N*-(3-Amino-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (10c).** Yield 85%, mp 99–101°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.15 d (6H, CH**Me**$_2$, J = 6.9 Hz), 1.86 s (3H, 2-Me), 2.90–3.02 m (1H, C**H**Me$_2$), 3.18 s (3H, CH_3SO_2), 5.06 br.s (2H, NH_2), 7.61 s (1H, 6-H). Found, %: N 10.89, 10.95; S 12.49, 12.52. $C_{11}H_{14}N_4O_3S$. Calculated, %: N 10.93; S 12.51.

***N*-(3-Amino-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (10d).** Yield 77%, mp 118–120°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.24 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.00 s (3H, 5-Me), 3.20–3.31 m (1H, C**H**Me$_2$), 3.20 s (3H, CH_3SO_2), 5.15 br.s (2H, NH_2), 7.64 s (1H, 6-H). Found, %: N 10.91, 10.97; S 12.45, 12.49. $C_{11}H_{14}N_4O_3S$. Calculated, %: N 10.93; S 12.51.

***N*-(5-Amino-2,3-dimethyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (10e).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.20 s (3H, 3-Me), 2.32 s (3H, 2-Me), 3.01 s (3H, CH_3SO_2), 5.98 br.s (2H, NH_2), 6.93 s (1H, 6-H).

***N*-(3-Amino-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (11c).** Yield 78%, mp 164–165°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 d (6H, CH**Me**$_2$, J = 6.9 Hz), 1.91 s (3H, 2-Me), 2.92–3.06 m (1H, C**H**Me$_2$), 5.36 br.s (2H, NH_2), 7.34 s (1H, 6-H). ^{19}F NMR spectrum ($CFCl_3$): δ_F –81.18 ppm, s. Found, %: N 9.01, 9.07; S 10.30, 10.40. $C_{11}H_{13}F_3N_2O_3S$. Calculated, %: N 9.03; S 10.33.

***N*-(3-Amino-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (11d).** Yield 55%, mp 106–107°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.26 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.05 s (3H, 5-Me), 2.92–3.10 m (1H, C**H**Me$_2$), 5.58 br.s (2H, NH_2), 7.37 s (1H, 6-H). ^{19}F NMR spectrum ($CFCl_3$): δ_F –79.76 ppm, s. Found, %: N 8.97, 9.02; S 10.28, 10.35. $C_{11}H_{13}F_3N_2O_3S$. Calculated, %: N 9.03; S 10.33.

***N*-(5-Amino-2,3-dimethyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (11e).** Yield 58%, mp 180–182°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.05 s (3H, 3-Me), 2.13 s (3H, 2-Me), 5.73 br.s (2H, NH_2), 6.45 s (1H, 6-H). ^{19}F NMR spectrum ($CFCl_3$): δ_F –79.87 ppm, s. Found, %: N 9.85, 9.95; S 11.30, 11.38. $C_9H_9F_3N_2O_3S$. Calculated, %: N 9.93; S 11.36.

***N*-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (12c).** Yield 64%, mp 140–142°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 d (6H, CH**Me**$_2$), 2.18 s (3H, 2-Me), 2.88 s (3H, $MeSO_2$), 3.03–3.16 m (1H, C**H**Me$_2$), 6.38 s (1H, 3-H), 6.43 s (1H, 6-H) 8.68 s (1H, NH), 9.31 s (1H, OH).

Found, %: N 5.71, 5.78; S 13.20, 13.26. $C_{11}H_{15}NO_3S$. Calculated, %: N 5.76; S 13.18.

***N*-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dienylidene)methanesulfonamide (12d).** Yield 58%, mp 130–131°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.09 d (6H, CH**Me**$_2$), 2.07 s (3H, 5-Me), 2.91 s (3H, $MeSO_2$), 3.28–3.65 m (1H, C**H**Me$_2$), 6.71 s (1H, 3-H), 6.92 s (1H, 6-H), 8.68 s (1H, NH), 9.30 s (1H, OH). Found, %: N 5.77, 5.83; S 13.20, 13.24. $C_{11}H_{15}NO_3S$. Calculated, %: N 5.76; S 13.18.

***N*-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (13c).** Yield 83%, mp 95–97°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.12 d (6H, CH**Me**$_2$), 2.18 s (3H, 2-Me), 3.01–3.17 m (1H, C**H**Me$_2$), 6.66 s (1H, 3-H), 6.88 s (1H, 6-H), 9.53 s (1H, NH), 10.94 s (1H, OH). ^{19}F NMR spectrum ($CFCl_3$): δ_F –76.83 ppm, s. Found, %: N 4.65, 4.70; S 10.64, 10.71. $C_{11}H_{14}F_3NO_3S$. Calculated, %: N 4.71; S 10.79.

***N*-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dienylidene)trifluoromethanesulfonamide (13d).** Yield 80%, mp 115–116°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.02 d (6H, CH**Me**$_2$), 2.06 s (3H, 5-Me), 3.01–3.25 m (1H, C**H**Me$_2$), 6.73 s (1H, 3-H), 6.85 s (1H, 6-H), 9.53 s (1H, NH), 10.78 br.s (1H, OH). ^{19}F NMR spectrum ($CFCl_3$): δ_F –75.82 ppm, s. Found, %: N 4.70, 4.74; S 10.69, 10.77. $C_{11}H_{14}F_3NO_3S$. Calculated, %: N 4.71; S 10.79.

***N*-(3-Amino-2,5-dimethyl-4-oxocyclohexa-2,5-dienylidene)benzenesulfonamide (17a).** Yield 74%, mp 203–204°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.82 s (3H, 2-Me), 2.13 d (3H, 5-Me, J = 1.8 Hz), 4.93 br.s (2H, NH_2), 7.46–8.05 m (5H, Ph), 7.91 q (1H, 6-H). Found, %: N 9.57, 9.62; S 10.96, 11.03. $C_{14}H_{14}N_2O_3S$. Calculated, %: N 9.65; S 11.04.

***N*-(5-Amino-2,3-dimethyl-4-oxocyclohexa-2,5-dienylidene)-4-methylbenzenesulfonamide (17b).** Yield 70%, mp 188–190°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.00 s (3H, 3-Me), 2.05 s (3H, 2-Me), 2.44 s (3H, 4′-Me), 5.48 br.s (2H, NH_2), 6.91 s (1H, 6-H), 7.32–7.88 d.d (4H, C_6H_4, J = 8.1 Hz). Found, %: N 9.10, 9.17; S 10.51, 10.60. $C_{15}H_{16}N_2O_3S$. Calculated, %: N 9.20; S 10.54.

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