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Photolytic decarbonylation of *o*-benzoquinones

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ABSTRACT

It was established that photodecarbonylation of *o*-benzoquinones occurs by irradiation not only by UV-light, but visible light ($\lambda > 520$ nm) too. Study of the series of 4,5-di-substituted 3,6-di-*tert*-butyl-*o*-benzoquinones detected that the only product of photoreaction is the corresponding 3,4-di-substituted 2,5-di-*tert*-butyl-cyclopentadienone, which is formed in a yield close to quantitative. NMR monitoring of reaction of photodecarbonylation of *o*-benzoquinones detected that this is a two-stage process. In the first stage the photoexcited molecule of quinone rearranges into bicyclo compound (bicyclo[1.3.0]hexa-3-en-2,6-dione) containing five- and three- membered cycles, which spontaneously decomposes during the following dark stage into cyclopentadienone and a molecule of CO.

1. Introduction

Articles[1–4] dedicated to the photodecarbonylation of quinones describe studies of reactions occurring under UV-radiation. The following is known about the products of the decarbonylation reaction of *o*-benzoquinones: irradiation ($\lambda=254$ and 320 nm) of unsubstituted *o*-benzoquinone in an argon matrix ($T=10$ K) leads to the formation of cyclopenta-2,4-dienone.[2] It was established that 3,6-di-*tert*-butyl-*o*-benzoquinone decomposes to 2,5-di-*tert*-butyl-cyclopentadienone with CO elimination.[3] It is suggested[4,5] that irradiation ($\lambda<405$ nm) of a hexane solution of 3,5-di-*tert*-butyl-*o*-benzoquinone leads to formation of the corresponding 2,4-di-*tert*-butyl-cyclopentadienone (it was concluded on the base of fixation of the product of dimerization of 2,4-di-*tert*-butyl-cyclopentadienone by Diels–Alder reaction ($2\pi+4\pi$ addition)). Thus, reaction of decarbonylation of *o*-benzoquinones can be considered as method of synthesis of cyclopentadienones, which are widely used as ligands for organometallic compounds[6–14] and as reagents for binding of singlet oxygen.[15] Here, we report studies on the mechanism of decarbonylation of 3,6-di-*tert*-butyl-*o*-benzoquinone and its 4,5-derivatives under irradiation by visible light ($\lambda>520$ nm).

2. Results and discussion

The photolysis of series of benzene solutions of sterically hindered *o*-benzoquinones (**1**), such as 3,6-di-*tert*-butyl-*o*-benzoquinone (**1a**), 4,5-di-fluoro-3,6-di-*tert*-butyl-*o*-benzoquinone (**1b**), 4,5-di-chloro-3,6-di-*tert*-butyl-*o*-benzoquinone (**1c**), 4,5-di-methoxy-3,6-di-*tert*-butyl-*o*-benzoquinone (**1d**), 5,8-di-*tert*-butyl-2,3-dihydrobenzo-1,4-dioxine-6,7-dione (**1e**), 4,7-di-*tert*-butylbenzo-1,3-dithiole-2,5,6-trione (**1f**) and 5,8-di-*tert*-butyl-2,3-dihydro-1,4-ethanoquinoxaline-6,7-dion (**1g**) was studied upon irradiation with light, $\lambda>520$ nm. We established that *o*-benzoquinones undergo photochemical conversion under irradiation not only by UV-light, but also by natural light, $\lambda>520$ nm. It leads to decoloration of the quinone solution. Selection of benzene as solvent was determined by the relatively large energy of the C–H bond. It excludes the possibility of participation of *o*-benzoquinone in photoreduction.[16–18] The typical changes in the spectral characteristics of benzene solution of 4,5-di-chloro-3,6-di-*tert*-butyl-*o*-benzoquinone are presented in Figure 1.

A decrease in the absorption bands intensities of quinone is accompanied by an increase of the absorption of solution in $440<\lambda<500$ nm region (this absorption band is attributed to the product of photoreaction; the spectrum does not change more than this), which is followed by appearance of two distinct isobestic points. The presence of isobestic points was observed in the photolysis of all *o*-benzoquinones (excluding **1d**).

NMR monitoring of the photoreaction of all *o*-benzoquinones detected that decarbonylation occurs in all cases to give a single (the main for **1d**) final product—the corresponding 3,4-di-substituted 2,5-di-*tert*-butyl-cyclopentadienones (**2**) (Scheme 1).

