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Photodecomposition of Substituted *o*-Benzoquinones in Solutions of Saturated Hydrocarbons: II.[1] Transformation Products

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Abstract — The products of photolytic decomposition of a series of *o*-benzoquinones in paraffin solutions under the action of the radiation with λ 405 nm were identified. The influence of the quinone structure on the reaction pathway and the composition of the final products was elucidated.
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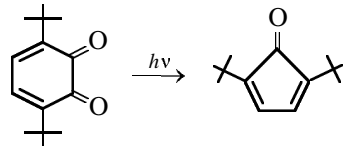
Photochemical reactions of *p*-benzoquinones are being actively studied [2]. However, the related studies concerning *o*-benzoquinones are much fewer, and they deal mainly with the photoreduction of these compounds in the presence of hydrogen donors [3, 4]. Virtually no data are available on the photolytic transformation of *o*-benzoquinones.

The goal of this study was to elucidate the nature of primary photolytic reactions of *o*-benzoquinones, the composition and structure of products formed by prolonged irradiation of the reaction mixture, and the influence of the substrate structure on the composition and yields of the reaction products.

Hexane solutions of 3,6-di-*tert*-butylbenzo-1,2-quinone **I**, 3,5-di-*tert*-butylbenzo-1,2-quinone **II**, 4,6-di-*tert*-butyl-3-nitrobenzo-1,2-quinone **III**, 4,6-di-*tert*-butyl-3-chlorobenzo-1,2-quinone **IV**, and 3,4,6-triisopropylbenzo-1,2-quinone **V** (10^{-2} M) were exposed to prolonged irradiation (λ 405 nm). The residual amount of the starting compounds did not exceed 3%. The solvent choice was governed by the feasibility of its removal from the reaction mixture.

According to the TLC and NMR data, the main product of transformation of quinone **I** was 2,5-di-*tert*-butylcyclopentadienone (yield 98%).

Photolysis of solutions of individual compound **II**–**V** yielded more complex mixtures of products. To determine their compositions and yields, along with TLC and NMR spectroscopy, we used gas chromatography–mass spectrometry (GC–MS) to identify the volatile products and single crystal X-ray diffraction for products that could be isolated in the crystalline form.



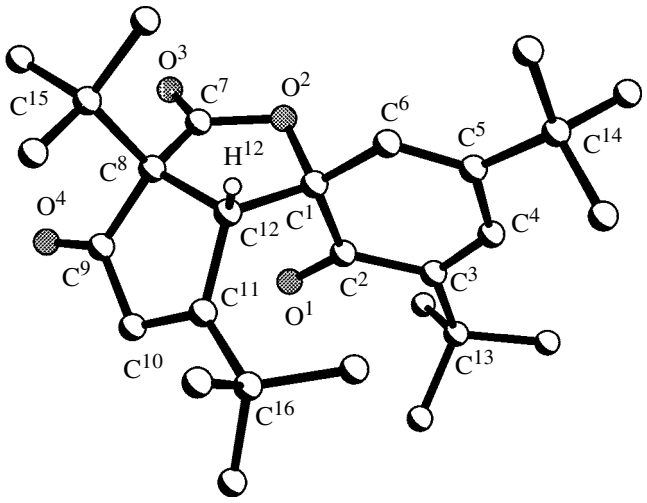
I (1)

TLC studies of the reaction mixtures from the photolysis of *o*-benzoquinones **IV** and **V** showed that the yellow spot with R_f 0.8–0.9 was present on the chromatograms. It was attributed to the substituted cyclopentadienones.

The products of photolytic decomposition of **II** were analyzed in most detail. The starting dark green solution of **II** in hexane after the photolysis acquires a bright yellow color, and a yellowish crystalline precipitate is formed. The band at 1670 cm^{-1}, characteristic of the starting quinone, disappears from the IR spectrum of the liquid phase. The ^1H and ^{13}C NMR spectra also contain no signals characteristic of **II**. The photolytic transformation of **II** occurs along several pathways.

