Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2016, **26**, 552–554

Mendeleev Communications

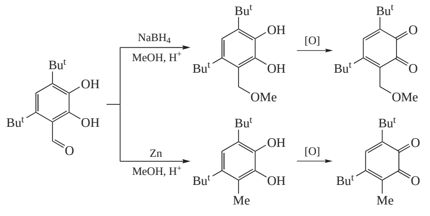
New sterically-hindered catechols/*o*-benzoquinones. Reduction of 4,6-di-*tert*-butyl-2,3-dihydroxybenzaldehyde

Maxim V. Arsenyev,* Eugene V. Baranov, Margarita P. Shurygina,
Sergey A. Chesnokov and Gleb A. Abakumov

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 603950 Nizhnii Novgorod, Russian Federation. Fax: +7 831 462 7497; e-mail: mars@iomc.ras.ru

DOI: 10.1016/j.mencom.2016.11.032

Reduction of aldehyde group in 4,6-di-*tert*-butyl-2,3-dihydroxybenzaldehyde leads to methoxymethyl ($NaBH_4$, MeOH) or methyl (Zn, MeOH) analogues, which were further oxidized into the corresponding *o*-benzoquinones. Their photostability in benzene increases substantially on replacement of the 6-positioned Me substituent with the CH_2OMe group.



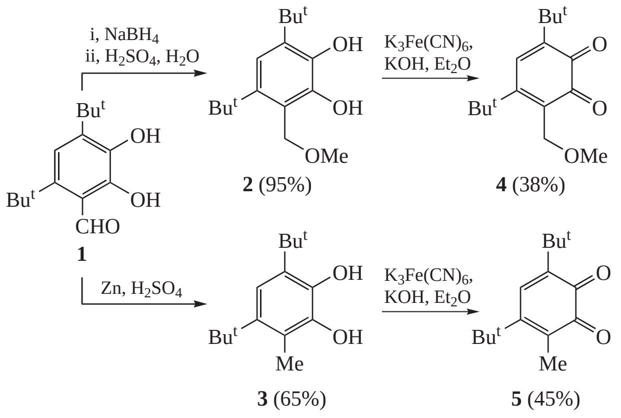
Alkylated catechols and their oxidized analogues, *o*-quinones, have been of interest for past few decades. The most explored *o*-quinones, 3,5- and 3,6-di-*tert*-butyl-*o*-benzoquinones (3,5-Q and 3,6-Q, respectively), are used as non-innocent ligands[1] and inhibitors or photoinitiators of free-radical polymerization.[2] The usual access to substituted sterically hindered catechols/*o*-quinones is addition of O-, N-, S-, C-nucleophiles to *o*-quinones. For example, 4-C-substituted 3,6-di-*tert*-butylcatechols were synthesized by the nucleophilic addition of organometallic compounds[3] or C–H acids[4] to 3,6-Q. The corresponding three-alkylated quinones would transform to *p*-quinomethide form (for example, 4-methyl-3,6-Q[3]) since substituent at 4-position contains a labile hydrogen atom. The natural three-alkylated quinones (*e.g.*, celastrol,[5] taxodione,[6] kendomycin[7]) and the oxidized forms of three-alkylated catechols (*e.g.*, barbatusol,[8] carnosol[9]) also exist in the *p*-quinomethide form.

Recently, three-alkylated catechols[10] were synthesized from 3,5-di-*tert*-butylcatechol by the Mannich reaction. The relative *o*-quinones are stable only in dry solution in the dark.

Previously, we have synthesized 4,6-di-*tert*-butyl-2,3-dihydroxybenzaldehyde **1** which seems to be a universal precursor for polyfunctional sterically hindered catechols.[11] The aldehyde group in **1** appreciably influences spectral and chemical properties of both catechol and the corresponding quinone. Reduction of aldehyde group should lead to localization of catechol π-system, so this method claims to be a simple synthetic way to three-alkylated catechols.