At room temperature, all 3,4-di-substituted 2,5-di-*tert*-butyl-cyclopentadienones are formed with yields close to quantitative. The products of photolysis of *o*-benzoquinones were isolated and

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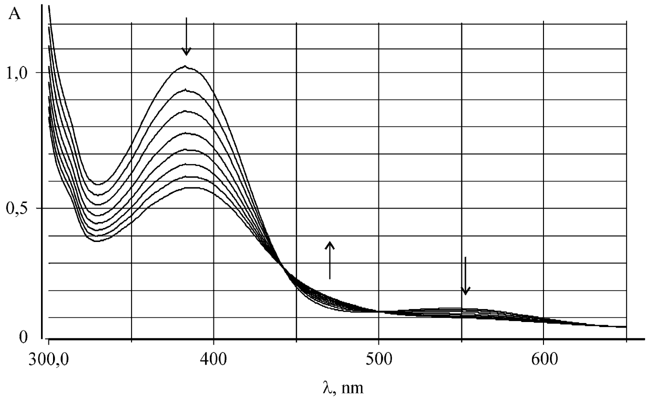
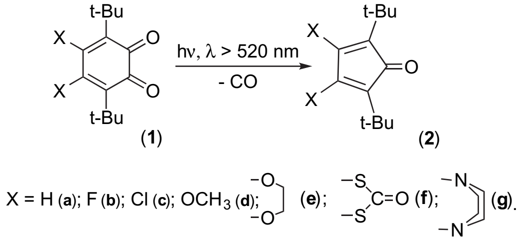


Figure 1. Spectral changes upon irradiation with the light, λ>520 nm, at equal time intervals (60 s) of benzene solution of 4,5-di-chloro-3,6-di-*tert*-butyl-*o*-benzoquinone (5×10^{-4} M) (deaerated solution was saturated with Ar, 298 K).



Scheme 1.

characterized by IR, NMR spectroscopy and element analysis (see Section 3).

The detailed NMR study of reaction of *o*-benzoquinones allowed us to detect the formation of an unstable intermediate product. The NMR spectra illustrating the evolution of phototransformation of quinone **1d** is shown in Figure 2. The irradiation (yellow light, λ>520 nm for 20 h) of a benzene solution of **1d** (in deaerated and soldered NMR tube) (Fig. 2a) results in the almost total disappearance of signals of the initial quinone (Fig. 2b). Simultaneously, the appearance of new signals attributed to protons of the *tert*-butyl groups (δ=1.39 ppm), methoxy groups (δ=3.32 ppm) of 3,4-di-methoxy-2,5-di-*tert*-butyl-cyclopentadienone (**2d**) and nonequivalent protons of two *tert*-butyl groups (δ=1.13 and 1.23 ppm) and two methoxy groups (δ=3.16 and 3.53 ppm), conceivably, of 1,3-di-*tert*-butyl-4,5-di-methoxy-bicyclo[3.1.0]hexa-3-en-2,6-dione (**3**) (Scheme 2) were observed in the ^{1}H NMR spectrum (Fig. 2b). Heating (at 333 K for 10 h) of reaction mixture leads to almost total disappearance of signals of protons of compound **3** and simultaneous accumulation of signals attributed to **2d** (Fig. 2c).

Earlier[2] the formation of intermediate, hexa-1,3,5-triene-1,6-dione, at the investigation of reaction of photodecarbonylation of unsubstituted *o*-benzoquinone in argon matrix (10 K) by UV-light was observed. However, the ^{1}H NMR spectrum of the intermediate, the product of decomposition of **1d**, contains signals of the nonequivalent protons of *tert*-butyl groups, which exclude the possibility of formation of derived hexa-1,3,5-triene-1,6-dione. Apparently photodecarbonylation of substituted *o*-benzoquinones in the solution at T=298 K occur in other way, namely, through formation of intermediate, which has the structure of bicyclo[3.1.0]hexane. Formation of bicyclo[3.1.0]hexane-type compounds is described in reports dedicated to photochemistry of various cyclohexanenones[19–21] and cyclohexanedienones.[22–24] It is supposed[16] that rearrangement of cyclohexanenones and cyclohexanedienones occur through the triplet excited state (n, π*) with the formation of transient zwitterion and is similar to di-π-methyne rearrangement of 1,4-dienes.[25–27] The rearrangement of *o*-benzoquinone into bicyclo[3.1.0]hexane-3-en-2,6-dione was unknown until the present investigation.