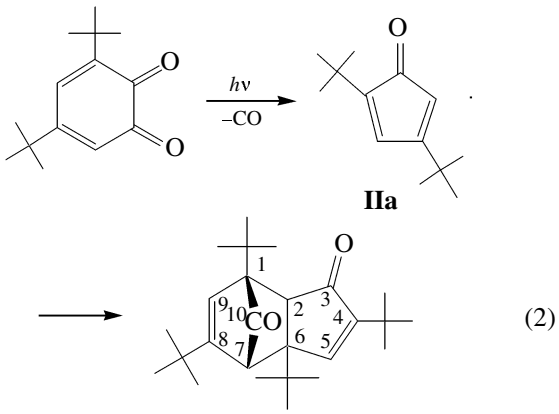
The major fraction of **II** decomposes with the CO_2

[1] For communication I, see [1].



Molecular structure of 3,3a',6,6'-tetra-*tert*-butyl-3a',6a'-dihydro-2*H*-spiro{cyclohexa-3,5-diene-1,1'-cyclopenta-[*c*]furan}-2,3',4'-trione **IIc**.

liberation and formation of 2,4-di-*tert*-butylcyclopentadienone **IIa**.

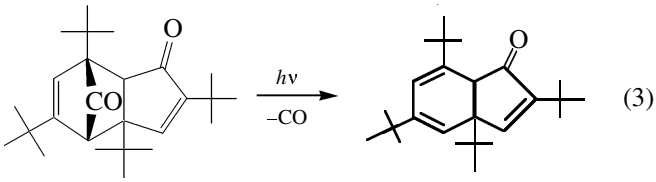


(2)

Cyclopentadienone **IIa** undergoes the Diels–Alder dimerization ($2\pi+4\pi$ addition) [5] to form 1,4,6,8-tetra-*tert*-butylbicyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione [Eq. (2)]. This compound was identified by ^{1}H and ^{13}C NMR spectroscopy after partial dissolution of the liquid phase in $CDCl_3$. The yield of the dimer was about 36%.

It should be noted that GC–MS examination of the final reaction mixture showed the presence of the monomer **IIa** only. Apparently, at relatively high temperatures necessary for the analysis, the dimer decomposes by the retro-Diels–Alder reaction.

2,4-Di-*tert*-butylcyclopentadienone dimer undergoes further photodecomposition to give product **IIb** in 15% yield.



(3)

