1 H, H-13, $J_{12,13}$ = 6.0), 3.42 and 3.39 (s, 6 H, 2 OCH_3), 3.19 (complex m, 1 H, H-8), 2.97 (br t, 1 H, H-12, J = 7.0), 2.77 (dd, 1 H, H_{A-7}, J_{AB} = 18.0, $J_{A,8}$ = 7.2), 2.54 (dd, 1 H, H_{B-7}, J_{AB} = 18.0, $J_{B,8}$ = 10.2), 1.83 (s, 3 H, 11-CH_3); ^{13}C NMR ($CDCl_3$) δ 177.65 (s, C-6), 147.01 (s, C-11), 125.66 (d, C-10), 105.20 (d, C-13), 87.12 (d, C-9), 54.98 and 54.70 (q, 2 OCH_3), 51.58 (d, C-12), 39.01 (d, C-8), 31.02 (t, C-7), 16.07 (q, 11-CH_3).

Registry No. **1**, 479-98-1; **2**, 63879-67-4; **3**, 86537-27-1; **4**, 111795-30-3; **10**, 111795-31-4; 6,10-dideoxyaucubin, 31655-27-3.

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p-Benzoquinone *O*-Oxide

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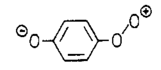
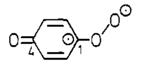
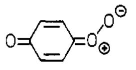
Carbonyl *O*-oxides and their isomeric dioxiranes are important intermediates in many oxidation processes.[1] Whereas some substituted dioxiranes are stable enough to be investigated in solution,[2,3] the very unstable carbonyl oxides only have lifetimes in the range of microseconds at room temperature.[4] During the last few years several carbonyl oxides have been characterized spectroscopically by using the matrix isolation technique.[5-7]

In this paper we report the matrix isolation and spectroscopic characterization of *p*-benzoquinone oxide (**1**). This allows for the first time a comparison of a carbonyl oxide and a carbonyl functional group in the same molecule spectroscopically. By comparison of the vibrational frequencies of both functional groups it is possible to gain information about the electronic structure of **1** and the relative importance of the resonance structures **1a–c**.[8]

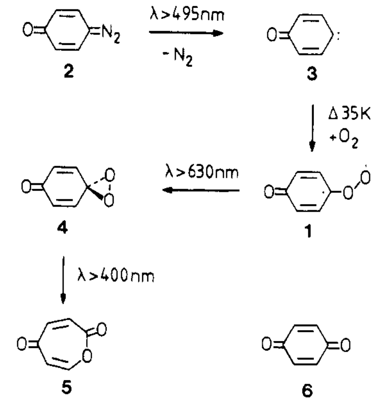

1a


1b


1c

Photolysis (λ > 475 nm) of *p*-benzoquinone diazide (**2**),[9] matrix isolated in Ar at 9 K, gave 4-oxo-2,5-cyclohexadienylidene (**3**)[10] in a clean reaction (Scheme I). The IR spectrum of **3** shows an intense absorption at 1496 cm^{-1},[10] assigned to the C–O stretching mode. This vibration is found half-way between the C=O stretching mode of *p*-benzoquinone (**6**) (1682 cm^{-1})[11] and the C–O stretching mode of phenol (1250 cm^{-1}),[12] and thus a bond order of approximately 1.5 can be deduced. This finding is in agreement with ESR investigations[13] and trapping ex-

Scheme I



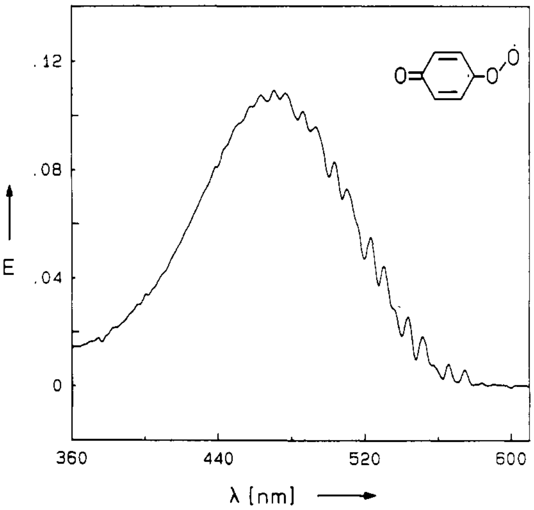


Figure 1. Vis spectrum of **1**. The band is assigned to the intense $\pi \rightarrow \pi^*$ transition with λ_{max} at 462 nm.