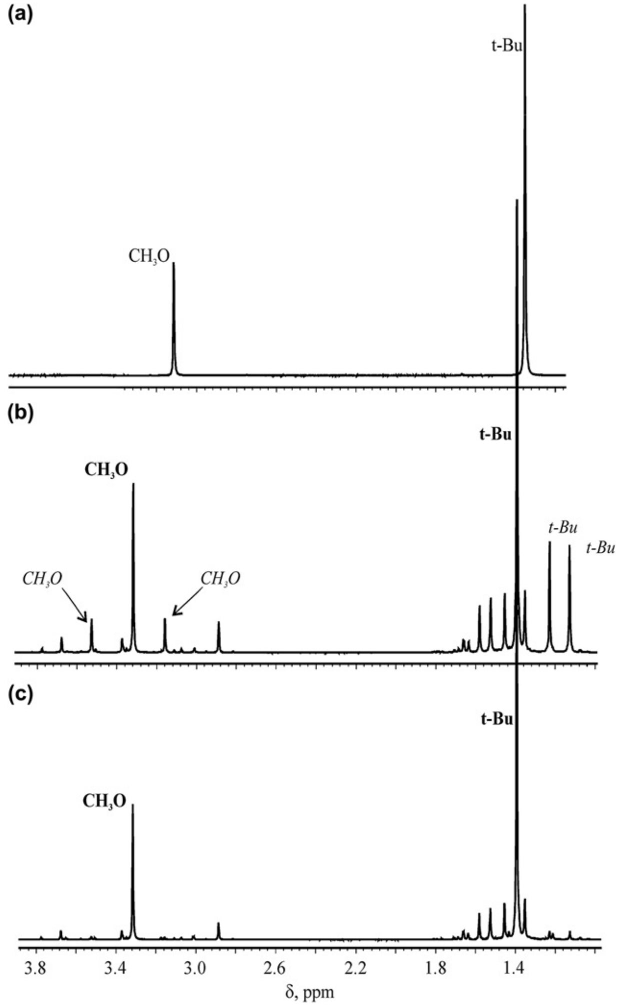
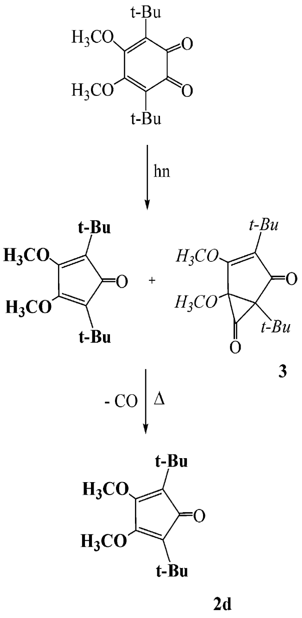


Figure 2. Changes in the ^{1}H NMR spectrum of a solution of 4,5-di-methoxy-3,6-di-*tert*-butyl-*o*-benzoquinone (1×10^{-2} M, C_6D_6, T=298 K) before irradiation (a); after 20 h of irradiation by light, λ>520 nm (b); after heating at 333 K during 10 h (c). (Labels: the protons of *tert*-butyl groups and methoxy groups of 3,4-di-methoxy-2,5-di-*tert*-butyl-cyclopentadienone (**2d**) marked by bold; the protons of *tert*-butyl groups and methoxy groups of 1,3-di-*tert*-butyl-4,5-di-methoxy-bicyclo[3.1.0]hexa-3-en-2,6-dione (**3**) marked by italic).

To isolate compound **3** the following experiment was carried out. The irradiation of solution of **1d** at low temperature (284 K) leads to the formation of mixture containing **2d** and **3** in the ratio 2:1. Unfortunately, we were unable to isolate **3**. The NMR tube containing deaerated solution of this mixture in benzene with CH_2Cl_2 as internal standard was heated at T=368 K for 1.5 h in the dark. Under these conditions conversion of compound **3** into **2d** was equal to 98%. Thus, in the case of photolysis, quinone itself does not undergo decarbonylation but rather CO is lost from the bicyclo compound formed from photoexcited molecule of *o*-benzoquinone; removal of CO occurs not from the cyclohexanediendione but from the cyclopropane ring. Thus, compound **2d** is the single product of thermal decomposition of **3**.

Long-term irradiation (284 K, λ>520 nm, 100 h) of 4,5-di-methoxy-3,6-di-*tert*-butyl-*o*-benzoquinone results in the formation of 2,3a,6,8-tetra-*tert*-butyl-1,9,9a,9b-tetra-methoxy-9a,9b-di-hydrocyclopentachromene-3,4,7-(3a*H*)-trione (**4**)—another product of photoreaction. Compound **4** was isolated as colourless crystals and analyzed by IR, NMR spectroscopy, element analysis and X-ray



Scheme 2.

diffraction study (Fig. 3). In the ^{1}H NMR spectra (Fig. 2b and c) weak signals in the range δ=1.35–1.58 ppm was attributed to protons of the four nonequivalent *tert*-butyl groups and in the range δ=2.89, 3.37 and 3.68 ppm of four methoxy groups of compound **4** was observed. X-ray analysis has shown that long-term irradiation forms a tricyclic product. The central six-membered oxygen containing cycle has a distorted half-chair conformation. The mean deviation of C(9a), C(9b), C(3a), C(4), O(5) from plane is 0.164 Å whereas the deviation of C(5a) atom from the same plane is 0.747 Å. The five-membered cycle has a cover conformation. Four atoms (C(1), C(2), C(3a), C(9a)) are disposed in the plane whereas the C(3) atom deviates from it by 0.429 Å. The six-membered carbonic cycle is a practically plane. The mean deviation from plane is 0.086 Å. It should be noted that five- and six-membered carbonic cycles situated at cis-position relatively of central ring. The torsion C(1)C(9a)C(9b)C(9) angle is −49.7°. Apparently, it leads to elongation of C(9a)–C(9b) (1.5935(13) Å), C(9a)–C(3a) (1.5864(13) Å) and C(3a)–C(But) (1.5923(13) Å) distances in comparison with typical ones for sp^{3}–sp^{3} carbon bond (Table 1).