IIb

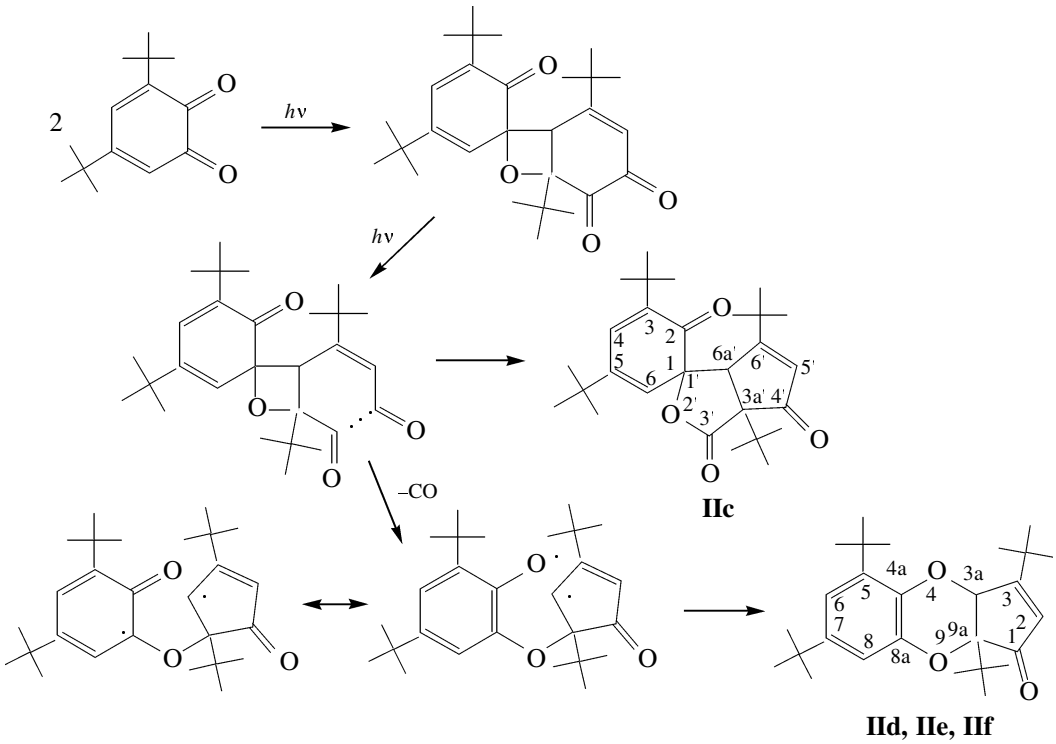
The second pathway of photolysis of **II** is the cycloaddition of the carbonyl group from one molecule to the C=C bond of another molecule (photochemical $2\pi+2\pi$ addition) [2]. This was suggested by the formation of a precipitate **IIc** in the course of the reaction. The yield of crystals of **IIc** was about 10% based on the starting quinone. In addition, according to GC–MS analysis, the liquid fraction of the reaction mixture contained about 2% of this substance. The IR spectrum of **IIc** contained three absorption bands of C=O groups. The band at 1685 cm^{-1} belongs to the ester C=O group. The band at 1715 cm^{-1} was assigned to the cyclopentadiene C=O group, and that at 1780 cm^{-1}, to the cyclohexadiene carbonyl absorption. The ^{1}H and ^{13}C spectra, along with four signals of the nonequivalent *tert*-butyl groups, contained the signals of 12 nonequivalent carbon atoms.

The X-ray studies of compound **IIc** showed that it is a tricyclic spiro compound containing one six-membered and two five-membered rings (see figure). The five-membered [C^{8-12}] and six-membered [C^{1-6}] rings of **IIc** are planar with the mean deviations of 0.040 and 0.015 Å, respectively. On the contrary, the five-membered oxygen-containing ring has a dihedral angle of 20° between the $C^1O^2C^7$ and $C^1C^{12}C^8C^7$ fragments. The dihedral angle between the five-membered rings is 57.3°. The C^1 spiro atom has the distorted tetrahedral surrounding. The bond angles $O^2C^1C^2$ [101.6(2)°] and $C^6C^1C^2$ [115.8(2)°] of the spiro carbon atom significantly differ from the characteristic value for the sp^3-hybridized carbon atom. The distances between the carbonyl oxygen and carbonyl carbon fall into the typical range [1.197(2)–1.221(3) Å]. The O^2–C^1 [1.464(2)Å], O^2–C^7 [1.359(2) Å], and C=C [1.332(3)–1.337(3) Å] bond lengths in the rings are typical of the cyclic systems [6].

Compound **IIc** is formed by rearrangement of the intermediate resulting from cycloaddition of two quinone molecules [Eq. (4)].

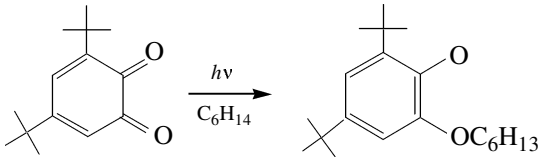
In addition, GC–MS analysis of the liquid phase of the photolysis products showed that isomers **IId**–**IIf** are formed in a total yield of 32% based on the starting quinone. They result from cycloaddition of the C=C bond to the carbonyl group, followed by

decarbonylation of the *o*-quinone dimer [Eq. (4)]. In the mass spectra of **IId**–**IIf**, the quinone and cyclopentadiene components are identified. The content of the major isomer **IIf** reaches 27%. According to the NMR data, it is 3,5,7,9a-tetra-*tert*-butyl-3a,9a-dihydro-1*H*-benzo[*b*]cyclopenta[*e*][1,4]dioxin-1-one.