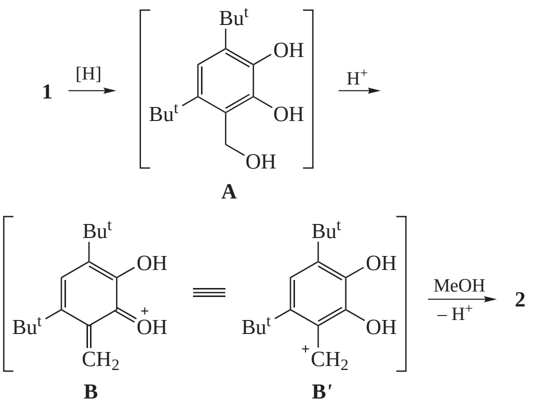
Herein, we report on the synthesis of two new three-alkylated catechols and two *o*-quinones from aldehyde **1** (Scheme 1). Treatment of **1** with $NaBH_4$ in methanol leads to a discoloration of reaction mixture. Instead of expected benzylic alcohol, methyl ether **2** was isolated after the addition of aqueous H_2SO_4 solution to the reaction mixture at room temperature.[†]

Apparently, ‘catecholbenzyl’ alcohol **A** is initially formed (Scheme 2). This compound, by the analogy with well known *o*-hydroxybenzyl alcohol, can be a precursor for *o*-quinomethide by the thermo- or photoinduced dehydration.[12] However, the formation of free *o*-quinomethide from **A** is unlikely under the reaction conditions (mixture of methanol and 20% aqueous solution of H_2SO_4, 25 °C). The more likely intermediate is a protonated form of corresponding *o*-quinomethide **B**, whose resonance structure is carbocation **B′** (see Scheme 2). Trapping methanol molecule gives ether **2**. The cation **B′** and its quinomethide, by analogy with 2,6-di-*tert*-butyl-*p*-quinomethide,[13] can be constitutive particles for the formation of new derivatives of 3,5-di-*tert*-butylcatechol. This synthetic way with the use of cation **B′** may be realized without protective groups in contrast to traditional methods for obtaining new catechols.[14]



Scheme 1

[†] *3,5-Di-*tert*-butyl-6-(methoxymethyl)catechol* **2**. 4,6-Di-*tert*-butyl-2,3-dihydroxybenzaldehyde[15] **1** (5.0 g, 20 mmol) was dissolved in methanol (200 ml) and $NaBH_4$ (4 × 0.38 g, 40 mmol) was added to the solution. The mixture was stirred for 30 min, then the 20% H_2SO_4 solution (100 ml) was added. The product was extracted with hexane (3 × 50 ml). The extract was dried with Na_2SO_4. The solvent was evaporated and the product was dried *in vacuo* to give light yellow powder. Yield 5.09 g (95%), mp 56–57 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.10 (s, 1H, OH), 6.87 (s, 1H, H_{Ar}), 5.97 (s, 1H, OH), 4.95 (s, 2H, CH_2), 3.52 (s, 3H, OMe), 1.42 and 1.38 (s, 2 × 9H, Bu^t). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 144.55, 142.08, 137.61, 133.96, 118.58, 115.55, 71.17, 58.19, 35.35, 34.92, 32.13, 29.45. IR (Nujol, ν/cm^{-1}): 3528, 3418, 3239 (OH), 1620, 1571 (C_{Ar}–C), 1261, 1057 (C–O), 889, 869. Found (%): C, 72.02; H, 9.90. Calc. for $C_{16}H_{26}O_3$ (%): C, 72.14; H, 9.84.



Scheme 2

Treatment of **1** with Zn/H_2SO_4 in methanol causes reduction of aldehyde group into a methyl one and affords catechol **3** in high yield (see Scheme 1).[‡] Ether **2** also forms under such conditions in amount less than 5% (NMR data).

Changing C^6-positioned aldehyde group in **1** to CH_2OMe and Me groups in catechols **2** and **3**, respectively, shifts dramatically the signals of phenolic protons in ^1H NMR spectra. The signals of O^1H^1 and O^2H^2 protons are observed at 10.71 and 5.99 ppm for **1**;[15] 8.10 and 5.97 ppm for **2**; 5.53 and 4.81 ppm for **3**. These values indicate decreasing H-bonding between H^1 and O^3 for compounds **1** and **2** and the absence of such H-bond in compound **3**.