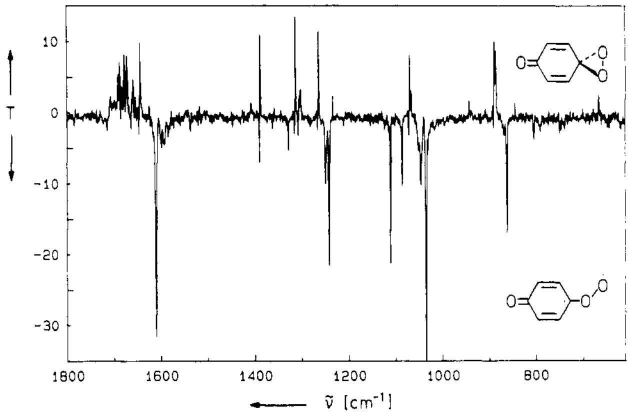


Figure 2. Difference IR spectrum showing the photochemistry of **1**. Bottom: bands assigned to **1**, disappearing on irradiation (λ > 630 nm). Top: new bands of **4** growing in.

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(9) **2**: IR (Ar, 9 K) 2084 (s), 2074 (vs), 1635 (s), 1628 (s), 1591 (m), 1406 (m), 1241 (m), 1145 (m), 845 (m) cm^{-1}. **2**-d_4: IR (Ar, 9K) 2080 (vs), 2044 (m), 1630 (s), 1616 (s), 1562 (s), 1304 (s), 1140 (m), 830 (m), 745 (m), 657 (m) cm^{-1}.

(10) **3** is the primary product of the photolysis of **2**. On irradiation (λ 543 ± 20 nm) an isomer **3a** of unknown structure is formed. The photochemistry of **3** is currently under investigation. **3**: IR (Ar, 9 K) 1496 (s), 1375 (m), 1260 (m), 1076 (m), 937 (m), 819 (s) cm^{-1}; UV (Ar, 9 K) 290, 297, 338, 351, 367, 379, 496, 508, 521, 535, 550, 566 nm. **3a**: IR (Ar, 9 K) 1720 (s), 1713 (vs), 1305 (w), 1005 (m), 843 (m), 797 (m), 743 (w), 582 (s) cm^{-1}.

(11) **6**: IR (Ar, 9 K) 1707 (w), 1682 (m), 1672 (s), 1658 (m), 1596 (w), 1301 (m, δ C–H), 1066 (m, δ C–H), 942 (w), 885 (m, δ C–H). For a vibrational analysis of **6**, see: Becker, E. D.; Charney, E.; Anno, T. *J. Chem. Phys.* **1965**, *42*, 942.

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0022-3263/88/1953-2091$01.50/0

Table I. IR Spectroscopic Data of Four Isotopomers of Carbonyl Oxide 1, Matrix Isolated in Ar at 9 K (Some Bands Are Split by Fermi Resonance)

IR, cm^{-1}				
$^{16}OC_6H_4{}^{16}O_2$	$^{16}OC_6H_4{}^{18}O_2$	$^{16}OC_6D_4{}^{16}O_2$	$^{16}OC_6D_4{}^{18}O_2$	
1609 (s)	1609 (s)	1602 (s)	1603 (s)	C(4)=O str.
1327 (w)	1311 (w)	1285 (m)	1280 (m)	C(1)–O str.
1248 (w)	1247 (w)	1268 (w)	1265 (m)	C–C str.[a]
1241 (m)	1235 (m)	1153 (s)	1144 (s)	
1110 (m)	1106 (m)			
1085 (w)	1084 (w)	1001 (m)	1017 (m) 965 (w)	C–H def.[b]
1045 (m) 1034 (vs)	985 (s) 977 (s)	1048 (w) 1039 (s)	980 (w) 973 (s)	O–O str.
861 (m)	861 (m)	757 (w)	756 (m)	C–H def.[c]
606 (w)	600 (w)	581 (vw)	580 (w)	
570 (w)	559 (m)	555 (m)	543 (m)	C(1)–O–O def.

[a] Corresponding band in **6**: 1301 cm^{-1}. [b] **6**: 1066 cm^{-1}. [c] **6**: 885 cm^{-1}.

periments in solution[14] which indicate that the electronic structure of **3** resembles the phenoxyl radical (π-system) as well as the phenyl radical (σ-system).