(4)

The third reaction pathway is the reduction of quinone **II** [Eq. (5)] accompanied by formation of the isomeric phenol ethers **IIg** and **IIh** in a total yield of about 5%. Their origination may be caused by different location of the alkoxy group in relation to the *tert*-butyl substituents, as well as by the possibility of addition of the hexyl radical to the quinone oxygen atom through different carbon atoms. It should be noted that the structure of the phenol ether isomers obtained is not unambiguously established.



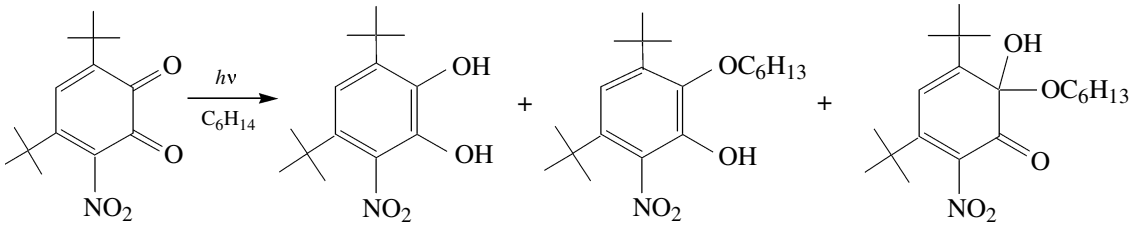
(5)

A GC–MS analysis showed that prolonged photolysis of **III** in hexane led to a mixture of its photoreduction products [Eq. (6)].

Selected interatomic distances (*d*) and bond angles (ω) in **IIc**

Bond	*d*, Å	Angle	ω, deg
O^2–C^7	1.359(2)	$O^2C^1C^6$	107.6(2)
O^2–C^1	1.464(2)	$O^2C^1C^2$	101.6(2)
O^3–C^7	1.197(2)	$C^6C^1C^2$	115.8(2)
O^4–C^9	1.221(3)	$O^2C^1C^{12}$	104.3(2)
O^1–C^2	1.218(3)	$C^6C^1C^{12}$	113.1(2)
C^5–C^6	1.332(3)	$C^2C^1C^{12}$	113.0(2)
C^3–C^4	1.337(3)		
C^9–C^{10}	1.337(3)		
C^1–C^6	1.487(3)		
C^1–C^2	1.545(3)		
C^1–C^{12}	1.579(3)		

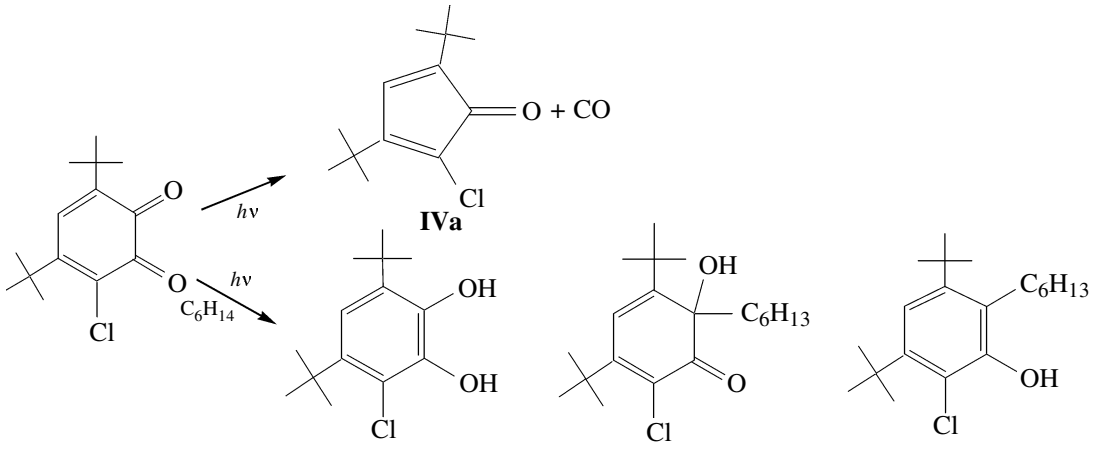
The cyclopentadienone corresponding to starting compound **III** was not found. The ratio of 4,6-di-*tert*-butyl-3-nitropyrocatechol **IIIa**, isomeric phenyl ethers **IIIb**–**IIIf**, and keto alcohols **IIIg** + **IIIh** is 1 : 15 : 3.



