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Reaction on the addition of some organometallic compounds to 3,6-di-*tert*-butyl-*o*-benzoquinone: new *o*-quinones

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Abstract

3,6-Di-*tert*-butyl-*o*-benzosemiquinone is very convenient for the investigation of the interaction between organometallic R_2M and carbonyl compounds. The reaction of organometallic compounds R_2M with *o*-quinone, where R = Ph, Me, Et, Pr, ^{i}Pr or ^{t}Bu and M ≡ Zn, Cd, and Al, proceeds in two ways: (1) the single-electron oxidation of the organometallic compound by *o*-quinone, resulting in derivatives of alkyl(phenyl)oxyphenols; (2) the polar 1,2 and 1,4 addition of organometallic molecules to *o*-quinone as to conjugated ketone, which produces hydroxycyclohexadienones after hydrolysis.

The relationship between these two is defined by the nature of the organometallic compound. The products of polar addition are rearranged easily in different ways, finally resulting in new *o*-quinones: 3-(R)-6-*tert*-butyl-*o*-benzoquinones and 3,6-di-*tert*-butyl-4-(R)-*o*-benzoquinones, where R ≡ alkyl.

Keywords: Zinc; Cadmium; Aluminium; *O*-quinones; Electron transfer

1. Introduction

Many papers have been dedicated to the problems of the carbonyl compound interaction with organometallic compounds because these processes are widely used in organic synthesis. Their interaction mechanism description has been presented, some of them we should like to consider [1–3]. The main conclusion shown from data in the literature indicates that the reaction of organometallic compounds with different ketones proceeds in two different ways: (1) reagent interaction in accordance with the one-electron transfer mechanism; (2) organometallic molecule polar addition to the carbonyl group.

However, the ratio of these two in the real chemical process is rarely defined, because of the recombination of ion-radical particles due to the single-electron transfer which results in the same products as those produced in the polar addition reaction [4]. Efforts undertaken to find a model system in which a certain product series would separate the two different ways have not been successful [5].

o-Quinone interaction with organometallic compounds has not been researched so intensively. In one of the first studies of this problem [6] using the reactions of phenanthrenequinone and a number of naphthoquinones with dimethylzinc and diethylzinc it was shown that different products are produced depending on the alkyl group nature; Me_2Zn gives 1,2-addition products to one of the carbonyl groups of *o*-quinone, and the reaction of Et_2Zn produces ethoxyphenols. In work presented earlier [7] the reaction of *o*-quinones with ^{t}BuMgCl was shown to result finally in the new *o*-quinones, in which one of the ring protons was substituted by a radical from the organometallic molecule.

Among other data in the literature we should like to mention Refs. [8 and 9], which are devoted to investigation of the interaction mechanism of the sterically hindered *o*-benzoquinones with ethyl derivatives of the Group 12 and Group 13 elements. The reactions were carried out in toluene at a low temperature. Product composition—ethoxyphenols (> 95%), ethane and ethylene—together with the intermediate paramagnetic

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substance observation during the process allowed the reaction mechanism to be interpreted as the one-electron oxidation of organometallic compound by *o*-benzoquinone.

2. Results and discussion

The literature data mentioned above give us an opportunity to suppose that the organometallic compound interaction with *o*-quinone, as well as with other carbonyl compounds, may proceed by two concurrent mechanisms. In order to the clarify this phenomenon, the reactions of the sterically hindered *o*-benzoquinones with the series of organometallic compounds were investigated by varying the alkyl(aryl) radicals. Organometallic compounds of Zn and Cd were used as the reagents. 3,6-Di-*tert*-butyl-*o*-benzoquinone (3,6-DTBQ) was chosen since, first, the more reactive 4,5 ring positions of this quinone do not contain any substituents and are open to attack by the different reagents and, secondly owing to its symmetric structure the minimum number of possible isomers would be present in the reaction products. The reactions were carried out in tetrahydrofuran (THF) in the temperature range from −60 to +60°C. It is interesting that all the investigated processes occur rapidly in the whole temperature range.

