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New tri-*tert*-alkyl substituted *o*-quinones of tetraline family

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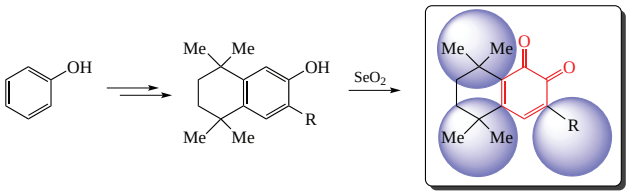
New tri-*tert*-alkyl substituted *o*-quinones of 3-*tert*-alkyl-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-1,2-dione chemotype were obtained from phenol and 2,5-dichloro-2,5-dimethylhexane, with the SeO_2 oxidation of the sterically hindered phenol moiety having been performed at the final step. The electrochemical reduction of these quinones proceeds in two stages: the first reduction wave ($E_{1/2}$ = –0.60 ÷ –0.62 V) is reversible, while the second stage is irreversible.

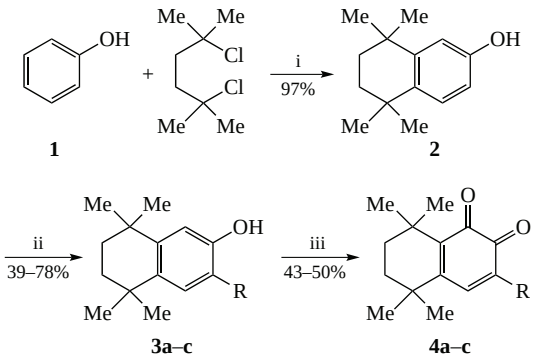


Keywords: *o*-quinones, phenol, tetralines, alkylation, oxidation, selenium dioxide, X-ray study, electrochemistry.

o-Quinones are important intermediates in many biological processes,[1,2] they are used as oxidizing agents of organic[3,4] and inorganic substrates,[5–7] and they possess different biological activities.[8] *tert*-Alkyl-substituted sterically hindered *o*-quinones occupy the special place. They are used as redox-active ligands in coordination chemistry[9,10] and as photoinitiators[11] and photoinhibitors[12] of radical processes controlled by visible light irradiation. The most studied 3,5-, 3,6- and 4,5-di-*tert*-alkyl-substituted *o*-quinones can serve as photoinitiators, however they undergo Michael addition with compounds of photo-polymerizable composition like alcohols, secondary and primary amines, thereby worsening the performance properties of the composition. The transition from di- to tri-alkyl substituted *o*-benzoquinones should reduce the reactivity of *o*-quinones in these reactions. Earlier, tri-alkyl-substituted *o*-quinones have been prepared by oxidation of the corresponding catechols. These *o*-quinones have either two *tert*-alkyl and one primary/secondary alkyl[13–15] or three secondary alkyl substituties.[16–18] The presence of primary and secondary alkyl substituents in the *o*-quinone structure allows one to isomerize them into *p*- or *o*-quinone methides.[19] These isomerizations are undesirable for *o*-quinone derivatives chemistry. We anticipate that tri-*tert*-alkyl substituted *o*-quinones can be resistant to such unwanted *o*-quinone reactions, however such compounds have not been previously reported. In this paper, we report on the synthesis of 3-*tert*-alkyl-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-1,2-diones, which are the first examples of tri-*tert*-alkyl-substituted *o*-quinones.

Compounds herein prepared contain 1,1,4,4-tetramethyl-butane-1,4-diyl fragment fused to positions 3 and 4 along with 6-positioned *tert*-alkyl fragment in the *o*-quinone structure. In principle, they could be prepared by oxidation of the corresponding 3,4,6-substituted catechol. However, a simple alkylation of catechol does not allow the synthesis of such *o*-quinones. The predominant products of catechol alkylation with tertiary alcohols (*tert*-butanol, *tert*-pentanol, 1-adamantanol) are 4-substituted products instead of the desired 3-substituted catechol.[20,21] The alkylation of catechol with 2,5-dimethyl-2,5-dichlorohexane leads to 4,5- but not to the desired 3,4-substituted catechols.[15] So, we suggest a different access to the target quinones, namely, the synthesis of 2,4,5-tri-alkyl-substituted phenols with further oxidation to quinone (Scheme 1). Alkylation of phenol **1** with 2,5-dimethyl-2,5-dichlorohexane in the presence of $AlBr_3$ afforded bicyclic phenol **2** of tetraline series. Its alkylation with tertiary alcohols in the presence of strong acids leads to 2,4,5-tri-alkyl-substituted phenols **3a–c** with high yield. Many oxidants were documented for the further oxidation of phenols to *o*-quinones.[22] In this study, we used SeO_2 in acetic acid to prepare *o*-quinones **4a–c**.