When **2** was irradiated (λ >475 nm, 9 K) in O_2-doped Ar matrices (0.5–5% O_2), free carbene **3**, dioxirane **4**, and traces of quinone **6** (only at >5% O_2 content) were formed (Scheme I). At 0.5% O_2 content **3** was the major product, whereas at 5% O_2 the oxidation was almost complete. The diffusion of O_2 in solid Ar is slow at 9 K;[6b] therefore the photooxidation at this temperature results from the reaction of **2** and O_2 in the same matrix cage. If a statistical distribution is assumed, the chance of carbene **3** having an O_2 molecule as nearest neighbor is high at 5% O_2 but low at 0.5% O_2 concentration.

When the matrix containing **2** and O_2 was annealed at a temperature where the diffusion of O_2 is rapid, the thermal reaction of **3** and O_2 to give *p*-benzoquinone oxide (**1**) was observed. At 30 K the reaction was complete within 4 h; at 40 K within 3 min. The progress of the reaction was followed spectroscopically by UV–vis or IR (Figure 1 and 2).

In the UV–vis spectrum of **1** transitions with maxima at 462, 328, 273, and 262 nm were observed. The most intense band in the spectrum (λ_{max} 462 nm) is assigned to a $\pi \rightarrow \pi^*$ transition also found in other carbonyl oxides.[4–7] At the long wavelength side of this band a vibrational fine structure is observed (Figure 1).

By use of CNDO/S[15a] calculations on MINDO/3-UHF[15b] optimized geometries, strong transitions at 468 nm (log ϵ = 4.1), 362 (2.1), 265 (3.2) and 241 (3.3) were calculated, in good agreement with the observed transitions. The calculated weak $n \rightarrow \pi^*$ transition (λ_{max} 859 nm, log ϵ = 1.1) could not be observed due to the highly scattering background of the matrix.

The most intense band in the IR spectrum of **1** (Figure 2) was found at 1034 cm^{-1} (Table I). When the experiment was repeated with $^{18}O_2$, doubly ^{18}O-labeled **1** ([$^{18}O_2$]-**1**) was formed. The band at 1034 cm^{-1} was shifted 57 cm^{-1} (5.5%) toward lower frequencies and thus assigned to the O–O stretching mode. The splitting of this band in two components (1045 and 1034 cm^{-1}) is due to Fermi resonance. In [$^{18}O_2$]-**1** the relative intensity of these bands is, as expected, changed (Table I).

Compared to benzophenone oxide[6a] the O–O stretching mode in **1** is shifted by 137 cm^{-1} to higher frequencies, indicating a stronger O–O bond in **1**. Thus the tendency of the O–O stretching mode to shift to higher frequencies by substitution with electron-withdrawing groups[16] is confirmed.

Table II. IR Spectroscopic Data of Four Isotopomers of Dioxirane 4, Matrix Isolated in Ar at 9 K (Some Bands Are Split by Fermi Resonance)

IR, cm^{-1}				
$^{16}OC_6H_4{}^{16}O_2$	$^{16}OC_6H_4{}^{18}O_2$	$^{16}OC_6D_4{}^{16}O_2$	$^{16}OC_6D_4{}^{18}O_2$	
1687 (m) 1677 (m) 1644 (s)	1703 (m) 1688 (m) 1666 (m) 1647 (m) 1642 (s)	1683 (s) 1666 (m)	1684 (m) 1680 (m) 1663 (s) 1632 (m)	C(4)=O str.[a]
1388 (m)	1392 (m)	1308 (s)	1294 (s)	
1313 (s)	1311 (s)	1258 (w)		C–C str.[b]
1263 (s)	1247 (m)	1252 (s)	1248 (s)	C(1)–O str.
1070 (m)	1069 (m)	871 (w)	864 (w)	C–H def.[c]
889 (s)	885 (s)			C=H def.[d]
		865 (w)	859 (w)	
		821 (w)	817 (w)	
		798 (w)	750 (w)	

[a] Corresponding band in **6**: 1707–1658 cm^{-1}. [b] **6**: 1301 cm^{-1}. [c] **6**: 1066 cm^{-1}. [d] **6**: 885 cm^{-1}.

The intense band at 1609 cm^{-1} (Figure 2) does not show any isotopic shift and is assigned to the C(4)–O stretching vibration. Compared to quinone **6** this band is shifted 60 cm^{-1} toward lower frequencies but still occurs in the "normal" carbonyl range.