IIIa **IIIb, IIIc, IIId, IIIe, IIIf** **IIIg, IIIh** (6)

The isomerism of the ketones is due to the fact that the hexyl radical adds to the benzene ring through either the second (**IIIh**) or third (**IIIg**) carbon atom.

A GC–MS analysis of photolysis products of quinone **IV** showed the presence of 3,5-di-*tert*-butyl-2-chlorocyclopentadienone **IVa**, 4,6-di-*tert*-butyl-3-chloropyrocatechol **IVb**, keto alcohol **IVc** with the hexyl radical bonded to the first carbon atom of the six-membered ring, and phenyl ethers of various structures. The ratio of the decarbonylation and reduction products is 1.0 : 1.2, which shows that the rates of reactions (7) and (8) are approximately equal.



IVa (7)

IVb **IVc** **IVd, IVe, IVf, IVg, IVh** (8)

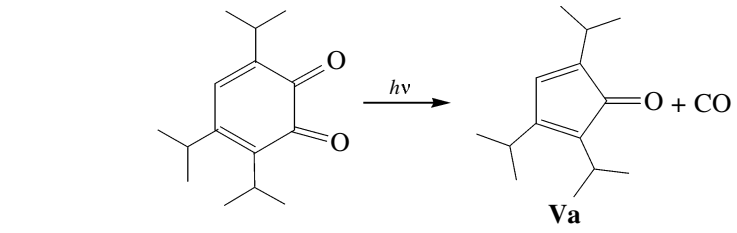
Irradiation of a solution of quinone **V** gives 2,3,5-tripropylcyclopentadienone **Va** in 54% yield based on the starting compound [Eq. (9)]. The isomeric phenyl ethers resulting from photoreduction of the starting quinone are formed in a total yield of 25% [Eq. (10)]. Compounds containing the fragments of cyclopentadienone and quinone structures are formed by cycloaddition in a total yield of 13% [Eq. (11)].

They are presumably formed by the scheme similar to that for the analogous products of photodecomposition of quinone **II**. Structures **Vg**–**Vi** may be formed by photoaddition of the cyclopentadienone double bond to the carbonyl group of quinone. The structure of these compounds was not determined unambiguously.

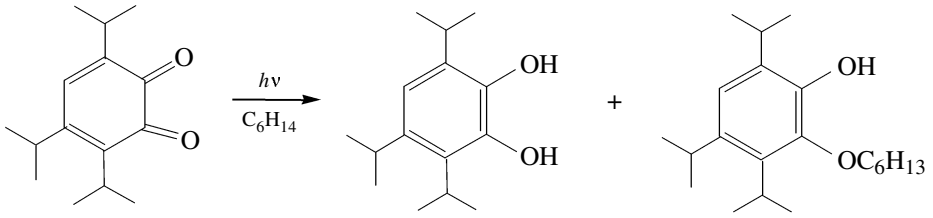
Along with the above-considered pathways of photolysis of quinone **V**, there is one more pathway: intramolecular reduction (up to 2%). Its realization is favored by the presence of isopropyl radicals having labile hydrogen atoms in the methine groups.