This strategy allowed us to obtain sterically ultra-hindered *o*-quinones **4a–c** from unsubstituted phenol **1** in three-step with an overall yield of up to 39%. These *o*-quinones have high solubility, even in hexane. The ^1H, ^{13}C NMR, and IR spectroscopy



Scheme 1 *Reagents and conditions*: i, $AlBr_3$, CH_2Cl_2, 0–5 °C; ii, ROH, H_2SO_4 (for **3a**,**b**) or CF_3COOH (for **3c**), 60 °C, 8 h; iii, SeO_2, AcOH, 100 °C, 20 h.

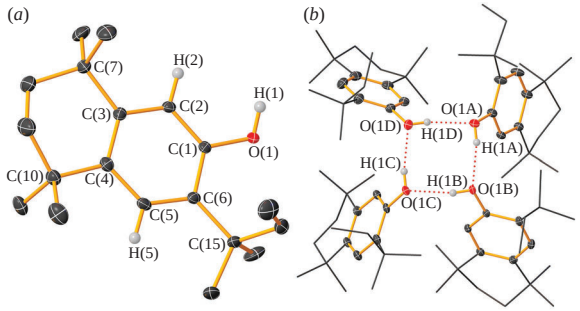


Figure 1 Molecular structure of (*a*) phenol **3b** and (*b*) its tetramer associate in the crystal. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are not shown except for H(1), H(2) and H(5). Selected bond lengths (Å) and angles (°): C(1)–O(1) 1.3911(18), O(1)–H(1) 0.80(2), C(1)–C(6) 1.404(2), C(6)–C(15) 1.541(2), C(1)–O(1)–H(1) 108.6(17), C(2)–C(1)–O(1) 118.88(14), C(2)–C(1)–C(6) 121.46(14), and C(5)–C(6)–C(15) 122.28(15).

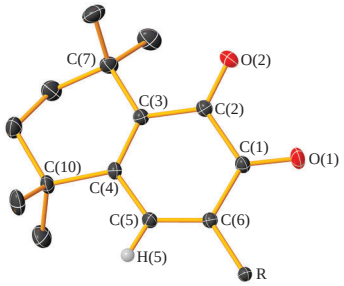


Figure 2 Molecular structure of *o*-quinones **4a**/**4c** (R = Bu^t/1-adamantyl) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are not shown except for H(5). Selected bond lengths (Å) and angles (°): C(1)–O(1) 1.213(4)/1.2169(15), C(2)–O(2) 1.230(4)/1.2197(14), C(1)–C(6) 1.472(5)/1.4759(16), C(6)–R 1.528(5)/1.5235(15), O(1)–C(1)–C(6) 124.8(3)/125.33(11), C(6)–C(1)–C(2) 118.2(3)/117.71(10), O(2)–C(2)–C(3) 123.4(5)/123.73(11), C(3)–C(2)–C(1) 119.8(3)/119.45(10).

data confirm the structures of new compounds. The crystals of **3b**, **4a** and **4c** were grown from hexane solution, and their molecular structures were determined by X-ray analysis.† Figure 1(*a*) shows the molecular structure of phenol **3b**. Four independent molecules (**A**–**D**) were observed in the crystal of **3b**. They form the ring structure [Figure 1(*b*)] *via* intermolecular hydrogen bonds with graph set notation $R_4^4(8)$.[23]

o-Quinones **4a** and **4c** have similar molecular structures (Figure 2). The alternation of bonds in the O(1)C(1–6)O(2) fragment confirms their quinonoid structures. The O(1)–C(1)–C(2)–O(2) torsion angles in **4a** and **4c** are 17.4° and 20.2°, respectively.

The electrochemical properties of compounds **4a**–**c** were studied by cyclic voltammetry (CV) in MeCN solutions. Figure 3 shows the CV curves of *o*-quinone **4c**. The first stage is reversible with the $E_{1/2}$ value of –0.62 V. This process corresponds to the reduction wave '*o*-quinone/*o*-benzosemiquinone' with the formation of stable radical anion *o*-benzosemiquinone. The second stage at –1.37 V is irreversible and corresponds to the reduction wave '*o*-benzosemiquinone/catecholate' with the protonation of the thus formed catecholate. The oxidation of protonated form of catecholate was observed at –0.33 V as the new anodic peak at the CV curve (see Figure 3). So, this form of CV curves is typical for *o*-quinones.[24,25]

The cathodic shift of the reduction potentials for tri-*tert*-alkyl-*o*-quinones compared to di-*tert*-alkyl- ($E_{1/2}$ = –0.51 V)[11,26] and tri-*sec*-alkyl-*o*-quinones ($E_{1/2}$ = –0.53 V)[17,18] is observed. The values of $E_{1/2}$ for **4a**, **4b** and **4c** are –0.60, –0.60 and –0.62 V, respectively. Thereby new *o*-quinones are weaker oxidants than di-*tert*-alkyl- and tri-*sec*-alkyl-*o*-quinones.

