Low Temperature Photolysis of *o*-Benzoquinones. Spectroscopic Detection of Cyclopentadienones and Bis-Ketenes[1)]

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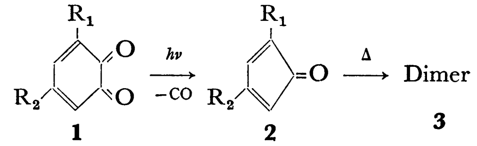
(Received June 10, 1977)

The photodecarbonylation of *o*-benzoquinone to cyclopentadienone at low temperature was monitored by infrared and ultraviolet spectra which showed that the reaction is highly sensitive to substituents. 3,5-Di-*t*-butyl-*o*-benzoquinone undergoes clean decarbonylation to give cyclopentadienone under irradiation at −170 °C. Similar irradiation of 4-*t*-butyl-, 4-methyl-, 3-methyl-, and unsubstituted *o*-benzoquinones also leads to decarbonylation to cyclopentadienones. However, competitive α-cleavage to bis-ketene becomes important in these systems. Direct spectroscopic observation of the elusive cyclopentadienone was unsuccessful because of the overlapping absorption of the by-product. The infrared spectrum of bis-ketene from 4-*t*-butyl-*o*-benzoquinone shows that it exists as a mixture of rotamers, not undergoing thermal interconversion even at −170 °C.

Much attention has been paid to the preparation and properties of cyclopentadienones[2)] because of the theoretical interest in this system. The classic problem concerning their isolation and direct spectroscopic observation as a monomer is their pronounced facility to dimerize in a mode of the Diels-Alder reaction. While relatively many tri- and tetra-substituted derivatives have been isolated as monomer, minimally substituted derivatives thus far isolated were di-*t*-butyl derivatives.[3)] Further, it was not until 1971 that the parent compounds was detected spectroscopically in the pyrolytic decarbonylation of *o*-benzoquinone.[4)] Recently, however, a similar decarbonylation was observed[5)] also in the UV irradiation of 3,5- and 3,6-di-*t*-butyl-*o*-benzoquinones at room temperature to yield the corresponding cyclopentadienones. During the course of studies on the low temperature photochemistry of organic molecules,[1,6)] it was found that the photodecarbonylation of 3,5-di-*t*-butyl-*o*-benzoquinone occurs equally efficiently upon irradiation in infrared cell even at low temperature. Although there have been many reports on the syntheses of cyclopentadienones, only a few examples[7)] exist on the ingenious approaches for the generation of cyclopentadienone and its simply substituted derivatives under the conditions associated with general spectroscopic observation.

The present reaction, thus, might be expected to provide another convenient route which permits the spectroscopic observation of unstable cyclopentadienones as monomer if the reaction could be applied to the other simply substituted *o*-benzoquinones (**1b**—**d**) as well as the parent. The irradiation of *o*-benzoquinones at low temperature monitored by infrared and ultraviolet spectroscopy revealed that the photodecarbonylation is highly sensitive to the substituents on benzoquinone and the competitive α-fission to give interesting bis-ketene becomes more important in simpler benzoquinones.



a: $R_1=R_2={}^tBu$
b: $R_1=H$, $R_2={}^tBu$
c: $R_1=H$, $R_2=Me$
d: $R_1=Me$, $R_2=H$
e: $R_1=R_2=H$

Results and Discussion

A thin film of 3,5-di-*t*-butyl-*o*-benzoquinone (**1a**) as a suspension in Nujol in a liquid nitrogen-cooled infrared cell equipped with a vacuum shroud and dewar was irradiated with a 250 W mercury lamp through a pyrex window and monitored by infrared spectra. As shown in Fig. 1, irradiation led to rapid disappearance of the absorption of the starting material and concurrent appearance of new bands at 2138, 1702, 1320, 1300, 1196, 1145, 1003, 956, and 867 cm^{-1}. A strong and sharp band appearing at 2138 cm^{-1} is easily attributable to carbon monoxide by comparison with the reported value.[8)] The new carbonyl band at 1702 cm^{-1} did not change upon warming the cell slowly to room temperature. After the photomixture had been allowed to stand at room temperature for one day, a new band appeared at 1768 cm^{-1} concomitant with slight shift and change in shape of the original carbonyl band. 2,4-Di-*t*-butylcyclopentadienone (1708 cm^{-1}) is thermally stable at room temperature but slowly dimerizes to