The first investigated reaction was the interaction of Me_2Zn (Cd) with 3,6-DTBQ [10]. The process occurs in accordance with a classical scheme of the polar addition of organometallic reagents to conjugated ketones. The total yield and the ratio of 1,2- to 1,4-addition products (80% and 20% at −60°C) at a fixed temperature remain constant and do not depend on the solvent nature (THF, diethyl ether, toluene or hexane); the introduction of complexable reagents, such as pyridine and α,α′-dipyridyl also have no influence on the process. It should be emphasized that no products of the one-electron oxidation of Me_2Zn were

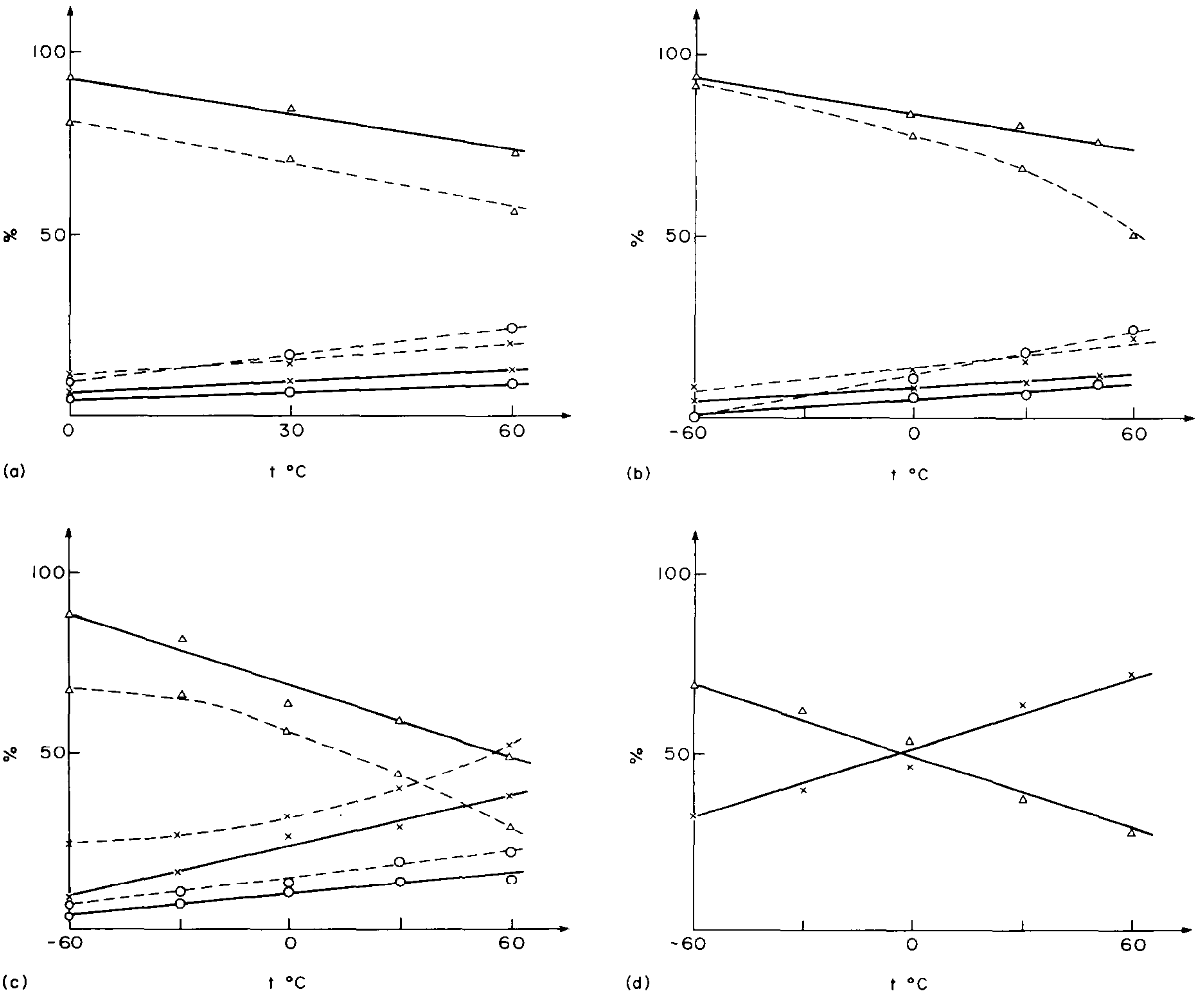


Fig. 1. The dependence of product I (×), II (○) and III (△) yields on temperature in the reaction of 3,6-DTBQ with R_2M, where M = Zn (———) and Cd (- - - - -): (a) $Et_2Zn(Cd)$; (b) $^nPr_2Zn(CD)$; (c) $^iPr_2Zn(Cd)$; (d) $^tBu_2Zn$.