Oxidation of catechols **2** and **3** with $K_3Fe(CN)_6$ at pH > 7 leads to new *o*-quinones **4** and **5** in 38% and 45% yields, respectively (see Scheme 1).[§] The catechol fragment is oxidized easier than a substituent at C^6 under these conditions. Three characteristic vibration bands are observed at 1610–1680 cm^{-1} in IR spectra of quinones **4** and **5**. Two signals of carbonyl groups manifest themselves in ^{13}C NMR spectra: at 182.48, 179.57 and 182.99, 180.24 ppm for **4** and **5**, respectively. The UV spectra reveal two characteristic bands with maxima at 403 nm (lgε = = 3.39) and 580 nm (lgε = 1.85) for **4** and at 421 nm (lgε = 3.27) and 576 nm (lgε = 1.85) for **5**, which can be attributed to π–π* and n–π* transitions, respectively.[16]

The single crystals of quinones **4** and **5** were grown and investigated by X-ray analysis (Figure 1).[¶] The bond distances and angles in O(1,2)C(1–6) fragments for **4** and **5** are typical of *o*-quinones: the values of C–O distances are characteristic of a double bond, and the explicit alternation of short and long C–C distances in six-membered ring C(1–6) is observed.

The *o*-quinone fragment in **4** is more planar than that in **5**. Atoms O(1) and O(2) of **4** lie in the C(1–6) plane and these atoms deviate out from six-membered ring at 0.009(1) and 0.003(1) Å, respectively. The corresponding values of deviation for **5** are 0.159(1) and 0.102(1) Å, respectively. The torsion angles O(1)–C(1)–C(2)–O(2) are 0.5° for **4** and 8.3° for **5**. The distances of C(5)–Bu^t bonds [1.5456(11) (**4**) and 1.5473(10) Å (**5**)] are longer than C(3)–Bu^t [1.5263(11) (**4**) and 1.5271(10) Å (**5**)]. Apparently, this fact represents steric repulsion between *tert*-butyl group at C(5) and substituent at C(6). Methoxy group C(16)O(3) in **4** is located out of the quinone plane and torsion angle C(1)–C(6)–C(15)–O(3) is 77.8(1)°.

All quinones undergo the photodegradation in aprotic solvents under both the UV and visible light irradiation. It was demonstrated on the series of 3,6-Q derivatives that the *o*-quinones photorearrange to bicyclo[3.1.0]hex-3-ene-2,6-dione **6** under light with λ > 520 nm [the absorption band corresponding to the

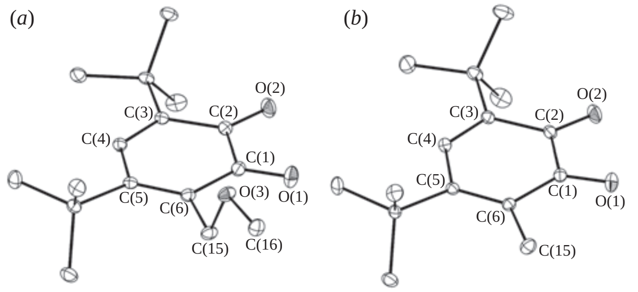


Figure 1 Molecular structures of *o*-quinones (*a*) **4** and (*b*) **5**. Thermal ellipsoids are given with 30% probability. Hydrogen atoms are not shown.

[‡] *3,5-Di*-tert-*butyl-6-methylcatechol* **3**. The water solution of H_2SO_4 (50%, 25 ml) was added dropwise to the methanolic solution (200 ml) of 4,6-di-*tert*-butyl-2,3-dihydroxybenzaldehyde **1** (5.0 g) with Zn (granular, 13 g, 0.2 mol) with vigorous stirring for 2 h. The colour of the solution changed from bright yellow to pale brown. Methanol was evaporated and the product was extracted with hexane. The extract was dried with Na_2SO_4. The solvent was evaporated. The crude product (~4.7 g) contained 5% of compound **2**. Pure product was obtained by the recrystallization from hexane, white crystals, yield 3.2 g (68%), mp 88–90 °C. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.95 (s, 1H, H_{Ar}) , 5.53 (s, 1H, OH), 4.81 (s, 1H, OH), 2.41 (s, 3H, Me), 1.44 and 1.42 (s, 2 × 9 H, Bu^t). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 142.61, 140.89, 139.08, 132.13, 120.00, 116.12, 35.70, 34.69, 31.40, 29.84, 14.51. IR (Nujol, ν/cm^{-1}): 3160–3400 (OH), 1616 (C_{Ar}–C), 852. Found (%): C, 76.12; H, 10.35. Calc. for $C_{15}H_{24}O_2$ (%): C, 76.23; H, 10.24.