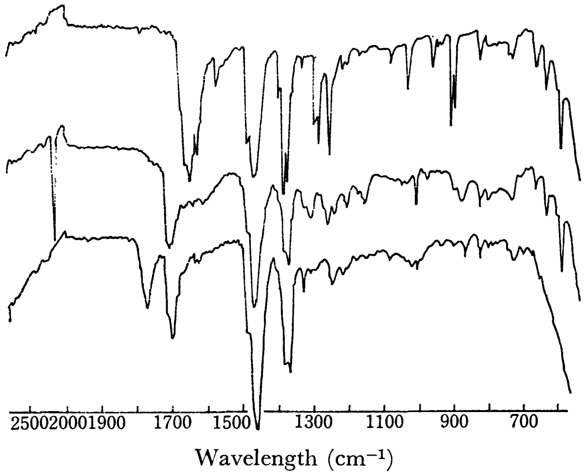


Fig. 1. IR spectra of **1a** in Nujol mulls at −170 °C before irradiation (top), after irradiation for 150 min (center), and after standing at room temperature for 1 day (bottom).

give a single Diels-Alder dimer (1700 and 1765 cm^{-1}) upon standing at the same temperature.[3] TLC analysis of the photomixture within the cell after standing overnight showed the presence of the dimer **3a**. The above results strongly suggest that the photodecarbonylation of **1a** to **2a** occurs within the infrared cell at low temperature.

A similar photolysis of 4-*t*-butyl-*o*-benzoquinone (**1b**) in the infrared cell, however, gave different results. Irradiation caused the starting band to disappear rapidly and the carbon monoxide band to appear along with a broad new absorption at around 1700 cm^{-1} (Fig. 2). Warming the cell to room temperature resulted in the disappearance of the 2138 cm^{-1} band but the broad carbonyl band remained unchanged and no new band appeared even on standing for 2 days. The results exclude the possible assignment of the broad carbonyl band to 3-*t*-butylcyclopentadienone **2b**, since it dimerizes rapidly above −80 °C to give **3b** which has new carbonyl bands at 1790 and 1710 cm^{-1}.[3] Inefficient increase in the intensity of a rather broad band at 2138 cm^{-1} on continued irradiation prompted us to investigate the reaction on a wider scale in the wave number range 2000—2300 cm^{-1}. The results (Fig. 3) revealed that two more new bands at 2125 and 2156 cm^{-1}, probably attributable to bis-ketene arising from the α-cleavage of *o*-benzoquinone, appear along with the carbon monoxide band in this region. Warming in the dark shows that one of the ketene bands at 2125 cm^{-1} rapidly disappears above −90 °C, while the other at 2156 cm^{-1} remains unchanged until −70 °C. This indicates that each band is associated with two different ketenes. Similar irradiation of 4-methyl-(**1c**), 3-methyl-(**1d**), and parent *o*-benzoquinones (**1e**) also resulted in rapid disappearance of the starting materials and concurrent formation of carbon monoxide and bis-ketene. No distinct new carbonyl band was observed in these compounds. Only one ketene band appeared at 2125 cm^{-1}, disappearing upon warming above −90 °C.

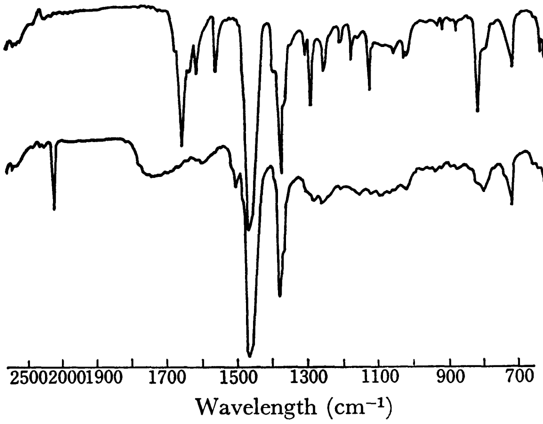


Fig. 2. IR spectra of **1b** in Nujol mulls at −170 °C before irradiation (top), after irradiation for 60 min (bottom).

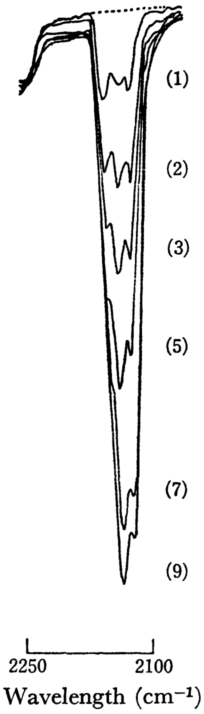


Fig. 3. IR spectra of **1b** in Nujol mulls at −170 °C in the region at 2100—2250 cm^{-1} in expanded scale, -----: before irradiation, ——: after irradiation. Numbers in parentheses refer to irradiation time in min.