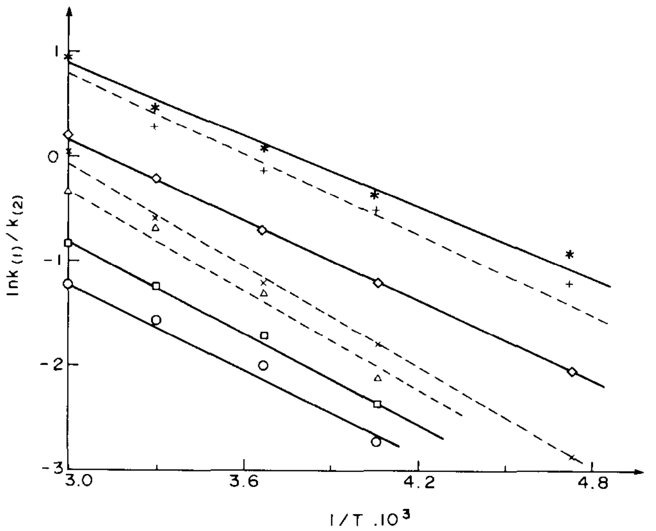


Fig. 2. The dependence of $\ln(k_{(1)}/k_{(2)})$ on $1/T$ in the reaction of 3,6-DTBQ with R_2M: ⊙, Et_2Zn: ⊡, $^nPr_2Zn$; △, Et_2Cd; ×, $^nPr_2Cd$; ◇, $^iPr_2Zn$; +, $^iPr_2Cd$ *, $^tBu_2Zn$.

observed over the temperature range. The only temperature influence consists in changing the product ratio of 1,2 to 1,4 additions.

To investigate the 3,6-DTBQ interaction with other R_2Zn (Cd) with R = Ph, Et, ^nPr, ^iPr or ^tBu, the same procedure for reaction mixture treatment was used as in [10] (excluding the $^tBu_2Zn$ reaction): heating to room temperature, acidification, oxidation by potassium ferrocyanide in alkali medium and the subsequent separation of products by chromatography on silica gel. Three types of substance have been identified: 3,6-di-*tert*-butyl-4-alkylbenzoquinones-1,2 (**I**), 3-alkyl-6-*tert*-butylbenzoquinones-1,2 (**II**) and alkoxyphenols (**III**). In order to prevent alkoxyphenol (**III**) oxidation, sodium carbonate was used as the alkali reagent. Even small amounts of sodium hydroxide added to the water solution result in oxidative coupling products of alkoxyphenols. The total yield of products was very close to the quantitative yield (greater than 98%) and their ratio depends greatly on the organometallic compound nature and the reaction temperature. The experimental temperature dependences of **I**, **II** and **III** product yield for Et_2Zn(Cd), $^nPr_2Zn$(Cd), $^iPr_2Zn$(Cd) and $^tBu_2Zn$ are shown in Figs. 1(a), 1(b), 1(c) and 1(d) respectively. The only phenoxyphenol as the unique product is formed in the reaction of Ph_2Zn(Cd) with 3,6-DTBQ in the temperature range from −20 to +20°C.

The general product composition in the processes researched is that the reaction occurs in two ways: (1) polar or nucleophilic addition of organometallic compound to *o*-quinone (products **I** and **II**); (2) one-electron transfer followed by the recombination of ion-radical particles (product **III**). This approach can be described by Scheme 1. In accordance with this scheme, discussed previously in [4], both processes are bimolecular and they conform to the second kinetic order. The following equation (1) is valid under this condition, i.e. the products ratio is determined only by the rate constant ratio of the two ways:

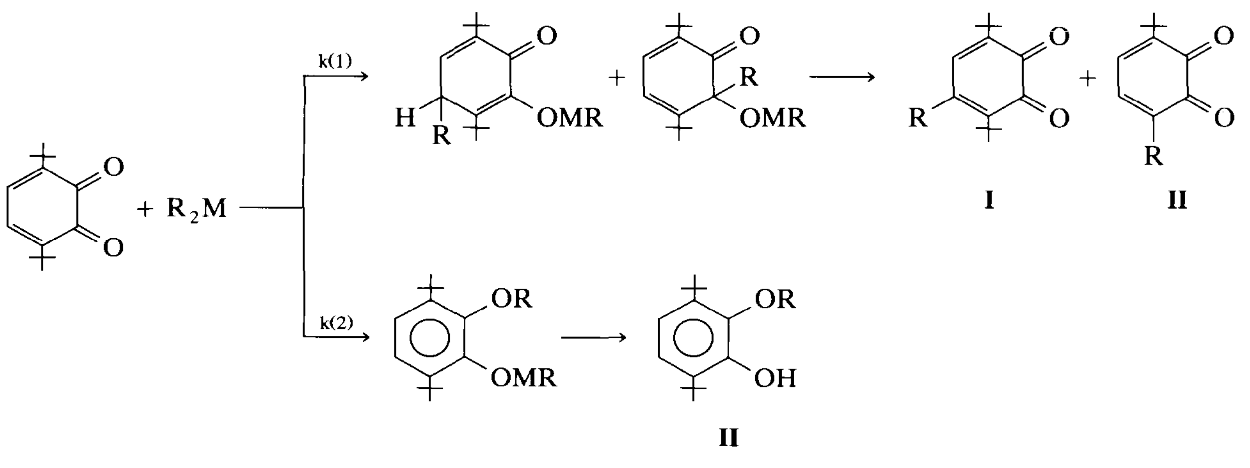
$$\frac{[\mathbf{I}+\mathbf{II}]}{[\mathbf{III}]}=\frac{k_{(1)}}{k_{(2)}} \tag{1}$$

