Photoinduced Electron Transfer Oxidation. I. 9,10-Dicyanoanthracene-sensitized Photooxidation of Hindered Phenols

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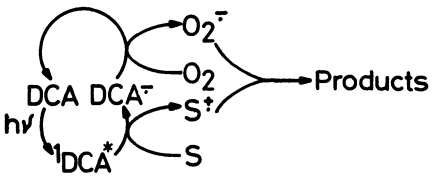
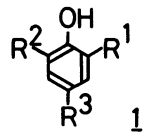
9,10-Dicyanoanthracene (DCA)-sensitized photooxidation reactions of hindered phenols and catechols (**1**) proceed *via* the initial electron transfer from **1** to ^{1}DCA*. 4-Hydroperoxy-2,5-cyclohexadien-1-ones and 4-hydroxy-2,5-cyclohexadien-1-ones are obtained from 2,4,6-trialkyl-substituted phenols, and an *o*-benzoquinone and furanone derivatives are afforded from 3,5-di-*t*-butylcatechol.

Oxygenation of the phenol and catechol has long been one of the current subjects in connection with model reactions for enzymes[1] and a number of reports both from a synthetic[2] and a kinetic[3,4] viewpoints have been accumulated in the literature. This problem is of interest because their oxidation products highly depend on the reaction conditions, *i.e.*, their substituents,[5] oxidizing reagents,[1,6–13] and solvent,[13] *etc.*

Recently, photoinduced electron transfer reactions have attracted much attention of photochemists.[14] 9,10-Dicyanoanthracene (DCA) can be a good electron deficient sensitizer in the electron transfer oxidation of electron-rich substrates[15] because the second electron transfer process from DCA$^{\cdot-}$ to O_2 (see Scheme 1) is exothermic ($E_{1/2}^{RED}$(DCA) = −0.97 V, $E_{1/2}^{RED}$(O_2) = −0.94 V, *vs.* SCE in MeCN). It is already reported that electron-rich substrates, such as olefins,[15] acetylenes,[16] aromatics,[17] and sulfides,[18] undergo DCA-sensitized photooxidation reactions as Scheme 1 shows.



Scheme 1.



1

	R^1	R^2	R^3
1a:	t-Bu	t-Bu	t-Bu
1b:	t-Bu	t-Bu	Me
1c:	Me	Me	Me
1d:	H	H	t-Bu
1e:	OH	t-Bu	t-Bu
1f:	OH	H	t-Bu
1g:	OH	H	H

Fig. 1.

We now wish to present in this paper the photoinduced electron transfer oxidations of hindered phenols and catechols using DCA as sensitizer.

Experimental

Materials. DCA(Kodak) was purified by silica gel column chromatography. Mp 250.0—251.0 °C. Phenols and catechols were recrystallized twice from hexane–benzene. 1,3,5- and 1,2,4-Trimethoxybenzenes, acetonitrile, and methanol (reagent special grade) were used without further purification.

Instrumental. The GC analyses were done on a Shimadzu GC-6A-FID apparatus equipped with a column of 5% OV 17 on Chromosorb P. The products were analyzed on a waters liquid chromatograph, Model 440-RCM 100 equipped with a column of Radial-PAK (silica gel). The products were isolated by silica-gel chromatography or by preparative TLC (silica gel). The IR spectra were taken on a Shimadzu IR-420 Infrared Spectrophotometer. The NMR spectra were obtained on a Varian EM 360A NMR Spectrometer (60 MHz), using Me_4Si as the internal standard. The UV spectra were recorded on a JASCO NEW-UV-210A Digital Double-beam Spectrophotometer. The fluorescence spectra were taken on a Shimadzu RF-502A Fluorescence Spectrophotometer. The melting points were measured by means of a Yazawa Hot Plate and are uncorrected.

DCA-sensitized Photooxidation of ***1****.* A 100 ml MeCN or MeOH solution of **1** (10^{-2} M) was irradiated externally in the presence of DCA (10^{-4} M) from a 400-W high-pressure mercury arc through an aqueous 75% $NaNO_2$ solution ($\lambda_{irrad.} \geq 410$ nm).