Thus, the results show that the photodecarbonylation is quite general for other *o*-benzoquinones, but the photo-α-cleavage to give the bis-ketene occurs concurrently as a relatively important pathway in the photolysis of less substituted *o*-benzoquinones (**1b**—**e**). However, direct observation of cyclopentadienones was unsuccessful since the broad and thermally stable band[9] in the carbonyl region interferes with the expected carbonyl absorption of cyclopentadienones.

The possibility that carbon monoxide can be formed in the photodecarbonylation[10] of bis-ketene initially formed was excluded, since plots of the intensities of carbon monoxide and ketene absorption as a function of irradiation time indicate that both compounds are the primary photoproduct of *o*-benzoquinones (Fig. 4). Strong chemical evidence of the intervention of cyclopentadienone and bis-ketene were provided by GLPC and TLC analyses of the photomixture obtained in the low temperature irradiation of *o*-benzoquinone (**1e**) in the presence of ethanol. Both analyses show the presence

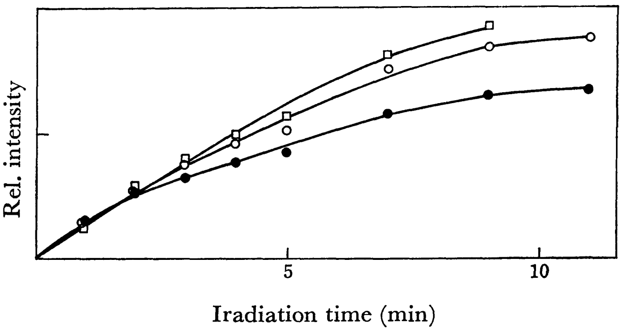
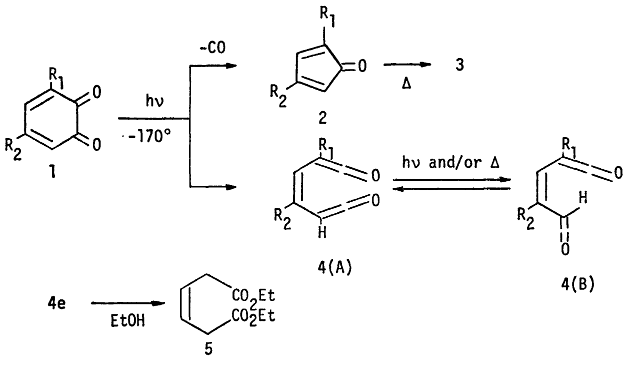


Fig. 4. Plot of relative intensity of bis-ketene and carbon monoxide bands as a function of irradiation time obtained from IR spectra on Fig. 3: -□-, CO (2138 cm^{-1}); -○-, $\nu_{C=O}$ (2125 cm^{-1}) and -●-, $\nu_{C=O}$ (2156 cm^{-1}) of bis-ketene **4b**.

of dicyclopentadienone (**3e**) and diethyl 3-hexenedioate (**5**), a trapped product of bis-ketene by ethanol.

The presence of two ketene bands with different thermal stability in the spectrum of photolyzed **1a** reminds us of the photochemical cleavage[11a–c] of α-pyrone to ketene–aldehyde in Ar matrix at 8 K. Four ketene bands observed at 2022, 2129, 2136, and 2146 cm^{-1} have been attributed to the four possible rotamers available by rotation about C–C single bond. Thus, we assigned the two ketene bands from **1a** to a mixture of bis-ketene rotamers **4A** and **4B**. The band at 2125 cm^{-1} would be associated with bis-ketene **4A**, which is formed first and rapidly rotates photochemically and/or thermally around C–C single bond to the more stable isomer **4B** (2156 cm^{-1}).[12]



Direct observation of a mixture of rotamers at −170 °C seems to have achieved for the first time. Apparently, the energy barrier to single bond rotation is large with respect to kT at 8 K and the rotamers are essentially different compounds at this temperature. However, the relative intensities of each ketene–aldehyde absorption in the spectrum of photolyzed α-pyrone change remarkably upon warming the sample to 35 K from 8 K in the dark,[11b] suggesting that thermal rotation around C–C single bond occurrs at this low temperature.[13] This, along with the failure to observe a mixture of rotamer in bis-ketene **4c**—**e** at −170 °C implies that the barrier to the rotation in bis-ketene **4b** is raised by the bulky group to the extent of permitting the observation of each rotamer at this temperature.

Photolysis of **1b**—**e** in EPA matrix at −196 °C monitored by ultraviolet spectra resulted in rapid decrease in the intensity of original absorption to a very broad and weak absorption at around 380 nm, which disappeared on thawing of the matrix. This might be attributed to either the elusive cyclopentadiene or bis-ketene.[14]

In conclusion we have found that *o*-benzoquinones undergo two important photochemical transformations, *i.e.*, decarbonylation and α-cleavage, depending on the position and bulkiness of the substituent. An interesting bis-ketene has been observed for the first time as a mixture of rotamers at −170 °C.