[§] *3,5-Di*-tert-*butyl-6-methoxymethyl*-o-*benzoquinone* **4**. The solutions of **2** (2.68 g, 10 mmol) in Et_2O and $K_3Fe(CN)_6$ (16.45 g, 50 mmol) with KOH (1.16 g, 20 mmol) in water (200 ml) were vigorously stirred for 30 min. Then the mixture was washed with water (3 × 100 ml) and the ethereal layer was dried with Na_2SO_4. The solvent was evaporated and the product was crystallized from hexane solution (5 ml). The powder was filtered, washed with cold hexane and dried *in vacuo*. Red-green crystals, yield 1.01 g (38%), mp 43–45 °C. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.08 (s, 1H, CH), 4.36 (s, 2H, CH_2), 3.35 (s, 3H, OMe), 1.38 and 1.23 (s, 2 × 9 H, Bu^t). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 182.48, 179.57, 159.71, 148.66, 137.12, 132.59, 63.87, 58.45, 38.70, 35.41, 30.02, 29.10. IR (Nujol, ν/cm^{-1}): 1676, 1653, 1614 (C=O and C=C), 1230, 1098 (CH_2OMe). Found (%): C, 72.60; H, 9.19. Calc. for $C_{16}H_{24}O_3$ (%): C, 72.69; H, 9.15.

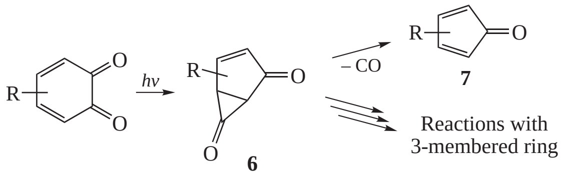
3,5-Di-tert-*butyl-6-methyl*-o-*benzoquinone* **5** was synthesized in the same manner as compound **4**. Green crystals, yield 1.05 g (45%), mp 47–49 °C. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.06 (s, 1H, CH) , 2.09 (s, 3H, Me), 1.34 and 1.22 (s, 2 × 9 H, Bu^t). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 182.99, 180.24, 154.96, 146.41, 137.29, 133.55, 37.32, 35.19, 30.02, 29.17, 13.82. IR (Nujol, ν/cm^{-1}): 1674, 1646, 1612 (C=O and C=C). Found (%): C, 76.78; H, 9.50. Calc. for $C_{15}H_{22}O_2$ (%): C, 76.88; H, 9.46.

[¶] *X-ray diffraction studies*. The crystals suitable for X-ray analysis were grown in hexane. The X-ray data were collected on an automatic Agilent Xcalibur E diffractometer (graphite-monochromated, MoKα-radiation, ω-scan technique, λ = 0.71073 Å) at 100 K. The intensity data were integrated by CrysAlisPro[19] program. SADABS[20] for **4** and SCALE3 ABSPACK[21] for **5** were used to perform area-detector scaling and absorption corrections. The structures were solved by dual-space method with SHELXT program[22] and were refined on F^2 using SHELXTL[23] package. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. The hydrogen atoms were placed in calculated positions and were refined in the riding model.

Crystal data for **4**. $C_{16}H_{24}O_3$, M = 264.35, crystal size 0.5 × 0.4 × 0.1 mm, monoclinic, space group $P2_1/c$, at 100 K: a = 10.5604(4), b = 13.2743(4) and c = 11.6629(4) Å, β = 114.921(4)°, V = 1482.73(10) Å^3, Z = 4, d_{calc} = 1.184 g cm^{-3}, μ = 0.08 mm^{-1}, F(000) = 576, 2θ = 60.9°, R_{int} = = 4491 (0.0482), R_1 [$I > 2\sigma(I)$] = 0.0382, wR_2 (all data) = 0.1054. Largest diff. peak and hole, e/Å^3 = 0.407/–0.189.

