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Photooxygenolysis of 3,6-Di-*tert*-butyl-*o*-benzoquinone

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Abstract—The photolysis of 3,6- and 3,5-di-*tert*-butyl-*o*-benzoquinones in benzene ($\lambda > 380$ nm, inert atmosphere) involves decarbonylation of the compounds to furnish respectively 2,5- and 2,4-di-*tert*-butylcyclopentadienones. The 2,5-isomer is stable, and the 2,4-di-*tert*-butylcyclopentadienone suffers a conversion into a Diels–Alder adduct. The participation of oxygen inhibited the decarbonylation and changed the directon of the photolysis: Here the products of the 3,5-di-*tert*-butyl-*o*-benzoquinones conversion were a di-*tert*-butylmuconic anhydride and dipivalylethylene. It was concluded that a singlet oxygen was involved in the process which formed by a triplet-triplet annihilation at the interaction of $^3O_2$ with a triplet-excited initial quinone.

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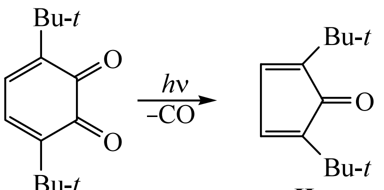
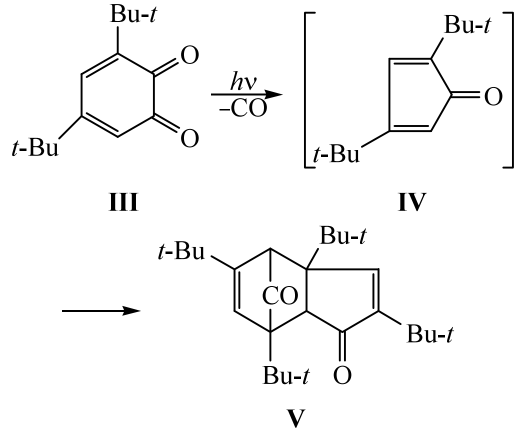
3,6-Di-*tert*-butyl-*o*-benzoquinone (**I**) irradiated with light in the visible region ($\lambda > 380$ nm) in the absence of oxygen in benzene or hexane solution suffered a phototransformation uncommon for quinones: a decarbonylation affording 2,5-di-*tert*-butylcyclopentadienone (**II**), the first example of a stable monomeric dialkyl-substituted cyclopentadienone [1].



I **II**

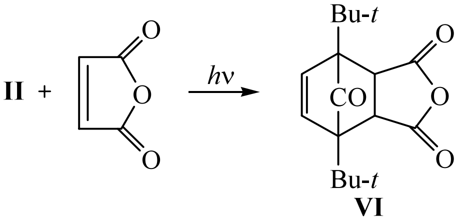
The isomer 3,5-di-*tert*-butyl-*o*-benzoquinone (**III**) reacts in the same fashion, but its decarbonylation product 2,4-di-*tert*-butylcyclopentadienone (**IV**) is a short-lived compound and even in the course of isolation it transforms into a Diels–Alder dimer, 2,3*a*,5,7-tetra-*tert*-butyl-3*a*,4,7,7*a*-tetrahydro-4,7-methanoindene-1,8-dione (**V**). The latter process can be visually observed by the disappearance of the characteristic orange-red cyclopentadienone color.



III **IV**

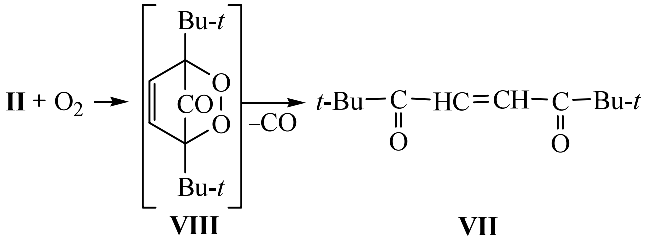
V

Dienone **II** sterically protected from the dimerization of the [4+2]-cycloaddition type is capable to react as a diene with less hindered dienophiles. For instance, in the photolysis of quinone **I** in the presence of maleic anhydride we isolated 1,8-di-*tert*-butyl-4-oxatricyclo-[5.2.1.0*2,6*]-dec-8-ene-3,5,10-trione (**VI**).