Experimental

The IR spectra were measured with a JASCO IR-G grating instrument and the UV spectra with a Shimadzu UV-200 spectrophotometer. The GLPC analysis was carried out on a Yanagimoto GC-1800 apparatus equipped with hydrogen-flame detectors using a column consisting of 5% silicone SE-30 on Diasolid L (5.0 mm × 2.0 m).

Materials. *o*-Benzoquinone (**1e**) was prepared[15] by the oxidation of catecohol with silver oxide in anhydrous ether. The fine red crystals of **1e** ($\nu_{C=O}$ 1662 cm^{-1}) turned to black powder upon standing and hence were used immediately. 3-Methyl derivative (**1d**) was similarly prepared immediately before use; IR (Nujol): $\nu_{C=O}$ 1660 cm^{-1}. **1a**, mp 113—114 °C (lit,[5a] mp 114—115 °C); **1b**, mp 67—67.5 °C (lit,[16] mp 68 °C); **1c**, mp 80—81 °C (lit,[16] mp 80—82 °C). Diels-Alder dimer (**3a**) of 2,4-di-*t*-butylcyclopentadienone was prepared by the irradiation[5a] of **1a** in acetonitrile, followed by standing for 2 days at room temperature, mp 152—153 °C (lit,[5a] mp 152.5—153.0 °C). Dicyclopentadienone (**3e**) was prepared[17] by the hydrolysis of the dimer of cyclopentadienone dioxime,[18] mp 101—102 °C (lit,[17] mp 101—101.5 °C). Diethyl *cis*-3-hexendioate (**5**) was prepared by the esterification[19] of the corresponding diacid, bp 125 °C/10 mmHg (lit,[19] bp 125—127 °C/10 mmHg.

Irradiation of 1 Monitored by Infrared Spectra. A thin film of *o*-benzoquinone as a suspension of Nujol was prepared between two polished sodium chloride plates which were mounted in the metal cell holder of the Air Product low temperature infrared spectroscopy unit fitted with a potassium bromide and pyrex windows. The cell was then cooled with liquid nitrogen and at the same time gradually evacuated in order to prevent the condensation of moisture and carbon dioxide. The temperature of the cell was monitored through a copper-constantan thermocouple during the course of the operation as well as irradiation. The infrared spectra of the sample at low temperature was recorded through the potassium bromide windows. A slight increase in intensity of all the peaks in the spectrum was observed upon cooling. The vacuum shroud was then rotated 90° for irradiation through the pyrex window with an Ushio 250 W high-pressure point-source mercury-arc lamp. The spectrum of the sample was recorded periodically until almost all the absorptions of the starting materials disappeared. When irradiation was accomplished, the liquid nitrogen was removed from the cooling unit of the cell and the temperature of the cell was continuously monitored while specific regions (*i.e.*, 2000—2300 and 1500—1850 cm^{-1}) of the spectrum were scanned to observed changes of reactive intermediates upon warming. At the end of warming, the sample was washed from the cell and further characterized by comparison of thin layer and gas chromatographic behavior with that of authentic specimens.

Irradiations of 1 Monitored by Ultraviolet Spectra. Photolysis of **1** in EPA at −196 °C was performed by immersing the reaction cell directly in a transparent quartz Dewar vessel containing liquid nitrogen. A rectangular quartz cell (1 × 0.2 × 5 cm) was used for the reaction.

The authors wish to express their thanks to Professor Jiro Tsuji, Tokyo Institute of Technology, for the supply of *cis*-3-hexenedioic acid and to Prof. Katsumasa Sakanishi, Suzuka College of Techlogy, for that of *o*-benzoquinones.

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9) Although the origin of this broad band is not clear at present, it might be related to an intractable black polymer formed upon standing of *o*-benzoquinone at room temperature, since the polymer shows similar carbonyl absorption.

10) The photodecarbonylation of ketene to carbene is known; W. Kirmse, "Carbene Chemistry," 2nd ed, Academic press, New York, N. Y. (1971), p. 14.

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12) Thermal instability of structure **A** would be related to the thermal electrocyclic closure reaction to *o*-benzoquinone, since **A** is favored over **B** for such closure reaction. Although we could not demonstrate the back reaction spectroscopically, there are examples demonstrating the electrocyclic closure reaction of ketene–aldehyde[11a–c)] and diene–ketene,[11d–e)] which are closely analogous to the present system.

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