In this case the temperature dependence of the product ratio in terms of a semilogarythmic anamorphosis, i.e. ln [1 + 2] against $1/T$ (Fig. 2) allows us to calculate the difference between the Arrhenius activation energies ($\Delta E_a = E_{a(1)} - E_{a(2)}$) of the two parallel processes of the reactions, except for the reactions of interaction 3,6-DTBQ with diphenyl and dimethyl organometallic derivatives, where one of the ways completely prevails over the other.

On the basis of the data given in Fig. 2, in accordance with

$$\ln\left(\frac{k_{(1)}}{k_{(2)}}\right)=-\frac{\Delta E_a}{RT}+\ln\left(\frac{A_{(1)}}{A_{(2)}}\right) \tag{2}$$

the following results were obtained (Table 1).



Scheme 1.

Table 1
Parameters of equation (2) for different organometallic compounds

R_2M	ΔE_a [a] (cal mol^{-1})	$\ln(A_{(1)}/A_{(2)})$
Et_2Zn	2600	2.72
Et_2Cd	3300	4.69
$^nPr_2Zn$	2800	3.31
$^nPr_2Cd$	3300	4.94
$^iPr_2Zn$	2600	4.16
$^iPr_2Cd$	2700	4.83
$^tBu_2Zn$	2300	4.31

[a] Correlation coefficients for all equations of type (2) are near to 0.99.

The Arrhenius equation parameters obtained testify, on the one hand, to the lower activation energy of the one-electron transfer reaction (which was to be expected) and, on the other hand, to the more difficult entropy control of this process, in comparison with that in the reaction of nucleophilic addition.

ΔE_a values for the corresponding cadmium compounds are slightly higher than for organozinc compounds, and correspondingly the product yields for nucleophilic addition for compounds of Cd are approximately 15–20% higher. However, it is known that the ionization potentials for organometallic compounds of Cd are lower than for those of Zn, at least for Me and Et derivatives (Me_2Zn, 9.4 eV; Me_2Cd, 8.76 eV; Et_2Zn, 8.6 eV; Et_2Cd, 8.2 eV [11]). The radical nature influence upon ΔE_a remains unrevealed. However, $\ln(k_{(1)}/k_{(2)})$ values depend linearly on the Taft constants of organometallic compound radicals. The corresponding correlation expressions are follows: for Cd at 273 K,

$$\ln\left(\frac{k_{(1)}}{k_{(2)}}\right) = -14.395\sigma^* - 2.79 \qquad (r = 0.99)$$

and for Zn at 273 K,

$$\ln\left(\frac{k_{(1)}}{k_{(2)}}\right) = -10.416\sigma^* - 3.02 \qquad (r = 0.98)$$

Unfortunately, the results of 3,6-DTBQ interaction with phenyl and methyl organometallic compounds could not be included in this relation.

To elucidate the general trend of influence of the organometallic compound nature on the ratio of the polar addition and the one-electron oxidation reactions, the plot of total yield of reaction (1) products (I + II) (at a certain temperature) as a function of the Taft inductive constants of R substituents in R_2M was constructed (Fig. 3). The ionization potential values are more convenient for organometallic compound characterization, but many of these data cannot be found in the literature.