VI

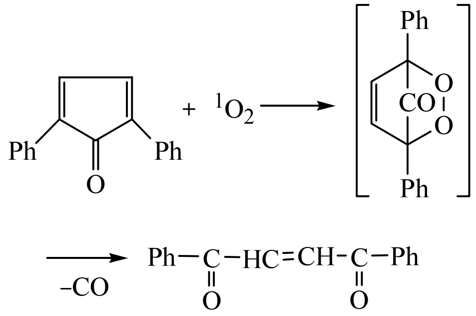
In photolysis carried out in the presence of oxygen the formation of 1,2-dipivaloylethylene (**VII**) was observed



VIII **VII**

whose precursor was a cyclic peroxide **VIII**, an adduct of dienone **II** with oxygen.

This process is a full analog of the reaction of 2,5-diphenylcyclopentadienone with a singlet oxygen that is used as one among chemical tests for the singlet oxygen [2].

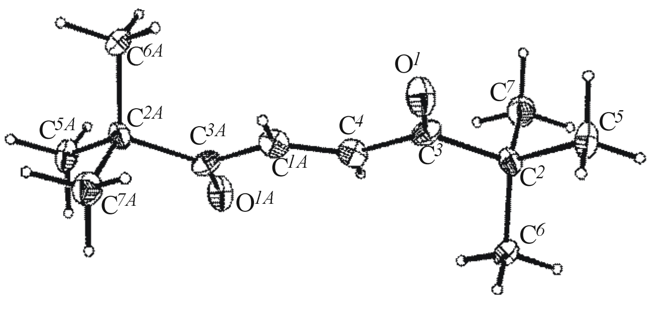


The data on the structure of compound **VII** are presented on the figure.

In our case dienone **II** turned out to be an indicator of a singlet oxygen formed *in situ*. The most probable mechanism of its generation is a triplet-triplet annihilation at the interaction of $^3O_2$ with a triplet-excited quinone [3]: $^3(I) + {}^3O_2 \rightarrow (I)_0 + {}^1O_2$. The quenching of quinone triplets in this process with the simultaneous decrease in the yield of the decarbonylation products (sum of compounds **II** and **VII**) makes it possible to identify the excited state of the quinone responsible for the decarbonylation as a triplet state.

The participation of oxygen inhibits the decarbonylation and changes the direction of the photoprocess. The main pathway becomes photooxygenolysis giving as products the above-mentioned 1,2-dipivaloylethylene (**VII**) and di-*tert*-butylmuconic anhydride (**IX**), the prevailing product arising from the reaction of $^1O_2$ with quinone **I**.

This reaction in comparison with the formation of anhydride **IX** from quinone **I** and $PhCO_3H$ or H_2O_2 in acid medium supports the conclusion of Denny and Nickon [4] on similarity of oxidation results of certain organic compounds with $^1O_2$ and of the nonradical reactions of the same organic compounds with peroxides.



Structure of 1,2-dipivaloylethylene (**VII**).

Apparently quinone **I** being indifferent to $^3O_2$ but capable to add $^1O_2$ can be used as chemical indicator for $^1O_2$ along with cyclopentadienones. The ability of quinone **I** to react with $^1O_2$ combined with the high antioxidant activity of the redox-conjugate 3,6-di-*tert*-butylpyrocatechol (**X**) [5] permits an assignment of the redox-couple pyrocatechol–quinone to the series of "universal" antioxidants.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord M-80 from KBr pellets, ^1H NMR spectra were registered on a spectrometer WH-250 (250 MHz), internal reference TMS. Crystals of alkene **VII** were studied by X-ray diffraction method. Colorless plates $C_{12}H_{20}O_2$ (M 196.28), triclinic, at 110 K a 5.609(6), b 5.933(6), c 9.863(10) Å, α 79.98(2), β 78.93(2), γ 64.37(2)°, V 288.9(5) Å^3, space group P-1, Z 2, C_{calc} 1.128 g/cm^3. The experimental set of 2499 reflections was obtained with diffractometer Bruker SMART CCD area detector [7] at 110 K (λMoK_α-radiation, $2\theta_{max}$ 46°) from a single crystal of the size 0.30×0.15×0.05 mm. After averaging the equivalent reflections we obtained 1027 independent reflections (R_{int} 0.0972) used in solving and refining of the structure. The extinction (μ 0.075 mm^{-1}) was not taken into account, the values T_{max} and T_{min} (0.928 and 0.676 respectively) were estimated using SADABS routine [8]. The structure was solved by the direct method, all the nonhydrogen atoms were localized in the difference synthesis of the electron density and refined by F^2_{hkl} in the anisotropic approximation; all hydrogen atoms were placed into the geometrically calculated positions and refined in the *rider* model with U(H) = 1.2 U(C) where U(C) is the equivalent thermal factor of the carbon linked to the corresponding hydrogen atom. The final values of the uncertainty factors are as follows: R_1 0.0551 [calculated by F_{hkl} for 278 reflections with $I > 2\sigma(I)$], wR_2 0.0645 (calculated by F^2_{hkl} for all 1027 reflections), GOOF 0.756.66 of refined parameter.