EXPERIMENTAL

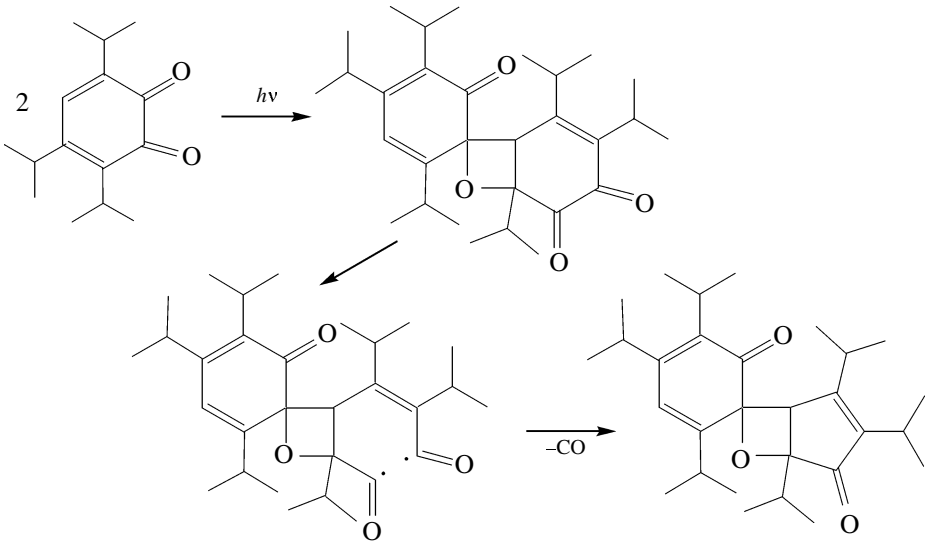
Hexane and nonane of chemically pure grade were purified and dried by standard procedures [7]. The fractions with bp 68.6–69.0°C and 149–151°C were collected for hexane (bp 69.0°C [7]) and nonane (bp 150.7°C [7]), respectively. A DRSh-500 high-pressure mercury lamp was used as the source. The radiation flow was focused with a quartz lens and



Va (9)



Vb **Vc, Vd, Ve, Vf** (10)



Vg, Vh, Vi (11)

passed through a ZhS-10 filter to cut out the radiation with λ 405 nm. The quinone solutions were degassed by multiple freeze–pump–thaw cycles.

The incident radiation intensity was measured with a potassium ferrioxalate actinometer [8].

The carbon monoxide yield was evaluated chromatographically on a Tsvet-104 device (1500 × 2.5-mm glass column packed with NaX zeolite, 5 Å; column and detector temperature 30°C; bridge current of thermal conductivity detector 250 mA; carrier gas helium, flow rate 40 ml min^{-1}). The concentration of quinones in solution was evaluated spectrophotometrically with an SF-46 device by the method of absolute calibration. The TLC was carried out on Sorbfil silica gel plates, elution with 17 : 3 hexane–ethyl acetate [9]. A spot was applied onto a plate with a glass capillary directly from the reaction mixture. After elution of the plate in a closed chamber, it was developed with iodine vapor, the positions of spots were determined, and the R_f values were calculated. TLC was also used for fractionation of the reaction mixtures for the subsequent NMR analysis.

The uni- and two-dimensional NMR spectra were taken on a Bruker Avance DPX-200 spectrometer (200 MHz for ^1H, 50 MHz for ^{13}C) in $CDCl_3$ against internal TMS. The ^1H and ^{13}C signals were assigned using the two-dimensional NMR techniques: scalar proton-carbon CHCORR and remote proton-carbon COLOC correlations, as well as the proton-proton dipole NOESY correlations.