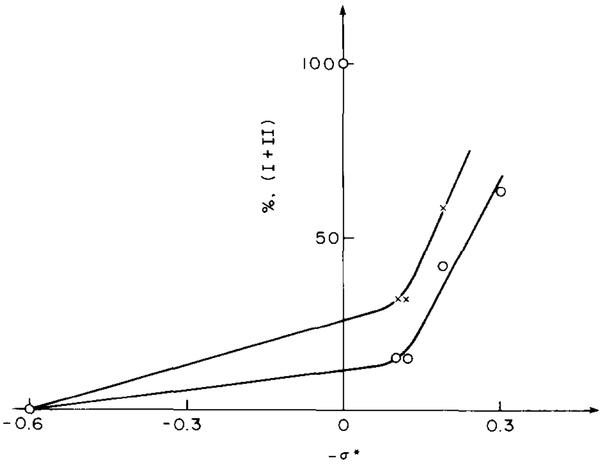
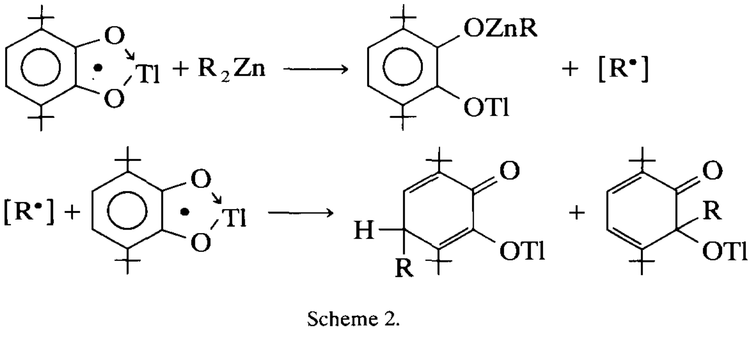


Fig. 3. The dependence of the summary yields of products **I** and **II** on the Taft constants σ^* of R (R_2M, where M ≡ Zn (⊙) or Cd (×)) at 30°C.

Nevertheless, it is well known that on increasing these constants the ionization potential of organometallic compound monotonically decreases [12]. For the organometallic compounds researched it is not that on increasing the Taft inductive constant from Ph to ^tBu, the contribution of the polar addition process monotonically increases in a range from 0% to 73% for Zn compounds. The exception is $Me_2Zn(Cd)$, which reacts with *o*-quinone in the polar addition way quantitatively, probably owing to the low steric constant of the methyl radical and the opportunity of a straight attachment of a negatively charged carbon atom of the organometallic compound to the *o*-quinone electron-deficient centres.

In spite of the observation of two definite product series there is not direct proof of the principal differ-



Scheme 2.

ences between their mechanism formation (free-radical and ionic pathways). Formally the 1,2- and 1,4-addition products can arise from free-radical recombination. Moreover, the preliminary investigation of R_2M ($M \equiv$ Zn or Cd) interaction with 3,6-DTBSQ-Tl, where ionic addition product formation is impossible, have demonstrated dienonic species of type **I′** and **II′**, whose origin should be only free-radicals recombination, as in Scheme 2.

On the basis of these data the following conclusion can be drawn for the reaction of 3,6-DTBQ with Zn and Cd organic derivatives: the relation between the changes in two processes increasingly favours the polar addition with decreasing organometallic compound ionization potentional.

This conclusion, at first sight, seems non-obvious, since the reaction rate of the one-electron transfer would also increase with decreasing ionization potential of the reacting organometallic compound [13].

Our experimental data demonstrate that the polar addition reaction is more sensitive to the energy change of the highest occupied molecular orbital (HOMO) of the organometallic compound than is the one-electron transfer process, i.e. with increasing energy of the HOMO the rate of nucleophilic addition to the quinone increases more than does the rate of the one-electron transfer process.

The reaction of the polar addition of organometallic compound to 3,6-DTBQ produces two products of 1,2 and 1,4 additions with respect to the carbonyl group, the ratio of which is mainly defined by the above-mentioned experimental data (see Fig. 1). The addition product ratio of 1,2 and 1,4 decreases as the radical changes from Me to ^{t}Bu, for both Zn and Cd compounds (Fig. 4) which obviously arises from the electron and steric characteristics of the radicals. On increasing the Taft constants the yield of the 1,2-addition product decreases monotonically. So, for example, in the reaction of 3,6-DTBQ with ^{t}Bu$_2$Zn (maximum σ^*) the 1,2-addition product is absent according to IR and ^{1}H NMR spectroscopy data, whereas the amount of the 1,4-addition product comes to about 63% in the total balance of this reaction at 30°C.

