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Cyclopentadienone *O*-Oxide: Spectroscopic Observation and Photochemistry of a Carbonyl Oxide

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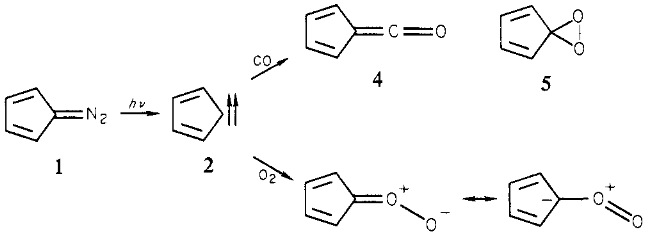
Carbonyl oxides have long been of interest as intermediates in the Criegee mechanism for the ozonolysis of olefins,[1] but the high reactivity of these intermediates has prevented physical characterization. We wish to describe the preparation, photochemistry, and spectroscopic observation of a carbonyl oxide. Similar observations have been made by Bell and Dunkin.[2] Our approach to the preparation of the carbonyl oxide is based on the reaction of a carbene with oxygen. Kirmse first suggested this approach when he reported the photochemical reaction of diphenyldiazomethane and oxygen which gives benzophenone.[3] Subsequent studies showed that nitrous oxide (N_2O) was eliminated rather than nitrogen and thus suggested that the intermediate that produced benzophenone still contained nitrogen.[4] Bartlett[5] and Murray,[6] however, produced evidence for the formation of a carbonyl oxide by isolation of the dimer and by trapping the carbonyl oxide with benzaldehyde as the ozonide of triphenylethylene. We have found that irradiation ($\lambda > 514$ nm) of diphenyldiazomethane matrix isolated in argon/oxygen (1:800:200) at 10 K gave only benzophenone, ozone, and nitrous oxide.

Diazocyclopentadiene (**1**) was chosen as the starting point for our studies for two reasons. first, it was known to give a stable, triplet carbene **2** on irradiation at low temperature,[7] and second, valence-bond resonance structures **3a,b** suggest that it should give a relatively stable carbonyl oxide because of the contribution of the cyclopentadienyl anion resonance structure **3b**. Irradiation ($\lambda > 418$ nm) of diazocyclopentadiene matrix isolated in argon/oxygen (1:800:200) at 10 K gives no nitrous oxide, in sharp contrast to the irradiation of diphenyldiazomethane. It is thus clear that in the irradiation of diazocyclopentadiene molecular nitrogen is lost. Confirmation of the fact that oxygen reacts with free cyclopentadienylidene (**2**) comes from experiments in which argon/oxygen/carbon monoxide matrices are used. the ratio of ketene[8] **4** to oxygen-trapped product is related directly to the ratio of carbon monoxide to oxygen in the matrix. Carbonyl oxide **3** and dioxirane **5** are reasonable products for the reaction of cyclopentadienylidene with oxygen. Three examples of 1,2-dioxiranes have been characterized[10–12] in the literature (two highly fluorinated derivatives have been isolated[10]), but no carbonyl oxide has been characterized spectroscopically. We turn now to the identity of the species produced in the irradiation of diazocyclopentadiene in an argon/oxygen matrix.



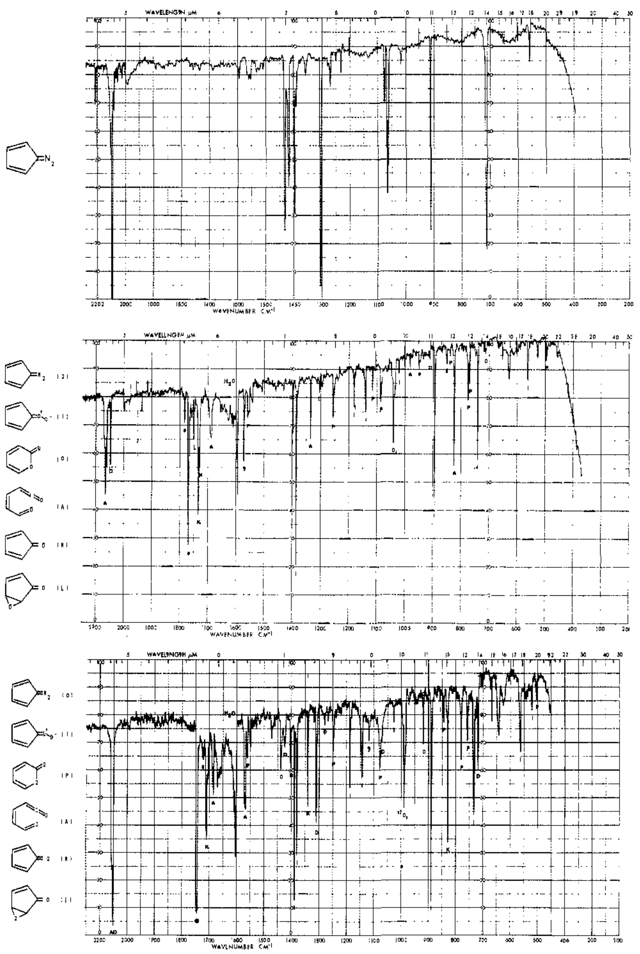
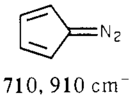
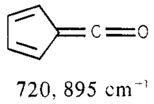