The mass-spectroscopic analysis was carried out on a FISONS MD 800/GC 8060 gas chromatograph–mass spectrometer equipped with an HP-5MS column, 60 m × 0.32 mm, coated with phenylmethylsiloxane (0.25-μm film). Helium of M60 grade was used as a

carrier gas, flow rate 1 ml min^{-1}. The injector temperature was 250°C, and the column temperature was changed from 70 to 250°C over a period of 30 min. Samples (1 μl) were injected with a syringe. The ionizing electron energy was 70 eV. The mass spectra were recorded in the range *m/z* 33-450.

The X-ray diffraction experiment was performed with a Smart APEX automatic diffractometer. The structure of **IIc** was solved by the direct method and refined by the least-squares method on F^2_{hkl} in the anisotropic approximation for all the nonhydrogen atoms. All hydrogen atoms were found from the differential Fourier synthesis and refined isotropically. The calculations were carried out using the SHELXTL v. 6.12 software [10].

2,5-Di-*tert*-butylcyclopentadienone: mp 58.9°C (published data: 59°C [11]). The R_f value (0.88) of the reaction product coincides with that of the authentic sample (0.88).

2,4-Di-*tert*-butylcyclopentadienone IIa is formed in the course of the GC–MS analysis of the photolysis products of **II**. Mass spectrum, *m/z* (*I*, %): 57 (38), 65 (11), 77 (15), 79 (12), 91 (32), 93 (43), 105 (25), 107 (27), 108 (58), 119 (18), 121 (18), 133 (20), 134 (18), 135 (12), 136 (12), 149 (100), 150 (12), 164 (11), 177 (17), 192 (23).

1,4,6,8-Tetra-*tert*-butylbicyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione [cyclopentadienone IIa dimer]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.98, 1.04, 1.14, and 1.19 all s [9H, $C(CH_3)_3$]; 2.96 s (1H, CH^2); 3.19 d (1H, CH^7, *J* 1.4); 5.89 d (1H, CH^9, *J* 1.4); 6.79 s (1H, CH^5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.2. 27.7, 28.5, and 28.8 [all $C(CH_3)_3$]; 32.1, 32.3, 33.9, and 36.1 (all CMe_3); 50.7 (CH^7); 53.6 (CH^2); 56.9 (C^6); 67.3 (C^1); 122.5 (CH^9); 154.1 (C^4); 154.9 (CH^5); 159.0 (C^8); 198.4 (C^3=O); 206.0 (C^{10}=O).

2,3a,5,7-Tetra-*tert*-butyl-3a,7a-dihydro-1*H*-inden-1-one (IIb). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.15, 1.25, 1.29, 1.41 all s [9H, $C(CH_3)_3$]; 4.82 d (1H, CH^{7a}, *J* 2.0); 6.73 d (1H, CH^3, *J* 2.0); 6.85 and 6.98 two d (1H, CH^4 and 1H, CH^6, *J* 2.3). Mass spectrum, *m/z* (*I*, %): 56 (5), 57 (100), 58 (4), 159 (4), 243 (62), 244 (12), 298 (5), 299 (35), 300 (7).