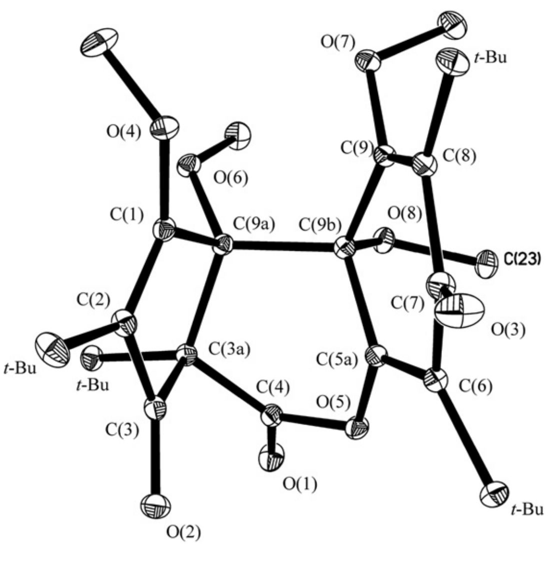


Figure 3. The molecular structure of 2,3a,6,8-tetra-*tert*-butyl-1,9,9a,9b-tetra-methoxy-9a,9b-di-hydrocyclopentachromene-3,4,7-(3a*H*)-trione (**4**). Hydrogens and *tert*-butyl groups are omitted for clarity.

Based on the structure **4** we suppose that the single possible route of its formation is the interaction between two molecules of compound **3** (Scheme 3). It was shown above that heating a mixture **3** and **2d** does not lead to formation of tree-cycle product **4**; it is formed only upon photoreaction. Thus, the formation of compound **4** is also the argument of existence of bicyclo compound **3**.

In the case of photoreaction of **1g**, irradiation of a benzene solution also results in the appearance in the ^{1}H NMR spectra not only of signals attributed to corresponding cyclopentadienone **2g** but signals of the intermediate product, derivative of bicyclo[1.3.0]-hexa-3-en-2,6-dione, attributed to protons of two nonequivalent *tert*-butyl group (δ=1.36 and 1.38 ppm) as well. But in contrast to **3**, this compound is noticeably less stable and decomposes at room temperature. The apparent rate constant of decomposition of intermediate compound determined using previously described procedure[26] is 6.1×10^{-4} s^{-1}.

Intermediate bicyclo[1.3.0]hexa-3-en-2,6-dione observed in present work allows us to interpret the previous data[4] otherwise. 3,3a′,6,6′-Tetra-*tert*-butyl-3a′,6a′-dihydro-2*H*-spirocyclohexa-3,5-dien-1,1′-cyclopentafuran-2,3′,4′-trione was isolated earlier as one of products of photoreaction of 3,5-di-*tert*-butyl-*o*-benzoquinone. Now we suppose that in the first stage, a bicyclic compound is formed. The spiro-compound is the product of interaction of this bicycle compound with initial quinone (Scheme 4). The less hindered carbonyl group of quinone takes part in the reaction. It is interesting to note that more hindered carbonyl group of the quinone takes part in rearrangement of photoexcited *o*-quinone into the bicycle compound.

It should be noted that during the photolysis of *o*-benzoquinones investigated in this work, the product from their reaction with the intermediate bicycle compound doesn't form. Presumably this is connected with the greater steric hindrance of both carbonyl groups of 3,6-di-*tert*-butyl-*o*-benzoquinone compared to 3,5-di-*tert*-butyl-*o*-benzoquinone.

Thus, on the basis of experimental and literature data we can suggest the mechanism of photolytic decarbonylation of *o*-benzoquinone, which is described in Scheme 5.

Photolytic decarbonylation of *o*-benzoquinones is a two-stage process. In the first stage the cyclohexadiendione ring of photoexcited molecule of *o*-benzoquinone is rearranged into the corresponding bicyclo[1.3.0]hexa-3-en-2,6-dione. In the second stage, elimination of CO from the cyclopropanone fragment and the formation of the final product—cyclopentadienone with the yields close to quantitative is observed.

3. Experimental

3.1. General

3,6-Di-*tert*-butyl-*o*-benzoquinone (**1a**), 4,5-di-fluoro-3,6-di-*tert*-butyl-*o*-benzoquinone (**1b**), 4,5-di-chloro-3,6-di-*tert*-butyl-*o*-benzoquinone (**1c**), 4,5-di-methoxy-3,6-di-*tert*-butyl-*o*-benzoquinone (**1d**), 5,8-di-*tert*-butyl-2,3-dihydrobenzo-1,4-dioxine-6,7-dione (**1e**), 4,7-di-*tert*-butylbenzo-1,3-dithiole-2,5,6-trione (**1f**) and 5,8-di-*tert*-butyl-2,3-dihydro-1,4-ethanoquinoxaline-6,7-dion (**1g**) were synthesized according to previously described procedures.[28–34]

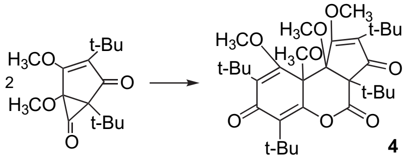
A KGM-24-150 lamp with a focusing device was used as the light source. Radiation with λ>520 nm was separated from the luminous flux of the lamp using the light filter GS-16.