Figure 1. (Top) Infrared spectrum of diazocyclopentadiene matrix isolated in argon/oxygen (1:800:200) at 10 K. (Middle) The same sample after 70 min of irradiation ($\lambda > 418$ nm). (Bottom) Diazocyclopentadiene matrix isolated in argon/$^{18}O_2$ (1:800:200) at 10 K after irradiation for 66 min ($\lambda > 418$ nm).

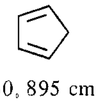
Irradiation ($\lambda > 418$ nm) of diazocyclopentadiene matrix isolated in argon/oxygen (1:800:200) at 10 K gave a new species with infrared bands at 1395 (s), 1385 (vs), 1184 (m), 1179 (w), 1142 (m), 1023 (w), 983 (w), 938 (vw), 895 (vs), and 741 (s) cm^{-1} (Figure 1). The product behaves as a single chemical entity; i.e., the infrared bands appear and disappear simultaneously. The intense bands at 741 and 895 cm^{-1} in the infrared spectrum of the product are characteristic C–H deformation modes of the cyclopentadiene ring, and it is clear from the model compounds shown (all values refer to the argon matrix isolated molecule at 10 K) that the cyclopentadiene ring has been retained. The infrared bands at 1395 and 1385 cm^{-1} are not found in the other cyclopentadiene derivatives and are not found in the infrared spectrum of bis(tri-fluoromethyl)dioxirane.[10] We tentatively assign



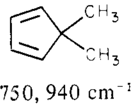
710, 910 cm^{-1}



720, 895 cm^{-1}



660, 895 cm^{-1}



750, 940 cm^{-1}

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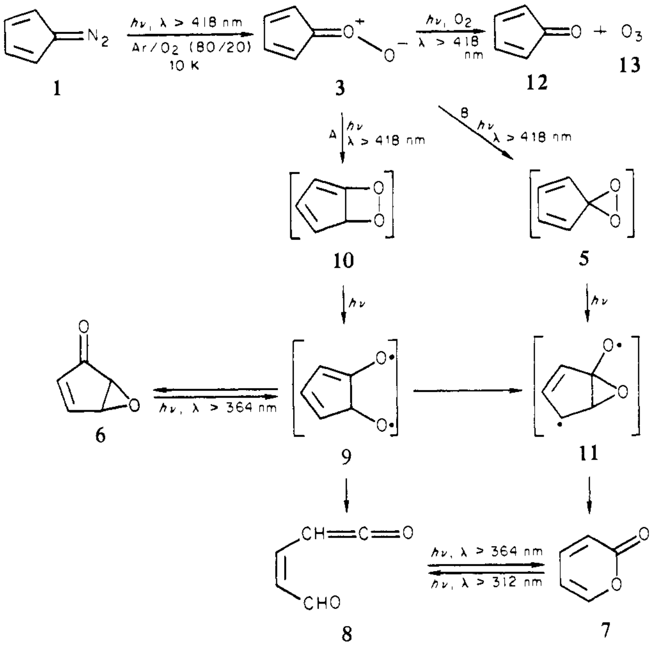
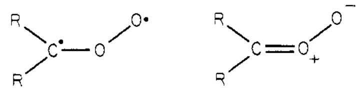
these bands to the O⋯O stretch in the carbonyl oxide **3**. It is significant that this stretching frequency comes approximately midway between carbon–oxygen double- (~1700 cm^{-1}) and single-bond (~1150 cm^{-1}) frequencies. The corresponding band in ozone comes at 1110 cm^{-1}.[13] When $^{18}O_2$ (99% double label) is used in the matrix, new bands at 1383 and 1373 cm^{-1} are observed. Both bands show intensity perturbations and are shifted. When a mixture of unlabeled oxygen and $^{18}O_2$ (99% double label) is used, four bands (1395, 1385, 1383, and 1373 cm^{-1}) are observed. These experiments show that both the 1395 and 1385 cm^{-1} bands are due to a carbon–oxygen bond.