*2,6-Di-t-butyl-4-methyl-4-hydroperoxycyclohexadien-1-one (**2b**).* Mp 115.2—115.6 °C (lit,[12a] 115—116 °C). NMR (δ): 1.22 (s, 18H), 1.35 (s, 3H), 6.55 (s, 2H), 7.70 (s, 1H). IR (cm^{-1}): 3400, 1667, 1646, 881. UV (EtOH): λ_{max} = 235 nm (ε = 11000). Found: C, 71.27; H, 9.63%; Calcd for $C_{15}H_{24}O_3$: C, 71.45; H, 9.52%.

*2,6-Di-t-butyl-4-methyl-4-hydroxycyclohexadien-1-one (**3b**).* Mp 107.0—108.0 °C (lit,[12a] 110 °C). NMR (δ): 1.24 (s, 18H), 1.39 (s, 3H), 1.57 (s, 1H), 6.54 (s, 2H). IR(cm^{-1}): 3370, 1660, 1640, 882. The spectra of **3b** were superimposable on those of the sample obtained by reducing **2b** with triphenylphosphine.

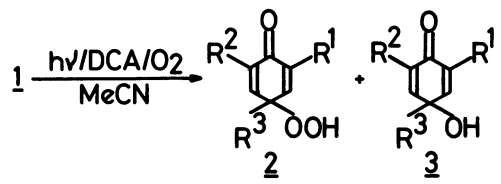
Table 2 summarizes the NMR and IR data of **2** and **3**.

*Bis(1,3,5-tri-t-butyl-4-oxo-2,5-cyclohexadienyl)peroxide (**4**).* **4** was synthesized according to Cook's method.[10] Mp 145.2—145.6 °C (lit,[10] 148—149 °C). NMR (δ): 0.84 (s, 18H), 1.31 (s, 36H), 6.66 (s, 4H). IR(cm^{-1}): 1667, 1643, 1365, 1248, 997.

5, **6**, and **7** were identified by comparison of their mp's and spectroscopic data with those of the authentic samples.[19,20]

Results and Discussion

DCA-sensitized Photooxidation of Phenols. As Table 1 shows, 4-hydroperoxy-2,5-cyclohexadien-1-ones (**2**) and 4-hydroxy-2,5-cyclohexadien-1-ones (**3**) were ob-



Scheme 2. DCA-sensitized photooxidation of phenols.

Table 1. DCA-sensitized photooxidation of phenols in acetonitrile

Compd	Irrad. time/h	Conv./%	Products (Selectivity/%)
1a	8	80	**2a**(43), **3a**(6)
1b	55	100	**2b**(80), **3b**(20)
1c	8	32	**2c**(100)
1d	23	33	a)

a) Not identified.

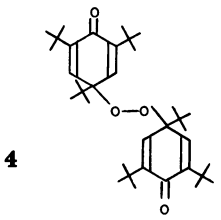


Fig. 2.

tained from 2,4,6-trialkyl-substituted phenols (**1a**—**c**) in good yields. On the other hand, monoalkyl-substituted phenol **1d** was photooxidized much slower and also its reaction was too complex to obtain isolable products.[21]

Refluxing **2** with the excess of triphenylphosphine in dichloromethane for 3 h gave **3** quantitatively and this fact supports the structure of **2**.

Although the effect of phenol concentration on its oxidation has been reported,[4] no concentration effect was observed concerning the product distribution in this reaction, and no bis(1,3,5-tri-*t*-butyl-4-oxo-2,5-cyclohexadienyl) peroxide (**4**) was formed even when the concentration of **1a** was increased to 10^{-1} M.

Formation of **3** urged us to ascertain the possibility that the redox decomposition of **2** or **4** should give **3**. Under the reaction conditions, however, both of them were highly stable in the absence or presence of hydrogen donor **1**, and **3** was not afforded at all. LC analysis also showed that **3** is a primary product and did not arise from **2** or **4**.

In methanol, the reaction rate was slower than in acetonitrile and **3** was not afforded.

Next, the quenching experiments of DCA fluorescence and the oxidation reaction were performed to obtain further information on the mechanism. The rapid quenching of ^{1}DCA* fluorescence by **1** (see Table 3) supports the occurrence of electron transfer from **1** to ^{1}DCA*, *i.e.*, formation of 1^+ and DCA^-. In fact, the relative rate, k_{rel} of **1** decreases as its oxidation potential increases.