3,3a',6,6'-Tetra-*tert*-butyl-3a',6a'-dihydro-2*H*-spiro{cyclohexa-3,5-diene-1,1'-cyclopenta[*c*]furan}-2,3',4'-trione (IIc) precipitates in the course of photolysis of **II** in hexane. Light yellow crystals were filtered off, washed with hexane, and dried; mp 224.5°C. Found, %: C 76.11; H 9.30. $C_{28}H_{40}O_4$. Calculated, %: C 76.32; H 9.15. UV spectrum, λ, nm (ε, l mol^{-1} cm^{-1}): 230 (7700), 330 (3100). IR spectrum (KBr), ν, cm^{-1}: 1685, 1715, 1780 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.07 s [9H, $C^{6'}C(CH_3)_3$], 1.11 s [9H, $C^{3a'}C(CH_3)_3$], 1.16 s [9H, $C^3C(CH_3)_3$], 1.20 s [9H, $C^5C(CH_3)_3$], 3.68 s (1H, $CH^{6a'}$), 5.99 s (1H, $CH^{5'}$=C), 6.03 d (1H, CH^6=C, *J* 2.2), 6.92 d (1H, CH^4=C, *J* 2.2). ^{13}C NMR spectrum, DEPT ($CDCl_3$), δ_C, ppm: 26.2 [$C^{3a'}C(CH_3)_3$], 28.5 [$C^5C(CH_3)_3$], 29.1 [$C^{6'}C(CH_3)_3$], 29.3 [$C^3C(CH_3)_3$], 34.90 [$C^3C(CH_3)_3$], 34.97 [$C^5C(CH_3)_3$], 35.4 [$C^{6'}C(CH_3)_3$], 38.3 [$C^{3a'}C(CH_3)_3$], 57.4 ($CH^{6a'}$), 69.2 ($C^{3a'}$), 79.2 ($C^{1,1'}$), 127.8 (CH^6), 130.7 ($CH^{5'}$), 136.1 (CH^4), 144.0 (C^3), 147.0 (C^5), 170.2 ($C^{3'}$=O), 179.5 ($C^{6a'}$), 195.4 (C^2=O), 200.4 ($C^{4'}$=O). The ^{1}H and ^{13}C NMR signals were assigned using two-dimensional NMR techniques: scalar proton–carbon CHCORR and long-range proton–carbon COLOC correlations, and also proton-proton dipole NOESY correlation. The X-ray data are presented in the figure and in the table. Crystallographic data for **IIc**: $C_{28}H_{40}O_4$, *M* 440.60, *T* 100(2) K, λ 0.71073 Å, space group $P2_12_12_1$, *a* 8.9977(6) Å, *b* 12.1100(7) Å, *c* 23.574(1) Å, *V* 2568.6(3) $Å^3$, *Z* 4; d_{calc} 1.139 g cm^{-3}, μ 0.074 mm^{-1}, *F*(000) 960, θ_{max} 26.0°. A total of 15541 reflections were collected, among them 5038 unique reflections (R_{int} 0.0712); final *R* factors for reflections with $I > 2\sigma(I)$: R_1 0.0474, wR_2 0.0751; final *R* factors (for all data) R_1 0.0885, wR_2 0.0839, $GOF(F^2)$ 0.966, absolute structural parameter 0.1(1), residual electron density 0.176/–0.157 e $Å^{-3}$.

3,5,7,9a-Tetra-*tert*-butyl-3a,9a-dihydro-1*H*-benzo[*b*]cyclopenta[*e*][1,4]dioxin-1-one IIf. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.03, 1.18, 1.22, and 1.33, all s [9H each, $C(CH_3)_3$], 4.53 s (1H, CH^{3a}), 6.86 m (*AB* system) (2H, CH^6 and CH^8, *J* 2.3, Δν 5 Hz), 7.07 s (1H, CH^2). ^{13}C NMR spectrum, DEPT ($CDCl_3$), δ_C, ppm: 25.0, 27.9, 30.0, and 31.4 [all $C(CH_3)_3$]; 32.0, 34.5, 34.6, and 36.5 (all CMe_3); 77.8 (CH^2); 87.2 (C^{9a}); 113.4 and 117.4 (CH^6 and CH^8); 138.4, 140.5, 144.4, and 144.6 (all C=C); 150.1 (CH^2); 151.1 (C^3); 202.7 (C=O). Mass spectrum, *m/z* (*I*, %): 57 (83), 79 (10), 91 (24), 93 (19), 105 (12), 107 (13), 108 (53), 119 (15), 121 (13), 133 (13), 135 (14), 136 (22), 137 (18), 149 (100), 150 (13), 164 (46), 177 (28), 192 (29), 355 (16), 397 (10), 412 (48), 413 (14).

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