All calculations were carried out applying the software package SHELXTL PLUS 5 [9].

3,6-Di-*tert*-butyl-*o*-benzoquinone (**I**) was prepared by oxidation of pyrocatechol (**X**) with Ag_2O in ethyl ether as described in [6].

Photolysis of 3,6-di-*tert*-butyl-*o*-benzoquinone (I) under nitrogen atmosphere. A solution of 0.22 g of quinone **I** in 20 ml of benzene was irradiated with light

($\lambda > 380$ nm) at room temperature under a nitrogen atmosphere till disappearance of quinone **I** traces. On removing the solvent the crystalline residue was purified by sublimation. We obtained 0.17 g (89%) of compound **II**, mp 59–60°C. IR spectrum, ν, cm^{-1}: 1720 (C=O), 1590 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.06 s (9H), 6.21 s (1H). Found, %: C 81.16; H 10.46. $C_{13}H_{20}O$. Calculated, %: C 81.17; H 10.48.

Photolysis of 3,6-di-*tert*-butyl-*o*-benzoquinone (I) in the presence of atmospheric oxygen. The photholysis of 0.22 g of quinone **I** was performed as described above but at access of air. The chromatographic analysis revealed the presence in the reaction mixture of a multitude of products. We isolated preparatively 20 mg (10%) of 1,2-dipivaloylethylene (**VII**) and 50 mg (20%) of di-*tert*-butylmuconic anhydride (**IX**). Compound **VII**, mp 108–109°C (after sublimation). ^{1}H NMR spectrum, δ, ppm: 1.4 s (9H), 7.1 s (1H). Found, %: C 73.55; H 10.25. $C_{12}H_{20}O_2$. Calculated, %: C 73.40; H 10.25. Anhydride **IX**, mp 100–101°C. ^{1}H NMR spectrum, δ, ppm: 1.24 s (9H), 6.37 s (1H). Found, %: C 70.81; H 8.29. $C_{14}H_{20}O_3$. Calculated, %: C 71.10; H 8.54.

Anhydride **IX** was also prepared by an independent synthesis by reacting quinone **I** with $PhCO_3H$ at boiling in benzene; it was isolated by TLC on Silufol UV-254 plates in a system hexane–ethyl ether, 4:1, v/v, yield 25%, mp 100–101°C , the mixed sample of compound **IX** prepared by both procedures melted without depression of the melting point.

Photolysis of 3,5-di-*tert*-butyl-*o*-benzoquinone (III). The photolysis conditions were similar to those described above. On evaporation of benzene we obtained colorless crystals of 2,3*a*,5,7-tetra-*tert*-butyl-3*a*,4,7,7*a*-tetrahydro-4,7-methanoindene-1,8-dione (**V**), mp 150–151°C (from methanol). ^{1}H NMR spectrum, δ, ppm: 0.98 s (9H), 1.05 s (9H), 1.14 s (9H), 1.19 s (9H), 2.96 s (1H), 3.18 d (1H, ^4J 1.1 Hz), 5.89 d (1H, ^4J 1.1 Hz), 6.77 s (1H). Found, %: C 81.51; H 10.50. $C_{26}H_{40}O_2$. Calculated, %: C 81.17; H 10.48.

1,8-Di-*tert*-butyl-4-oxatricyclo[5.2.1.0*2,6*]-dec-8-ene-3,5,10-trione (VI). A mixture of 0.22 g of quinone **I** and 0.1 g of maleic anhydride in 20 ml of anhydrous benzene was irradiated under nitrogen atmosphere till the quinone color disappeared. On evaporating the solvent and crystallization of the residue from hexane we obtained 0.23 g (81%) of adduct **VI**, mp 153–154°C. ^{1}H NMR spectrum, δ, ppm: 1.00 s (9H), 2.92 s (1H), 5.34 s (1H). Found, %: C 70.10; H 7.88. $C_{17}H_{22}O_4$. Calculated, %: C 70.34; H 7.64.

Adduct **VI** was also obtained by an independent synthesis by boiling equimolar amounts of cyclopentadienone **II** and maleic anhydride in benzene for 2 h.

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