Addition of 1,2,4-trimethoxybenzene (TMB) into the system of **1** and DCA causes the competition between Eqs. 2 and 3 because TMB is a better electron donor.[15] As r_1 and r_2 in Scheme 3 stand for the kinetic expressions for Eqs. 2 and 3, the calculated quenching ratio Q_{calcd} can be obtained by Eq. 6 if $\mathbf{1}^+$ is responsible for the oxidation of **1**.

$$DCA \xrightarrow{h\nu} {}^1DCA^* \quad (1)$$

$$^1DCA^* + \mathbf{1} \xrightarrow{kq} DCA^- + \mathbf{1}^+ \quad (2)$$

$$^1DCA^* + TMB \xrightarrow{kq'} DCA^- + TMB^+ \quad (3)$$

$$r_1 = k_q[\mathbf{1}][^1DCA^*] \quad (4)$$

$$r_2 = k_q[TMB][^1DCA^*] \quad (5)$$

$$Q_{calcd} = 1 - r_1/(r_1+r_2) = k_{q'}[TMB]/(k_q[\mathbf{1}]+k_{q'}[TMB]) \quad (6)$$

Scheme 3. Quenching of ^{1}DCA* fluorescence.

A good coincidence between Q_{calcd} and Q_{obsd} further confirms the involvement of the initial electron transfer process. DCA^- can reduce triplet molecular oxygen to generate O_2^-.[15] Therefore, **2** would be afforded in the subsequent deprotonation of $\mathbf{1}^+$ by O_2^-, followed by the coupling of $\mathbf{1}^\cdot$ with $HO_2^\cdot$. It is well known that a hindered phenoxyl radical is a good trap of a hydroperoxyl radical.[24] The alkylperoxyl radical could be excluded as a chain carrier since hindered phenols are known to act as a good radical inhibitor. They would rather couple with a phenoxyl radical to give **4**[4,10] when the concentration of the phenoxyl radical is high.

It is to note that **1** was stable on DCA-sensitized irradiation under nitrogen. This would be ascribed to the back electron transfer from DCA^- to $\mathbf{1}^+$ or the lack of the deprotonating reagent such as oxygen.[25]

The stability of **2** is delicate, and it rearranges to a 5,6-epoxy-4-hydroxy-2-cyclohexen-1-one under basic conditions,[12b] or it degrades to *p*-benzoquinones, diphenoquinones, *etc.* in the presence of a Cu(I)–amine complex.[11] Our reaction is clearly different from the base- or metal-catalyzed oxygenation of hindered phenols in that **2** is afforded in good yields, irrespective of the alkyl substituents although the path for formation of **3** has to be unraveled.

DCA-sensitized Photooxidation of ***1e****.* DCA-sensitized

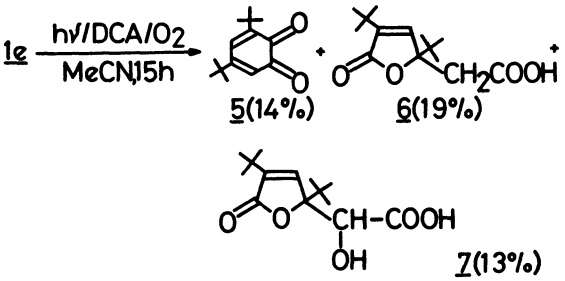
Table 2. Physical constants and spectroscopic data of **2** and **3**

Compd	Mp θ_m/°C	NMR δ	IR $\tilde{\nu}$/cm^{-1}
2a	75.8— 77.4	0.97(s, 9H), 1.25(s,18H), 6.10(s, 2H), 7.92(s,1H)	3400, 1660, 1628, 967
2b	115.3—115.6	1.22(s,18H), 1.35(s, 3H), 6.55(s, 2H), 7.70(s,1H)	3400, 1667, 1646, 1060
2c	63.1— 64.5	1.36(s, 3H), 1.90(s, 6H), 6.63(s, 2H), 8.52(s,1H)	3300, 1675, 1618, 1060
3a	80.9— 82.1	0.97(s, 9H), 1.05(s, 1H), 1.22(s,18H), 6.57(s,2H)	3520, 1653, 1627, 967
3b	107.0—108.0	1.24(s,18H), 1.39(s, 3H), 1.57(s, 1H), 6.54(s,2H)	3370, 1660, 1640, 1058
3c	40.8— 42.1	1.41(s, 3H), 1.84(s, 6H), 2.22(s, 1H), 6.60(s,2H)	3380, 1670, 1625, 1050