The investigation of products of photoreaction of 4,5-di-substituted 3,6-di-*tert*-butyl-*o*-benzoquinones was studied by NMR spectroscopy. The NMR spectra were recorded on a 'Bruker DPX-200' spectrometer (200 MHz).

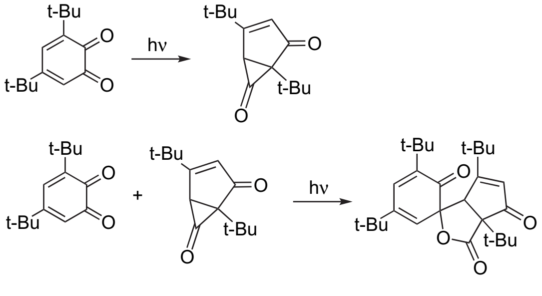
Table 1
Selected bond distances (*d*/Å) and angles (*ω*/°) of 2,3a,6,8-tetra-*tert*-butyl-1,9,9a,9b-tetra-methoxy-9a,9b-di-hydrocyclopentachromene-3,4,7-(3a*H*)-trione (**4**)

Distance	*d*	Distance	*d*	Distance	*d*
O(1)–C(4)	1.1933(12)	O(8)–C(9b)	1.4278(11)	C(5a)–C(6)	1.3309(13)
O(2)–C(3)	1.2158(11)	C(1)–C(2)	1.3408(13)	C(5a)–C(9b)	1.5113(13)
O(3)–C(7)	1.2185(13)	C(1)–C(9a)	1.5359(13)	C(6)–C(7)	1.5001(13)
O(4)–C(1)	1.5224(12)	C(2)–C(3)	1.4662(13)	C(7)–C(8)	1.5038(13)
O(5)–C(4)	1.3775(12)	C(3)–C(3a)	1.5563(13)	C(8)–C(9)	1.3406(13)
O(5)–C(5a)	1.3805(12)	C(3a)–C(4)	1.5224(12)	C(9)–C(9b)	1.5170(13)
O(6)–C(9a)	1.4057(11)	C(3a)–C(9a)	1.5864(13)	C(9a)–C(9b)	1.5935(13)
O(7)–C(9)	1.3769(11)				

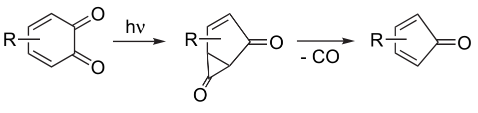
Angle	*ω*	Angle	*ω*
O(1)–C(4)–O(5)	117.02(8)	C(4)–O(5)–C(5a)	118.19(7)
O(1)–C(4)–C(3a)	128.20(9)	C(4)–C(3a)–C(3)	106.26(7)
O(2)–C(3)–C(2)	127.69(9)	C(4)–C(3a)–C(9a)	112.34(7)
O(2)–C(3)–C(3a)	122.78(8)	C(5a)–C(9b)–C(9)	113.05(7)
O(3)–C(7)–C(8)	120.78(9)	C(5a)–C(9b)–C(9a)	108.70(7)
O(3)–C(7)–C(6)	118.28(8)	C(5a)–C(6)–C(7)	114.64(8)
O(5)–C(4)–C(3a)	114.52(8)	C(6)–C(5a)–O(5)	122.16(8)
O(5)–C(5a)–C(9b)	111.72(7)	C(6)–C(5a)–C(9b)	125.30(8)
C(1)–C(2)–C(3)	107.12(8)	C(6)–C(7)–C(8)	120.94(8)
C(1)–C(9a)–C(3a)	101.70(7)	C(8)–C(9)–C(9b)	123.68(8)
C(2)–C(3)–C(3a)	109.53(7)	C(9)–C(9b)–C(9a)	111.69(7)
C(3)–C(3a)–C(9a)	100.21(7)	C(9)–C(8)–C(7)	116.60(8)
C(3a)–C(9a)–C(9b)	108.77(7)		



Scheme 3.



Scheme 4.



Scheme 5.

Solutions (1 mL) of 4,5-di-substituted 3,6-di-*tert*-butyl-*o*-benzoquinones (5×10^{-2} M) in C_6D_6 were degassed in an NMR tube, sealed and exposed at a distance of 2 cm from the focusing device. Solution irradiation times were varied taking into account the efficiency of decarbonylation of *o*-benzoquinones.

Electronic absorption spectra were recorded on 'Perkin–Elmer Lambda-25' spectrometer. The benzene solutions (5 mL) of *o*-benzoquinones **1a**–**g** (5×10^{-4} M) were deaerated, saturated with argon, placed in a spectrophotometric cell of 1 cm thickness and exposed at the distance of 11 cm from the focusing device.

All cyclopentadienones were synthesized using the single general procedure. The irradiation of ready solutions of *o*-benzoquinones **1a**–**g** was carried out at the room temperature with yields close to quantitative. After total decoloration of solution the solvent was removed at decreased pressure. The resulted cyclopentadienones were recrystallized from hexane. The physical–chemical data of reaction products are presented below. IR-spectra were recorded on 'Specord M-80'spectrometer. CHN-analyses were recorded by analytic group of G.A. Razuvaev Institute of Organometallic Chemistry RAS on 'EuroEA-3028-HT' elemental analyzer.