The photochemistry of the oxygen-trapped product is also explicable in terms of the carbonyl oxide **3**. Irradiation ($\lambda > 418$ nm) of the oxygen-trapped product partitions it between two reaction pathways. The first pathway involves reaction with oxygen giving cyclopentadienone (**12**)[14] and ozone (**13**).[15] The second pathway involves rearrangement to cyclopentadienone oxide (**6**), α-pyrone (**7**), and the aldehyde ene ketene **8**. It is probable that this rearrangement proceeds via the diradical **9**, which partitions between the observed products **6**–**8**. Identification of α-pyrone (**7**) and the aldehyde ene ketene **8** was based on comparison of infrared spectra with the authentic materials matrix isolated in argon[16] and on the previously described photochemical interconversion of **7** and **8**.[16] Photoisomerization of α-pyrone to the Corey–Streith β-lactone[17] provided confirmation of the identification. The epoxide **6** was synthesized independently and identified by comparison of the infrared spectrum with that of the authentic substance matrix isolated in argon.[18] Irradiation ($\lambda > 364$ nm) of cyclopentadienone epoxide (**6**) matrix isolated in argon gave α-pyrone (**7**) and the aldehyde ene ketene **8**. The photoisomerization of substituted cyclopentadienone oxides to pyrones has been described previously.[19]



Several reaction paths leading from the carbonyl oxide **2** to the diradical **9** may be considered, and two (A and B) are shown. Path A involves an eight-electron electrocyclic process to the dioxetane **10**. Cleavage of the peroxide bond would then give **9**. Path B involves a four-electron electrocyclic reaction giving the dioxirane **5**, which on cleavage of the peroxide bond could rearrange to **9** via **11**. Two arguments can be made that favor path A over path B. First, evidence is available that substituted diradicals related to **9** rearrange to pyrones via substituted derivatives of **11**,[19] but no evidence of the reverse process has been reported. Second, in orbital-symmetry-controlled pericyclic reactions, the more delocalized transition state is usually preferred.[20]

A final comment on the structure of the carbonyl oxide **3** is in order. Calculations on the simplest carbonyl oxide suggest that it is best described as the singlet diradical structure **14a** (R = H).[21]



14a **14b**

Addition of methyl groups stabilizes the carbonyl oxide relative to the singlet diradical structure, so that in the dimethyl compound **14** (R = CH_3) the singlet diradical structure **14a** (R = CH_3) is degenerate with the carbonyl oxide structure **14b** (R = CH_3).[21] The carbonyl oxide derived from cyclopentadienylidene is further stabilized by resonance (**3a**,**b**) and hence is properly described by the zwitterionic structure.

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Registry No. **1**, 1192-27-4; **3**, 88766-67-0; **4**, 4727-22-4; **6**, 68781-88-4; **7**, 504-31-4; **8**, 39763-18-3; **12**, 13177-38-3; 1,3-cyclopentadiene, 542-92-7; 5,5-dimethyl-1,3-cyclopentadiene, 4125-18-2.

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(15) Identified by comparison of the infrared spectrum with that of an authentic sample matrix isolated in an argon/oxygen matrix.

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On the Mechanism of the Triphenylphosphine–Azodicarboxylate (Mitsunobu Reaction) Esterification

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In the Mitsunobu reaction[1] of β-hydroxy acids **1** β-lactones **2** and/or alkenes **3** are formed, depending on the activation of hydroxy (HGA) vs. carboxy (CGA) groups.[2] These products are also obtained in the reaction of β-peroxy lactones **4** with phosphines (Scheme I).[3] The dipolar ions **5** and **6** are postulated as intermediates in the HGA and CGA routes of the acids **1**. Such intermediates presumably also intervene in the β-peroxy lactone–phosphine reaction, except that here biphilic insertion leads first to phosphorane **7**, which fragments to give **5** and **6**. However, in view of recent evidence,[4] the phosphorane **8** has been suggested[5] as precursor to the alkene products in the Mitsunobu reaction.

The latter interpretation cannot account for alkene formation from the β-peroxy lactones **4**. Thus, the β-peroxy lactone–

[†] Alexander von Humboldt postdoctoral fellowship, 1981–1983.

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