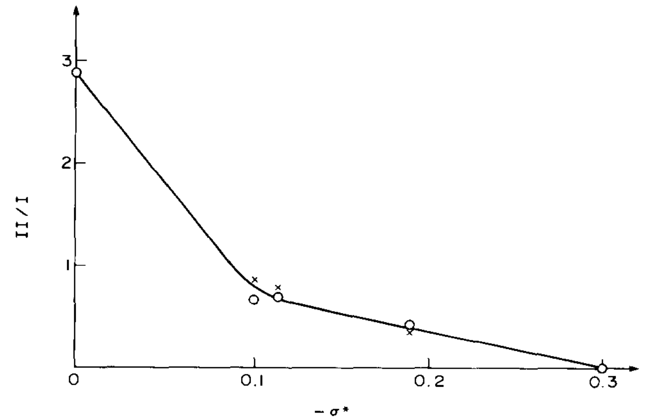


Fig. 4. The dependence of the ratio of product I and II yields on the Taft constants σ^* of R (R_2M, where $M \equiv$ Zn (⊙) or Cd (×)) at 0°C.

The difference between the Zn and Cd organic compounds is not great and it is determined by the radical nature mainly; however, for Al derivatives, e.g. the interaction of Me_3Al [10] with 3,6-DTBQ, the 1,4-addition product yield doubles in comparison with Zn(Cd) and is 42% at 20°C. So the relative yields of 1,2- and 1,4-addition products might be controlled by the choice of the metal in an organometallic compound.

In all the reactions investigated, the electron spin resonance (ESR) method was used, which detected the *o*-semiquinone Zn and Cd derivative signals; according to the hyperfine structure (HFS) constant analysis on magnetic isotopes of Cd (^{111}Cd, $J = \frac{1}{2}$; ^{113}Cd, $J = \frac{1}{2}$), primary products of the one-electron oxidation of R_2Cd by 3,6-DTBQ of the (DTBSQ)MR type were observed only for Me and Et derivatives ($a_{Cd} = 2.1$ G in pentane and 2.6 G in ether at 290 K). As for other alkyl substituents, ESR spectra were recorded of semiquinonic species, being the products of some secondary reactions, which correspond to more extensive organometallic compound molecule transformation. The HFS constant a_{Cd} values (8–10 G) are typical for the tetracoordinated cadmium atom [10].

The experimental features of the formation of products in the reaction of organometallic compounds with *o*-quinone, which are shown in this work make it possible to choose more efficient reagents for the synthesis of new *o*-quinones with alkyl or aryl substituents. For example, in the synthesis of 3,6-di-*tert*-butyl-4-arylbenzoquinone-1,2 the more active magnesium and lithium derivatives are required to achieve the maximum product yield.

3. Experimental details

IR spectra were recorded on UR-20 and Specord-80 spectrometers. ^{1}H NMR spectra were obtained with a 100 MHz Tesla BS-576A spectrometer, using the solvents CCl_4, $CDCl_3$ and acetone-d_6 and the integral standard hexamethyldisiloxane. ESR spectra were recorded on a Bruker ER-200D-SRC spectrometer. High performance liquid chromatography analyses were obtained a Milichrom-1A microcolumn liquid chromatograph. All solvents used were prepared in accordance with standard procedures [14]; Zn and Cd organic compounds were prepared as described in [15], and 3,6-di-*tert*-butyl-*o*-benzoquinone as in [16].

3.1. Reaction of 3,6-di-tert-butyl-o-benzoquinone with $Et_2Zn(Cd)$

To a solution of 0.05 mol of 3,6-DTBQ in 100 ml of THF, placed in an evacuated vessel, a solution of 0.05 mol of $Et_2Zn(Cd)$ in 30 ml of THF was added in small portions. After 15–20 min the reaction mixture was treated with a mixture of acetic and hydrochloric acids; the products were extracted with ether and washed with water up to a neutral medium. The ether solution obtained was oxidized by potassium ferricyanide in an alkaline medium. After oxidation the ether was changed to hexane and then the solution was chromatographed on a Silochrome column with hexane as eluent. The colourless zone was collected up to colour emergence, which indicates *o*-quinones. After evaporation of a portion of the solvent and on cooling, colourless crystals were precipitated from the solution. 2-ethoxy-3,6-di-*tert*-buthylphenol: melting point (m.p.), 61°C. IR (CCl_4, 5×10^{-3} M): ν(O–H) 3530 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ ^{t}Bu 1.37 (s, 18H); CH_3 1.45 (t, $J = 7.2$ Hz, 3H); CH_2Me 3.90 (q, $J = 7.2$ Hz 2H); OH 5.75 (s, 1H); H(4) 6.77 (d, $J = 8.5$ Hz, 1H); H(5) 6.93(d, $J = 8.5$ Hz, 1H). Anal. Found: C, 76.65; H, 10.75. $C_{16}H_{26}O_2$ Calc.: C, 76.80; H, 10.40%.