3.1.1. *2,5-Di-tert-butyl-cyclopentadienone (**2a**)*

Described in Ref. 3.

3.1.2. *3,4-Di-fluoro-2,5-di-tert-butyl-cyclopentadienone (**2b**)*

Red oil, mp=4–6 °C. [Found: C, 68.42; H, 7.96%. $C_{13}F_2H_{18}O$ requires: C, 68.40; H, 7.95; F, 16.67; O, 7.01%]; ν_{max}(neat) 670, 725, 780, 875, 960, 1030, 1080, 1185, 1210, 1280, 1315, 1360, 1400, 1450, 1470, 1490, 1670, 1725 cm^{-1}; δ_H (200 MHz, C_6D_6) 1.16 (18H, m, CMe_3); δ_C (50 MHz, C_6D_6) 193.8 (t, *J* 18.4 Hz, C=O), 160.3 (dd, *J* 33.4, 299.5 Hz, C(3) and C(4)), 112.6 (dd, *J* 2.2, 3.0 Hz, C(2) and C(5)), 31.8 (t, *J* 1.0 Hz, CMe_3), 29.1 (t, *J* 1.4 Hz, CMe_3).

3.1.3. *3,4-Di-chloro-2,5-di-tert-butyl-cyclopentadienone (**2c**)*

Orange oil, mp=15–16 °C. [Found: C, 59.90; H, 6.93%. $C_{13}Cl_2H_{18}O$ requires: C, 59.77; H, 6.95; Cl, 27.15; O, 6.13%]; ν_{max}(neat) 665, 738, 787, 845, 860, 1015, 1150, 1205, 1225, 1275, 1375, 1400, 1465, 1490, 1600, 1725 cm^{-1}; δ_H (200 MHz, C_6D_6) 1.25 (18H, s, CMe_3); δ_C (50 MHz, C_6D_6) 194.94 (C=O), 142.42 (C(2) and C(5)), 131.24 (C(3) and C(4)), 33.36 (CMe_3), 29.30 (CMe_3).

3.1.4. *3,4-Di-methoxy-2,5-di-tert-butyl-cyclopentadienone (**2d**)*

Orange solid, mp=18–20 °C. [Found: C, 71.23; H, 9.62%. $C_{15}H_{24}O_3$ requires: C, 71.39; H, 9.59; O, 19.02%]; ν_{max}(neat) 512, 735, 760, 775, 795, 880, 950, 1025, 1080, 1100, 1112, 1150, 1185, 1210, 1260, 1320, 1370, 1400, 1470, 1490, 1550, 1610, 1645, 1660, 1670, 1710 cm^{-1}; δ_H (200 MHz, C_6D_6) 3.32 (6H, s, CH_3O), 1.39 (18H, s, CMe_3); δ_C (50 MHz, C_6D_6) 199.28 (C=O), 162.46 (C(2) and C(5)), 118.59 (C(3) and C(4)), 59.45 (OCH_3), 32.17 (CMe_3), 29.91 (CMe_3).

3.1.5. *5,7-Di-tert-butyl-2,3-dihydrocyclopenta-1,4-dioxin-6-one (**2e**)*

Red crystals, mp=155–157 °C. [Found: C, 72.10; H, 8.84%. $C_{15}H_{22}O_3$ requires: C, 71.97; H, 8.86; O, 19.17%]; ν_{max}(liquid film)

575, 665, 730, 765, 780, 860, 870, 940, 1000, 1025, 1015, 1115, 1165, 1210, 1225, 1250, 1275, 1300, 1330, 1370, 1380, 1410, 1465, 1485, 1610, 1645, 1660, 1675, 1695 cm^{-1}; δ_H (200 MHz, C_6D_6) 3.10 (4H, s, CH_2O), 1.47 (18H, s, CMe_3); δ_C (50 MHz, C_6D_6) 197.59 (C=O), 154.91 (C(2) and C(5)), 108.80 (C(3) and C(4)), 64.77 (CH_2O), 32.31 (CMe_3), 30.42 (CMe_3).

3.1.6. *4,6-Di-tert-butyl-5H-cyclopenta-1,3-dithiole-2,5-dione (**2f**)*

Described in Ref. [28].

3.1.7. *5,7-Di-tert-butyl-2,3-dihydro-6H-1,4-ethanocyclopentapyrazin-6-one (**2g**)*

Orange crystals, mp=139–141 °C. [Found: C, 74.26; H, 9.53; N, 10.19%. $C_{17}H_{26}N_2O$ requires: C, 74.41; H, 9.55; N, 10.21; O, 5.83%]. ν_{max}(liquid film) 600, 660, 675, 740, 790, 810, 815, 850, 880, 930, 955, 990, 1040, 1050, 1195, 1225, 1280, 1300, 1315, 1345, 1350, 1365, 1380, 1465, 1650, 1715 cm^{-1}; δ_H (200 MHz, C_6D_6) 2.43–2.65 (8H, m, CH_2N), 1.43 (18H, s, CMe_3); δ_C (50 MHz, C_6D_6) 202,58 (C=O), 159.61 (C(2) and C(5)), 122.07 (C(3) and C(4)), 30.20 (CMe_3), 32.40 (CMe_3).