Crystal data for **5**. $C_{16}H_{22}O_2$, M = 234.32, crystal size 0.5 × 0.3 × 0.3 mm, monoclinic, space group $P2_1/n$, at 100 K: a = 9.5020(2), b = 12.0120(2) and c = 12.7785(3) Å, β = 109.101(2)°, V = 1378.21(5) Å^3, Z = 4, d_{calc} = = 1.129 g cm^{-3}, μ = 0.073 mm^{-1}, F(000) = 512, 2θ = 60°, R_{int} = 4004 (0.0377), R_1 [$I > 2\sigma(I)$] = 0.038, wR_2 (all data) = 0.110. Largest diff. peak and hole, e/Å^3 = 0.446/–0.168.

CCDC 1479163 and 1479164 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.



Scheme 3

$S(n \to \pi^*)$ electronic transition of carbonyl groups]. Further the intermediate **6** undergoes a decarbonylation with a formation of the corresponding cyclopentadienone **7** (in the case of 3,6-Q derivatives), or other reactions related to the opening of three-membered ring (in the case of 3,5-di-*tert*-butyl-*o*-benzoquinone)[17] (Scheme 3). The irradiation of **4** and **5** in benzene solutions leads to products which cannot be unambiguously identified by NMR spectroscopy. The investigation of photodegradation of 3,6-Q and *o*-quinones **4** and **5** in benzene[††] showed that the effective rate constants of photolysis of these quinones are 1.24×10^{-5}, 0.48×10^{-5} and 2.3×10^{-5} s^{-1}, respectively, and thus, the ratio of these values is 1 : 0.4 : 1.8. In other words, the photostability ($\lambda > 520$ nm) of *o*-quinone **4** in benzene solution is 4.5 times higher as compared to **5** and two times higher than for 3,6-Q. The reason for such differences in the *o*-quinone photostability has not been unambiguously established. Earlier, it was demonstrated on the series of 3,6-Q derivatives, that one of photostability criteria is a coplanarity of *o*-quinone fragment, in particular, the value of torsion angle between carbonyl groups:[18] increasing value of this torsion angle results in decreasing photostability of *o*-quinone. The values of torsion angle O(1)–C(1)–C(2)–O(2) are 1.1, 0.5 and 8.3° for 3,6-Q, **4** and **5**, respectively. Thus, this structural parameter can be used for prediction of photostability of different *o*-benzoquinones at a qualitative level.

In conclusion, two new three-alkylated catechols, 3,5-di-*tert*-butylcatechol derivatives, and the corresponding *o*-quinones have been synthesized. The proposed mechanism of the reactions involves the formation of relatively stable catecholbenzylic carbocation as intermediate. Photostability of new *o*-quinones in benzene correlates with the value of torsion angle between carbonyl groups.

The equipment of the center for collective use ‘Analytical Center IOMC RAS’ (Nizhnii Novgorod) was used in this study.

This work was supported by the Russian Science Foundation (project no. 15-13-00137).

References

1 (*a*) C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45; (*b*) C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **219**, 415; (*c*) P. Zanello and M. Corsini, *Coord. Chem. Rev.*, 2006, **250**, 2000; (*d*) C. G. Pierpont and C. W. Lange, *Prog. Inorg. Chem.*, 1994, **41**, 331; (*e*) C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **216–217**, 99; (*f*) O. Sato, J. Tao and Y. Z. Zhang, *Angew. Chem. Int. Ed.*, 2007, **46**, 2152; (*g*) A. I. Poddel’sky, V. K. Cherkasov and G. A. Abakumov, *Coord. Chem. Rev.*, 2009, **253**, 291.