The colour band was eluted with ether and the eluate was rechromatographed on Silochrome using a mixture of hexane and methylacetate (100 : 1) as eluent; so two fractions were separated. On distillation of a part of the solvent, green crystals were obtained from the first fraction. 4-ethyl-3,6-di-*tert*-butyl-o-benzoquinone: m.p., 59°C. IR (Nujol): ν(C=O) 1664, 1685 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ CH_3 1.19 (t, $J = 7.5$ Hz, 3H), ^{t}Bu(6) 1.22 (s, 9H), ^{t}Bu(3) 1.37 (s, 9H), CH_2Me 2.56 (q, $J = 7.5$ Hz, 2H), H(5) 6.55 (s, 1H). Anal. Found: C, 77.27; H, 9.63. $C_{16}H_{24}O_2$ Calc.: C, 77.42; H, 9.68%

Dark-brown needle-shaped crystals were isolated from the second fraction. 3-Ethyl-6-*tert*-butyl-*o*-benzoquinone: m.p., 97°C. IR (Nujol): ν(C=O) 1665, 1685 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ CH_3 1.08 (t, $J = 7.0$ Hz, 3H), ^{t}Bu 1.22 (s, 9H), CH_2Me 2.35 (q, $J = 7.0$ Hz, 2H), H(4.5) 6.7(m, 2H). Anal. Found: C, 75.01; H, 8.58. $C_{12}H_{16}O_2$ Calc.: C, 75.0; H, 8.33%.

3.2. Reactions of 3,6-di-tert-butyl-o-benzoquinone with $^nPr_2Zn$ (Cd) and $^iPr_2Zn$ (Cd)

These reactions and the product isolation were carried out similarly to the reaction of 3.6-DTBQ with $Et_2Zn(Cd)$. The following compounds were isolated.

2-Propoxy-3,6-di-*tert*-butylphenol: colourless crystals; m.p., 39°C. IR (CCl_4, 5×10^3 M): ν(OH) 3530 cm^{-1}. ^{1}H NMR (CCl_4): δ CH_3 1.08(t, $J = 7.0$ Hz, 3H), ^{t}Bu 1.34 (s, 9H) 1.35(s, 9H), CH_2Me 1.80 (m, 2H), OCH_2 3.76 (t, $J = 7.0$ Hz, 2H), OH 5.60 (s, 1H), H(4) 6.64 (d, $J = 8.4$ Hz, 1H), H(5) 6.80 (d, $J = 8.4$ Hz, 1H). Anal. Found: C, 76.85, H, 10.88. $C_{17}H_{28}O_2$ Calc.: C, 77.27; H, 10.61%.

2-Isopropoxy-3,6-di-*tert*-butylphenol: colourless crystals; m.p., 23–25°C. IR (CCl_4, 5×10^{-3} M): ν(OH) 3500 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ CH_3 1.28 (d, $J = 6.1$ Hz, 6H), ^{t}Bu 1.37 (s, 9H), 1.38 (s, 9H), $OCHMe_2$ 4.36 (sp, $J = 6.4$ Hz, 4H), OH 5.13 (s, 1H), H(4) 6.80 (d, $J = 8.5$ Hz, 1H), H(5) 6.91 (d, $J = 8.5$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ CH_3 21.9(q), $C(CH_3)_3(6)$ 29.2, $C(CH_3)_3(3)$ 31.3(q), $CMe_3(6)$ 34.0(s), $CMe_3(3)$ 34.8(s), OCH 76.1(d), C(5) 118.1(d), C(4) 121.1(d), C(3) 133.3(s), C(6) 140.1(s), C(1) 142.4(s), C(2) 149.5(S). Anal. Found: C, 77.66; H, 10.92. $C_{17}H_{28}O_2$ Calc.: C, 77.27; H, 10.61%.

4-Propyl-3,6-di-*tert*-butyl-*o*-benzoquinone: red–brown crystals; m.p., 72°C. IR (Nujol): ν(C=O) 1660, 1680 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ CH_3 1.05 (t, $J = 6.57$. Hz, 3H), ^{t}Bu 1.21 (s, 9H) 1.34 (s, 9H), CH_2Me 1.60-(m, 2H), CH_2Et 2.50 (m, 2H), H(5) 6.54 (s, 1H). Anal. Found: C, 77.56; H, 10.20. $C_{17}H_{26}O_2$ Calc.: C, 77.86; H, 9.92%.