3.2. Photochemical conversion of 4,5-di-methoxy-3,6-di-*tert*-butyl-*o*-benzoquinone

The irradiation (284 K, light $\lambda>520$ nm for 100 h) of benzene solution of **1d** was carried out using procedure described earlier. The solvent (benzene) was removed under reduced pressure without heating. The solid residue was washed with cold hexane and recrystallized from diethylether. Colourless rhombic crystals of *2,3a,6,8-tetra-tert-butyl-1,9,9a,9b-tetra-methoxy-9a,9b-di-hydro-cyclopentachromene-3,4,7-(3aH)-trione* (**4**) were isolated with ~20% yield. Mp=200–203 °C. [Found: C, 67.79; H, 8.84%. $C_{32}H_{48}O_8$ requires: C, 67.86; H, 8.82; O, 23.33%]; ν_{max}(liquid film) 670, 720, 730, 840, 870, 885, 930, 950, 9650, 1000, 1020, 1055, 1075, 1095, 1130, 1160, 1170, 1185, 1210, 1225, 1260, 1270, 1320, 1370, 1380, 1400, 1470, 1610, 1630, 1650, 1710, 1790 cm^{-1}; δ_H (200 MHz, C_6D_6) 3.68 (3H, s, OCH_3), 3.37 (3H, s, OCH_3), 2.89 (6H, s, OCH_3), 1.58 (9H, s, CMe_3), 1.52 (9H, s, CMe_3), 1.45 (9H, s, CMe_3), 1.35 (9H, s, CMe_3); δ_C (50 MHz, $CDCl_3$) 196.3 (C=O), 190.6 (C=O), 174.7 (O–C=O), 131.1, 135.5, 138.1, 150.3, 157.1, 163.2 (C(1), C(2), C(5a), C(6), C(8), C(9)), 72.1, 82.3, 92.3 (C(3a), C(9a), C(9b)), 159.61 (C(2) and C(5)), 64.6 (OCH_3), 61.4 (OCH_3), 57.6 (OCH_3), 51.8 (OCH_3), 38.3, 36.1, 35.9 (CMe_3), 32.8, 31.0, 30.4, 29.5 (CCH_3).

The hexane solution contains *1,3-di-tert-butyl-4,5-di-methoxy-bicyclo[3.1.0]hex-3-ene-2,6-dione* (**3**) and **2d** in the ratio 1:2. ^1H NMR of compound **3**: δ_H (200 MHz, C_6D_6) 3.53 (3H, s, OCH_3), 3.16 (3H, s, OCH_3), 1.23 (9H, s, CMe_3), 1.13 (9H, s, CMe_3); δ_C (50 MHz, C_6D_6) 196.31 (C=O), 188.26 (C=O), 179.5 (C(5)), 138.36 (C(4)), 94.56 (OCH_3), 57.9 (C(3)), 51.4 (C(2)), 31.3 (CMe_3), 30.9 (CMe_3), 30.3 (CMe_3), 27.9 (CMe_3).

The crystals of **4** suitable for X-ray structure determination were obtained from ether. Crystal data: $C_{32}H_{48}O_8$, $M=560.72$, monoclinic, $a=10.894(4)$ $b=22.695(8)$, $c=12.240(4)$ Å, $\beta=98.883(7)$, $V=2989.9(18)$ Å^3, $T=100(2)$K, space group $P2(1)/n$, $Z=4$, $\mu=0.088$ mm^{-1}, $d_{cal}=1.246$ g/cm^3, 28,770 reflections measured, 6853 unique ($R_{int}=0.0232$), which were used in all calculations. $R_1[I>2\sigma(I)]=0.0445$, $wR_2=0.1186$, wR_1(all data)=0.0522, GOF(F^2)=1.050. The structure was solved by direct method and refined on F^2 using SHELXTL package.[35] The H atoms were found from Fourier syntheses and refined isotropically.

CCDC-679033 (**4**) contains the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk.