TABLE 3. QUENCHING OF DCA-SENSITIZED PHOTOOXIDATION OF 1 BY TMB

Compd	$E_{1/2}^{ox}$/V	k_q^f/$M^{-1}s^{-1}$ a)	k_{rel}	Q_{calcd}/% b)	Q_{obsd}/% c)
1a	1.20 d)	2.45×10^{10}	6.4	37	31
1b	1.33 d)	2.85×10^{10}	4.9	33	36
1c		2.60×10^{10}	2.5	35	34
1d		2.06×10^{10}	1.0	41	43
TMB	1.12 e)	6.49×10^{10}			

a) Fluorescence quenching rate constant in acetonitrile under air at room temperature. $\tau_{DCA,Air}=\tau_{DCA,N_2}(I_{DCA,Air}/I_{DCA,N_2})=15.3\times0.52=8.0$ ns. ($\tau_{DCA,N_2}=15.3$ ns.)[22] b) Q_{calcd} was given by Eq. 6 when the conversion of **1** was around 10%. c) Q_{obsd} was given as $1-C_q/C_0$, where C_0 and C_q represent the conversions of **1** in the solutions containing only **1** and **1**–TMB when C_0 was around 10%, respectively. d) See Ref. 23. e) See Ref. 15.



Scheme 4. DCA-sensitized photooxidation of **1e**.

photooxidation of **1e** in acetonitrile gave 3,5-di-*t*-butyl-*o*-benzoquinone (**5**), 3,5-di-*t*-butyl-5-(carboxymethyl)-2(5*H*)-furanone (**6**), and 3,5-di-*t*-butyl-5-(carboxyhydroxymethyl)-2(5*H*)-furanone (**7**) in the yields shown above.

In MeCN–MeOH, **6** and the methyl ester of **7** were obtained in 20% and 10% yields, respectively, along with **5** (6%).

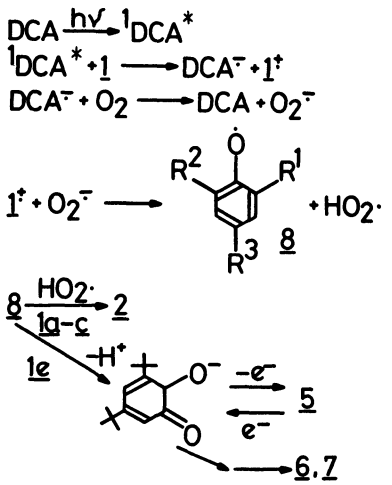
The relative rate of the catechol decreased in the order of **1e**>**1f**>**1g** and no isolable products were obtained from the less hindered catechols, **1f** and **1g**.

As has been discussed in the system of the phenol, the oxygenation of the catechol is also considered to proceed by an electron transfer mechanism because **1e** quenches ^{1}DCA* fluorescence at the diffusion-controlled rate limit ($k_q=1.21\times10^{10}$ $M^{-1}s^{-1}$) and its oxidation reaction is completely suppressed by 1,3,5-trimethoxybenzene.

5 is found to be an early product because **6** and **7** are afforded in the DCA-sensitized photooxidation reaction of **5** in acetonitrile.

The observed product distributions are less complicated than those reported by Foote and Moro-oka with KO_2.[9]

The different reactivities of **1a**—**c** and **1e** can be ascribed to the diphenolic character of **1e**. The phenoxyl radicals from **1a**—**c** couple together with a hydroperoxyl radical, while that from **1e** would further be deprotonated to afford a stable *o*-benzosemiquinone radical which leads to furanone derivatives in the subsequent oxygenation followed by ring cleavage and lactonization.[9]



Scheme 5. A presumed reaction scheme.

Scheme 5 shows a presumed reaction mechanism.[26]

In this paper, we have reported DCA-sensitized photooxidation of hindered phenols and catechols and have shown that the reaction proceeds *via* electron transfer mechanism.

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19) The IR and NMR spectra of **5** were identical with

those of the sample prepared by oxidizing **1e** in the presence of Co(salpr).

20) As to **6** and **7**, see Ref. 9.

21) The *ortho* substituent groups seem to be necessary to undergo the clean oxidation.

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25) DCA can be recovered quantitatively under nitrogen or oxygen.

26) The scheme merely shows a possible route leading to the products; other paths such as radical coupling between ArO· and $^3O_2$, and intervention of $^1O_2$ generated by the reaction of $ArO^+ + O_2^-$ would also be probable reactions. We thank the referee for this point.