4-Isopropyl-3,6-di-*tert*-butyl-*o*-benzoquinone: red–brown crystals; m.p., 97°C. IR (Nujol): ν(C=O) 1660, 1675 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ CH_3 1.14 (d, $J = 6.6$ Hz, 6H), ^{t}Bu 1.22 (s, 9H) 1.33 (s, 9H), CH 3.47 (sp, $J = 6.6$ Hz, 1H), H(5) 6.77(s, 1H). Anal. Found: C, 77.88; H, 9.97%. $C_{17}H_{26}O_2$ Calc.: C, 77.86; H, 9.92.

3-propyl-6-*tert*-butyl-*o*-benzoquinone: brown needle crystals; m.p., 70°C. IR (Nujol): ν(C=O) 1660, 1685 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ CH_3 0.93 (t, $J = 7.0$ Hz, 3H), ^{t}Bu 1.22 (s, 9H), CH_2Me 1.50 (m, 2H), CH_2Et 2.30 (t, $J = 7.0$ Hz, m, 2H), H(4) 6.70 (d, $J = 6.8$ Hz, t, $J = 0.94$ Hz, 1H), H(5) 6.75 (d, $J = 6.8$ Hz, 1H). Anal. Found: C, 75.85; H, 8.94. $C_{13}H_{18}O_2$ Calc.: C, 75.73; H, 8.74%.

3-Isopropyl-6-*tert*-butyl-*o*-benzoquinone: green–brown crystals; m.p., 96°C. IR (Nujol): ν(C=O) 1660, 1685 cm^{-1} ^{1}H NMR ($CDCl_3$): δ CH_3 1.10 (d, $J = 7.0$ Hz, 6H), ^{t}Bu 1.23 (s, 9H), $CHMe_2$ 2.92 (sp, $J = 7.0$ Hz, m, 1H), H(4) 6.68 (d, $J = 6.9$ Hz, d, $J = 1.0$ Hz, 1H), H(5) 6.67 (d, $J = 6.9$ Hz, 1H). Anal. Found: C, 75.67; H, 8.98. $C_{13}H_{18}O_2$ Calc.: C, 75.73; H, 8.74%.

3.3. The reaction of 3,6-di-tert-butyl-o-benzoquinone with $^tBu_2Zn$

This reaction was carried out under similar conditions. After the hydrolysis of the reaction mixture with acetic acid, the products were extracted with ether and washed with water up to a neutral medium; then ether was changed for hexane and colourless crystals were isolated.

2-*tert*-butoxy-3,6-di-*tert*-butylphenol: m.p., 101°C IR

(CCl_4, 5×10^{-3} M): ν(OH) 3535 cm^{-1}. u1H NMR ($CDCl_3$): δ ^tBu 1.37 (s, 9H), 1.40(s, 9H), O-^tBu 1.44 (s, 9H), OH 5.80 (s, 1H), H(5) 6.79 (d, $J = 8.5$ Hz, 1H), H(4) 6.89 (d, $J = 8.5$ Hz, 1H). Anal. Found: C, 78.22; H, 11.00. $C_{18}H_{30}O_2$ Calc.: C, 77.70; H, 10.79%.

Then the parent solution was evaporated and the residue was recrystallized from methanol, yielding colourless crystals as follows.

2-Oxy-3,4,6-di-*tert*-butylciclohexadienon-2,5: IR (Nujol): ν(OH) 3360, ν(C=O) 1640 cm. ^1H NMR ($CDCl_3$): δ ^tBu (4) 0.95 (s, 9H), ^tBu(6) 1.23 (s, 9H), ^tBu(3) 1.30 (s, 9H), H(4) 3.26 (d, $J = 5.6$ Hz, 1H), H(5) 7.01 (d, $J = 5.6$ Hz, 1H), OH 7.11 (s, 1H).

3.4. Reaction of 3,6-DTBQ with $Ph_2Zn(Cd)$

This reaction was carried out in the same conditions and resulted in only one product.

2-Phenoxy-3,6-di-*tert*-butylphenol: colourless crystals, m.p., 68°C, IR (CCl_4, 5×10^{-3} M): ν(OH) 3570 cm^{-1}. ^1H NMR ($CDCl_3$); δ ^tBu 1.25 (s, 9H) 1.32 (s, H), OH 5.29 (s, 1H), Ph 6.7–7.4 (m, 5H).

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