2 (*a*) N. Yu. Shushunova and S. A. Chesnokov, *Polym. Sci., Ser. B*, 2009, **51**, 427 (*Vysokomol. Soedin., Ser. B*, 2009, **51**, 2135); (*b*) S. A. Chesnokov, V. K. Cherkasov, G. A. Abakumov, O. N. Mamysheva, M. Yu. Zakharina, N. Yu. Shushunova, Yu. V. Chechet and V. A. Kuropatov, *Polym. Sci., Ser. B*, 2014, **56**, 11 (*Vysokomol. Soedin., Ser. B.*, 2014, **56**, 13); (*c*) G. A. Abakumov, O. N. Mamysheva, V. A. Muraev, V. D. Tikhonov, V. K. Cherkasov and S. A. Chesnokov, *RF Patent 2138070*, 1999; (*d*) G. A. Abakumov, O. N. Mamysheva, S. N. Mensov, Yu. V. Polushtajtsev and S. A. Chesnokov, *RF Patent 2472189*, 2011; (*e*) S. A. Chesnokov, S. N. Mensov, G. A. Abakumov, R. S. Kovylin, M. A. Baten’kin, A. N. Konev and Yu. V. Chechet, *RF Patent 2525908*, 2013.

3 (*a*) G. A. Abakumov, V. K. Cherkasov, L. G. Abakumova, N. O. Druzhkov, V. I. Nevodchikov, Yu. A. Kurskii and N. P. Makarenko, *Metalloorg. Khim.*, 1991, **4**, 925 (in Russian); (*b*) G. A. Abakumov, V. K. Cherkasov, L. G. Abakumova, V. I. Nevodchikov, N. O. Druzhkov, N. P. Makarenko and Ju. A. Kursky, *J. Organomet. Chem.*, 1995, **491**, 127.

4 (*a*) G. A. Abakumov, V. I. Nevodchikov, N. V. Zaitova, N. O. Druzhkov, L. G. Abakumova, Yu. A. Kurskii and V. K. Cherkasov, *Russ. Chem. Bull.*, 1997, **46**, 337 (*Izv. Akad. Nauk, Ser. Khim.*, 1997, 351); (*b*) G. A. Abakumov, V. I. Nevodchikov, N. V. Zaitova, N. O. Druzhkov, L. G. Abakumova, Yu. A. Kurskii and V. K. Cherkasov, *Russ. Chem. Bull.*, 1997, **46**, 2093 (*Izv. Akad. Nauk, Ser. Khim.*, 1997, 2206).

5 (*a*) L. Klaic, R. I. Morimoto and R. B. Silverman, *ACS Chem. Biol.*, 2012, **7**, 928; (*b*) A. M. Camelio, T. C. Johnson and D. Siegel, *J. Am. Chem. Soc.*, 2015, **137**, 11864.

6 (*a*) F. Schaller, L. Rahalison, N. Islam, O. Potterat, K. Hostettmann, H. Stoeckli-Evans and S. Mavi, *Helv. Chim. Acta*, 2000, **83**, 407; (*b*) A. J. Sanchez and J. P. Konopelski, *J. Org. Chem.*, 1994, **59**, 5445.

7 (*a*) J. T. Lowe and J. S. Panek, *Org. Lett.*, 2008, **10**, 3813; (*b*) H. J. Martin, T. Magauer and J. Mulzer, *Angew. Chem. Int. Ed.*, 2010, **49**, 5614; (*c*) T. Sengoku, S. Xu, K. Ogura, Y. Emori, K. Kitada, D. Uemura and H. Arimoto, *Angew. Chem. Int. Ed.*, 2014, **53**, 4213.

8 G. Majetich and G. Zou, *Org. Lett.*, 2008, **10**, 81.

9 (*a*) S. M. Petiwala and J. J. Johnson, *Cancer Lett.*, 2015, **367**, 93; (*b*) J. G. Marrero, L. Moujir, L. S. Andres, N. P. Montano, L. Araujo and J. G. Luis, *J. Nat. Prod.*, 2009, **72**, 1385.

10 Yu. A. Sayapin, I. O. Tupaeva, V. V. Tkachev and G. V. Shilov, *Russ. J. Org. Chem.*, 2016, **52**, 214 (*Zh. Org. Khim.*, 2016, **52**, 231).

11 M. V. Arsenyev, E. V. Baranov, S. A. Chesnokov, V. K. Cherkasov and G. A. Abakumov, *Russ. Chem. Bull, Int. Ed.*, 2013, **62**, 2394 (*Izv. Akad. Nauk, Ser. Khim.*, 2013, 2394).