Unlike the C(4)–O stretching mode, the C(1)–O stretching mode of the carbonyl oxide group is weak and not easily identified. A weak band at 1327 cm^{-1} shows an isotopic shift of 16 cm^{-1} (1.2%) and a medium intensity band at 1241 cm^{-1} shows an isotopic shift of 6 cm^{-1} (0.5%). Typical ^{16}O–^{18}O isotopic shifts of C=O stretching vibrations are 1.7–2%. Therefore the band at 1327 cm^{-1} is tentatively assigned to the C(1)–O stretching vibration. The low intensity of this band and the large shift towards lower frequencies (compared to C=O stretching modes) indicate that the C(1)–O bond is only weakly polarized and best described as a single bond. The C(4)–O bond is a double bond; therefore resonance structure **1b** is closest to the electronic structure of **1**. This is in good agreement with MINDO/3-UHF calculations. A singlet diradical **1b** is computed to be 12 kcal/mol more stable than the MINDO/3-RHF favored zwitterion **1c**.

To confirm the assignment of IR bands given above, all experiments were also performed using tetradeuteriated quinone diazide **2** (**2**-d_4). The IR data of the four isotopomers of **1** and a tentative assignment of some bands are given in Table I.

p-Benzoquinone oxide (**1**) is very photolabile. Long wavelength irradiation (λ >630 nm) rapidly produces dioxirane **4**. The IR spectrum of **4** (Figure 2, Table II) is similar to the spectrum of **6**.[11] The carbonyl vibration in the range 1687–1644 cm^{-1} (**6**: 1707–1658 cm^{-1}) is split into several bands (Fermi resonance). Vibrations at 1070 cm^{-1} (**6**: 1066 cm^{-1}) and 889 cm^{-1} (**6**: 885 cm^{-1}) are assigned to C–H deformation vibrations. These bands show only small ^{16}O–^{18}O isotopic shifts. The band at 1263 cm^{-1} shows the largest isotopic shift (16 cm^{-1}) and is assigned to a C–O stretching mode of the dioxirane unit. The corresponding band in the parent compound was calculated to appear at 1213 cm^{-1} (32-cm^{-1} isotopic shift).[17]

The UV–vis spectrum of **4** shows only a transition at 221 nm and no bands at longer wavelength. Although alkyldioxiranes appear to be yellow in concentrated solutions,[2] the low absorption coefficient (ϵ ≈10) of the bands at longest wavelength (λ_{max} 330–340 nm)[2] are well below the

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detection limit in the matrix experiments described above.

Shorter wavelength irradiation ($\lambda > 400$ nm) of **4** gives complete rearrangement to 2,5-oxepinedione (**5**), characterized IR and mass spectroscopically.[18] The lactone band at 1753 cm^{-1} (37-cm^{-1} isotopic shift) and the ketone band at 1660 cm^{-1} (no isotopic shift) are observed close to the corresponding bands in α-pyrone (1752 cm^{-1}) and γ-pyrone (1678 cm^{-1}). A small amount of **5** was isolated from the cold window after evaporating the matrix. The mass spectrum obtained from this sample[18] confirmed the assignment given above.

Chemiluminescence, observed in other thermal carbene oxidations[6,16,19] was not found. Quinone **6** does not show any fluorescence or phosphorescence on irradiation in Ar at 9 K, and thus chemiluminescence is not expected.

Experimental Section

p-Benzoquinone diazide (**2**) and *p*-benzoquinone-d_4 diazide[9] were synthesized by treating *p*-diazophenol hydrochloride with silver oxide according to the literature procedure.[20] *p*-Aminophenol-d_4 hydrochloride was synthesized by H-D exchange with D_2O at 220 °C.[21] The deuterium content was >95% (by mass spectroscopy).

Matrix experiments were performed by standard techniques,[6b,16] using an Air Products CSW-202 Displex closed cycle helium cryostat. The temperature of the matrix was controlled by a Lake Shore DRC 81 C controller (silicon diode sensor) interfaced to a HP 86 microcomputer. Argon (Messer Griesheim, 99.9995%), oxygen (Messer Griesheim, 99.998%), and [$^{18}O_2$]oxygen (Ventron, 99.8% isotopic purity) were mixed in a gas-handling system by standard manometric techniques. Infrared spectra were recorded on a Perkin Elmer PE 580 and UV–vis spectra on a Varian Cary 17D spectrometer. Both instruments were interfaced to a Hewlett Packard 86 microcomputer.