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References and notes

1. El'zov, A. V.; Studzin'skii, O. P.; Grebenkina, V. M. *Usp. Khim.* **1977**, *46*, 185–227.
2. Maier, G.; Franz, L. H.; Hartan, H.-G.; Lanz, K.; Reisernauer, H. *Chem. Ber.* **1985**, *118*, 3196–3204.
3. Vol'eva, V. B.; Ershov, V. V.; Belostozkaya, I. S.; Komisarova, N. L. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1974**, 739.
4. Vol'eva, V. B.; Belostozkaya, I. S.; Komisarova, N. L.; Starikova, Z. A.; Kurkovskaya, L. N. *Zh. Org. Khim.* **2006**, *42*, 243–245.
5. Kliment'eva, S. V.; Mischenko, O. G.; Kurskii, Yu. A.; Faerman, V. I.; Maslennikov, S. V.; Spirina, I. V.; Fukin, G. K.; Druzkov, N. O. *Zh. Org. Khim.* **2007**, *77*, 967–973.
6. Imbriglio, J. E.; Rainier, J. D. *Tetrahedron Lett.* **2001**, *42*, 6987–6990.
7. McDonnell Bushnell, L. P.; Evitt, E. R.; Bergman, R. G. *J. Organomet. Chem.* **1978**, *157*, 445–446.
8. Gesing, E. R. F.; Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem., Ind. Ed.* **1980**, *19*, 1023–1024.
9. Pearson, A. J.; Shively, R. J., Jr.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096–4104.
10. Pearson, A. J.; Shively, R. J., Jr.; Dubbert, R. A. *Organometallics* **1994**, *13*, 578–584.
11. Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1994**, *13*, 5054–5061.
12. Slugove, C.; Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 2954–2960.
13. Washington, J.; McDonald, R.; Takats, J.; Menashe, N.; Reshef, D.; Shvo, Y. *Organometallics* **1995**, *14*, 3996–4003.
14. Tamao, K.; Kohayashi, K.; Ito, Y. *Synlett* **1992**, 539–542.
15. *Einfuhrung in die photochemie, Von einem autorenkollektiv*; Bekker, G. O., Ed.; VEB Deutscher Verlag der Wissenschaften: Berlin, 1976; p 379.
16. Chesnokov, S. A.; Cherkasov, V. K.; Abakumov, G. A.; Kurskii, Yu. A.; Shurygina, M. P.; Mamysheva, O. N.; Shavyrin, S. A. *Russ. Chem. Bull., Int. Ed.* **2003**, *3*, 718–724.
17. Chesnokov, S. A.; Cherkasov, V. K.; Chechet, Yu. V.; Nevodchikov, V. I.; Abakumov, G. A.; Mamysheva, O. N. *Russ. Chem. Bull., Int. Ed.* **2000**, *9*, 1506–1511.
18. Shurygina, M. P.; Kurskii, Yu. A.; Chesnokov, S. A.; Druzkov, N. O.; Fukin, G. K.; Abakumov, G. A.; Cherkasov, V. K. *Russ. Chem. Bull., Int. Ed.* **2006**, *55*, 1585–1592.
19. Kropp, P. J. In *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, NY, 1967; Vol. 1, pp 125–131.
20. Dauben, W. G.; Spitzer, W. A.; Kellogg, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3674–3677.
21. Zimmerman, H. E. *Photochemistry* **1963**, *1*, 183–185.
22. Zimmerman, H. E. *Angew. Chem., Int. Ed. Engl.* **1969**, *1*, 1–11.
23. Barton, D. H. R.; de Mayo, P.; Shafiq, M. *J. Chem. Soc.* **1958**, 3314–3315.
24. Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551.
25. Barltrop, J. A.; Coyle, J. D. *Excited States in Organic Chemistry*; John Wiley and Sons: London, New York, NY, Sydney, Toronto, 1975; p 446.
26. Coyle, J. D. *Introduction to Organic Photochemistry*; John Wiley and Sons: London, 1989; p 176.
27. Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; John Wiley and Sons: London, New York, NY, 1976; p 586.
28. Kuropatov, V. A.; Cherkasov, V. K.; Kurskii, Yu. A.; Fukin, G. K.; Abakumova, L. G.; Abakumov, G. A. *Russ. Chem. Bull., Int. Ed.* **2006**, *4*, 708–711.
29. Garnov, V. A.; Nevodchikov, V. I.; Abakumov, G. A.; Abakumova, L. G.; Kurskii, Yu. A.; Cherkasov, V. K. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1985**, *34*, 2589–2591.
30. Abakumov, G. A.; Cherkasov, V. K.; Abakumova, L. G.; Nevodchikov, V. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1990**, *39*, 984–986.
31. Abakumov, G. A.; Cherkasov, V. K.; Abakumova, L. G.; Nevodchicov, V. I.; Druzhkov, N. O.; Makarenko, N. P.; Kursky, Ju. A. *J. Organomet. Chem.* **1995**, *491*, 127–133.
32. Abakumov, G. A.; Cherkasov, V. K.; Abakumova, L. G.; Druzhkov, N. O.; Nevodchicov, V. I.; Kursky, Ju. A.; Makarenko, N. P. *Metalloorg. Khim.* **1991**, *4*, 683–686.
33. Garnov, V. A.; Nevodchikov, V. I.; Abakumova, L. G.; Abakumov, G. A.; Cherkasov, V. K. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1987**, *36*, 1728–1730.
34. Abakumov, G. A.; Cherkasov, V. K.; Kocherova, T. N.; Druzkov, N. O.; Kurskii, Yu. A.; Bubnov, M. P.; Fukin, G. K.; Abakumova, L. G. *Russ. Chem. Bull., Int. Ed.* **2007**, *56*, 1849–1856.
35. Sheldrick, G. M. *SHELXTL v. 6.12, Structure Determination Software Suite*; Bruker AXS: Madison, WI, USA, 2000.