To conclude, three novel representatives of tri-*tert*-alkyl-*o*-quinones were synthesized in three simple steps, the key stage being the selenium dioxide oxidation of the intermediate tri-*tert*-alkylphenols. These *o*-quinones can be used as redox-active ligands to synthesize transition and non-transition metal complexes,[6,27] as redox-active components for creation of flow battery.[28] They are promising photoinitiators for one-stage curing of thick layers of acrylate resins under the action of visible light.[11]

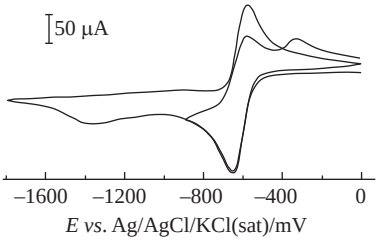


Figure 3 Cyclic voltammograms of compound **4c** in MeCN solution ([**4c**] = 0.005 M) in the ranges from –1.8 to 0.0 V and from –0.9 to 0.0 V, 0.1 M Bu_4NClO_4, argon, 20 °C, glassy carbon working electrode, 100 mV s^{-1}.

† *Crystal data for* **3b**. $C_{19}H_{30}O$, M = 274.43, triclinic, space group $P\bar{1}$, 100(2) K, a = 14.0868(6), b = 14.5367(6) and c = 19.9950(9) Å, α = 109.342(2)°, β = 97.588(2)°, γ = 109.642(2)°, V = 3499.5(3) Å^3, Z = 8, d_{calc} = 1.042 g cm^{-3}, F(000) = 1216. Colorless prism-shaped single crystal with dimensions 0.66 × 0.46 × 0.43 mm was selected and intensities of 48393 reflections were measured using a Bruker D8 Quest diffractometer (ω-scan, λ[MoKα] = 0.71073 Å, μ = 0.062 mm^{-1}, $2\theta_{max}$ = 57.52°). After merging of equivalents and absorption correction, 18045 independent reflections (R_{int} = 0.0319) were used for the structure solution and refinement. Final R factors: R_1 = 0.0666 [13047 reflections with $I > 2\sigma(I)$], wR_2 = 0.1836 (all reflections), GOF = 1.019.

Crystal data for **4a**. $C_{18}H_{26}O_2$, M = 274.39, monoclinic, space group $P2(1)/c$, 100(2) K, a = 5.9971(5), b = 19.5989(15) and c = 13.8438(10) Å, β = 90.628(3)°, V = 1627.1(2) Å^3, Z = 4, d_{calc} = 1.120 g cm^{-3}, F(000) = 600. Orange plate-shaped single crystal with dimensions 0.40 × 0.14 × 0.02 mm was selected and intensities of 18586 reflections were measured using a Bruker D8 Quest diffractometer (φ- and ω-scans, λ[MoKα] = 0.71073 Å, μ = 0.071 mm^{-1}, $2\theta_{max}$ = 50.19°). After merging of equivalents and absorption correction, 2840 independent reflections (R_{int} = 0.1035) were used for the structure solution and refinement. Final R factors: R_1 = 0.0956 [1883 reflections with $I > 2\sigma(I)$], wR_2 = 0.1945 (all reflections), GOF = 1.031.

Crystal data for **4c**. $C_{24}H_{32}O_2$, M = 352.49, monoclinic, space group $P2(1)/c$, 100(2) K, a = 6.5039(2), b = 21.4240(7) and c = 14.3529(5) Å, β = 99.261(1)°, V = 1973.86(11) Å^3, Z = 4, d_{calc} = 1.186 g cm^{-3}, F(000) = 768. Brown prism-shaped single crystal with dimensions 0.55 × 0.44 × 0.35 mm was selected and intensities of 25079 reflections were measured using a Bruker D8 Quest diffractometer (φ- and ω-scans, λ[MoKα] = 0.71073 Å, μ = 0.073 mm^{-1}, $2\theta_{max}$ = 56.00°). After merging of equivalents and absorption correction, 4763 independent reflections (R_{int} = 0.0275) were used for the structure solution and refinement. Final R factors: R_1 = 0.0465 [4104 reflections with $I > 2\sigma(I)$], wR_2 = 0.1222 (all reflections), GOF = 1.032.

The intensity data were collected by APEX3[29] and further integrated by the SAINT[30] program. SADABS[31,32] was used to perform area-detector scaling and absorption corrections. The structures were solved by a dual-space method with SHELXT program[33] and were refined by full-matrix technique on F^2 using SHELXTL[34] package. All non-hydrogen atoms were refined anisotropically. The H atoms were placed in the calculated positions and refined in the riding model except for those of OH groups in **3b**, located and refined isotropically from the difference Fourier synthesis of the electron density.

CCDC 2142056 (**3b**), 2142057 (**4a**) and 2142058 (**4c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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We dedicate this study to our teacher Academician G. A. Abakumov on the occasion of his 85th birthday.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.035.

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