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Registry No. **1**, 113567-56-9; [$^2H_4$]-**1**, 113567-58-1; [$^{18}O_2$]-**1**, 113567-57-0; [$^2H_4$,$^{18}O_2$]-**1**, 113567-59-2; **2**, 932-97-8; [$^2H_4$]-**2**, 113567-96-7; **3**, 3225-37-4; **4**, 113567-94-5; **5**, 113567-95-6.

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(18) **5**: IR (Ar, 9 K) 1769 (w), 1753 (m), 1748 (m), 1660 (m), 1638 (w), 1330 (s), 1296 (m), 1141 (m), 1048 (m), 869 (m) cm^{-1}; MS, *m/z* (relative intensity) 124 (M$^+$, 46), 96 (M$^+$ – CO, 100), 69 (55), 68 (43), 54 (41), 39 (32). [$^{18}O_2$]-**5**: IR (Ar, 9 K) 1716 (s), 1664 (s), 1647 (m), 1337 (w), 1320 (s), 1288 (s), 1132 (s), 1028 (m), 871 (m) cm^{-1}.

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Selective Halogenation of Aromatic Hydrocarbons with Alumina-Supported Copper(II) Halides

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Copper(II) halides have been used to halogenate aromatic hydrocarbons under heterogeneous conditions in nonpolar solvents. For example, anthracene and pyrene react with copper(II) chloride and bromide in heterogeneous conditions to give excellent yields of 9-haloanthracenes and 1-halopyrenes.[1,2] However, the process is not generally applicable for halogenation of all aromatic hydrocarbons. Aromatic hydrocarbons with ionization potentials (IP) higher than approximately 7.55 eV were found to be entirely unreactive toward chlorination with copper(II) chloride.[3] Even under reflux with copper(II) chloride in high-boiling solvents, e.g., nitrobenzene and chlorobenzene, chlorination of naphthalene (IP = 8.10[4]) or phenanthrene (IP = 8.03[4]) was not successful.[1,5]

Table I. Chlorination of Polycyclic Aromatic Hydrocarbons with $CuCl_2/Al_2O_3$[a]

aromatics	°C/h	products	total yield, %	ratio of products, %	
				mono-Cl	di-Cl
naphthalene	130/2	1-Cl, 1,4-Cl_2	94	94	6
1-methylnaphthalene	130/2	4-Cl	100	100	0
phenanthrene	130/2	9-Cl, 9,10-Cl_2	94	94	6
fluorene	130/1	2-Cl, 2,7-Cl_2	93	83	17
anthracene	50/1[b]	9-Cl, 9,10-Cl_2	99	95	5
	80/7[b]	9,10-Cl_2	99	0	100

[a] $CuCl_2$/aromatic = 5; solvent: chlorobenzene. [b] Carbon tetrachloride.

Previously, we reported that copper(II) halides supported on alumina halogenated phenylacetylene selectively to give 1-halo-2-phenylacetylene or 1,1,2-trihalo-2-phenylethylene in nonpolar solvents under mild conditions.[6] In the present paper, we report that aromatic hydrocarbons with ionization potentials higher than 7.55 eV were easily halogenated by alumina-supported copper(II) halides to give mono- or dihalogenated products. For example, while reaction of naphthalene, phenanthrene, and fluorene with copper(II) chloride in refluxing chlorobenzene produced negligible yields of chlorinated products, similar reaction with alumina-supported copper(II) chloride produced monochlorinated compounds in high yields, Table I. To examine what factors influence product yields, we examined the chlorination of naphthalene in more detail. Empirical testing of five supports (alumina, silica gel, molecular sieve, graphite, and Kieselguhr) revealed that alumina was most effective in activating copper(II) chloride. Kieselguhr was entirely ineffective. We postulated a reaction mechanism with participation of an aromatic radical cation which was formed by one electron transfer from an aromatic hydrocarbon to copper(II) chloride. Activated alumina has electron-acceptor properties, and formation of a radical cation of an aromatic hydrocarbon adsorbed on alumina has been observed by ESR.[7] Therefore, it seemed to us that alumina as a support facilitates the generation of the radical cation of the aromatic hydrocarbon.

Copper(II) bromide was more reactive than copper(II) chloride toward the aromatic hydrocarbons. Bromination of aromatic hydrocarbons proceeded in carbon tetrachloride to give the corresponding bromo compounds with high selectivity, Table II. Mono- or dibromo compounds were selectively obtained in high yield depending upon the reaction conditions. For instance, 1-bromonaphthalene was obtained from the reaction run at 80 °C in carbon

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