12 (*a*) M. S. Singh, A. Nagaraju, N. Ananda and S. Chowdhury, *RSC Adv.*, 2014, **4**, 55924; (*b*) E. Dorrestijn, M. Kranenburg, M. V. Ciriano and P. Mulder, *J. Org. Chem.*, 1999, **64**, 3012.

13 S. V. Bukharov, G. N. Nugumanova, N. A. Mukmeneva, A. R. Burilov, E. M. Kasymova, M. A. Pudovik and A. I. Konovalov, *Zh. Org. Khim.*, 2004, **40**, 327 (in Russian).

14 (*a*) A. E. V. Gorden, J. Xu, K. N. Raymond and P. Durbin, *Chem. Rev.*, 2003, **103**, 4207; (*b*) Q. Zhang, B. Jin, R. Peng, S. Lei and S. Chu, *Mendeleev Commun.*, 2015, **25**, 204.

15 M. V. Arsenyev, E. V. Baranov, A. Yu. Fedorov, S. A. Chesnokov and G. A. Abakumov, *Mendeleev Commun.*, 2015, **25**, 312.

16 (*a*) J. A. Barltop and J. D. Coyle, *Excited States in Organic Chemistry*, Wiley, London, 1975; (*b*) S. A. Chesnokov, V. K. Cherkasov, Yu. V. Chechet, N. I. Nevodchikov, G. A. Abakumov, O. N. Mamysheva and V. A. Muraev, *Russ. Chem. Bull, Int. Ed.*, 2000, **49**, 1506 (*Izv. Akad. Nauk, Ser. Khim.*, 2000, 1515).

17 (*a*) M. P. Shurygina, Yu. A. Kurskii, N. O. Druzhkov, S. A. Chesnokov and G. A. Abakumov, *High Energy Chem.*, 2010, **44**, 234 (*Khim. Vys. Energ.*, 2010, **44**, 262); (*b*) S. V. Klement’eva, G. K. Fukin, E. V. Baranov, V. K. Cherkasov and G. A. Abakumov, *High Energy Chem.*, 2011, **45**, 423 (*Khim. Vys. Energ.*, 2011, **45**, 457); (*c*) V. B. Vol’eva, I. S. Belostotskaya, N. L. Komissarova, Z. A. Starikova and L. N. Kurkovskaya, *Russ. J. Org. Chem.*, 2006, **42**, 227 (*Zh. Org. Khim.*, 2006, **42**, 243); (*d*) O. G. Mishchenko, S. V. Maslennikov, I. V. Spirina, N. O. Druzkov and Yu. A. Kurskii, *Russ. J. Gen. Chem.*, 2007, **77**, 2140 (*Zh. Obshch. Khim.*, 2007, **77**, 1997).

18 G. K. Fukin, A. V. Cherkasov, M. P. Shurygina, N. O. Druzhkov, V. A. Kuropatov, S. A. Chesnokov and G. A. Abakumov, *Struct. Chem.*, 2010, **21**, 607.

19 *Data Collection. Reduction and Correction Program. CrysAlisPro Software Package*, Agilent Technologies, Oxford, UK, 2012.

20 G. M. Sheldrick, *SADABS-2014/2. Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, USA, 2012.

21 *SCALE3 ABSPACK: Empirical Absorption Correction, CrysAlisPro Software Package*, Agilent Technologies, Oxford, UK, 2012.

22 G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3.

23 G. M. Sheldrick, *SHELXTL v. 6.14, Structure Determination Software Suite*, Bruker AXS, Madison, USA, 2003.

Received: 17th May 2016; Com. 16/4938

[††] The kinetic studies of *o*-benzoquinones photodegradation were carried out by UV spectroscopy using *o*-quinone absorption band. The benzene solutions of *o*-quinones (5×10^{-4} mol dm^{-3}) were degassed, saturated with Ar, and irradiated in air (lamp KGM-24-150, illuminance 16 kLx, filter ZhS-16, $\lambda > 520$ nm). The effective rate constants of *o*-quinone photodegradation were determined by the slope of the straight section depending $\ln([Q_0]/[Q_t])$ *vs*. t, where $[Q]$ is the concentration of *o*-benzoquinones to exposure and t is the total exposition time of irradiation of the solution. The values of the effective rate constants were averaged in three dimensions at the convergence of the results within 10%.