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AN INTRAMOLECULAR OXENOID OXIDATION

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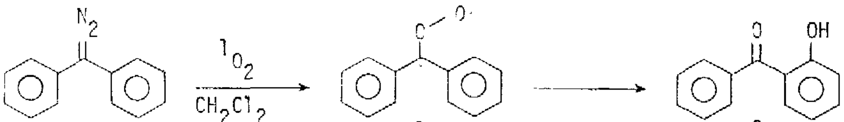
Abstract: Photooxidation of diphenyldiazomethane and 9-diazofluorene leads to the intramolecular oxenoid oxidation products, o-hydroxybenzophenone and 1-hydroxyfluorenone, respectively.

Carbonyl oxides have received attention as chemical models for the monooxygenase enzymes[1-7]. Hamilton has suggested that the enzymes and their chemical models, including carbonyl oxides, which accomplish oxygen atom transfer be termed oxenoids[8]. We have shown that singlet oxygen oxidation of diazo compounds[9-12] serves as a convenient source of carbonyl oxides which provides greater access to a study of the chemistry of these interesting intermediates. This method of generation has permitted us to show[13] that carbonyl oxides can oxidize naphthalene to a mixture of α and β naphthols as well as epoxidizing olefins[14] as also shown earlier[3] by Keay and Hamilton These reactions of carbonyl oxides and the earlier demonstration[15] that one of them accomplishes aromatic substrate oxidation accompanied by the NIH shift add to their attractiveness as suitable models for the enzymes.

We now wish to report examples of intramolecular oxidation by carbonyl oxide oxenoids. These results are of particular importance to the enzyme modeling aspect of this work because of the proximate oxygen atom transfer. Wasserman and Miller[16] have invoked intramolecular oxygen atom transfer from a carbonyl oxide in order to explain epoxide formation in the photosensitized oxidation of a pyrrole.

In a typical oxidation 4.68 mmol of diphenyldiazomethane in 550 ml of CH_2Cl_2 is photooxidized[17] using Ⓟ- Rose Bengal[18] sensitization. The intramolecular oxidation product, 2, is produced in 2.7% yield[19,20]. A similar procedure using 9-diazofluorene led to the production of the corresponding intramolecular oxidation product 1-hydroxyfluorenone, 4, in 4% yield[19,20]. Control experiments in which benzophenone or fluorenone are substituted for the respective diazo compounds indicate that the oxidations require the presence of the diazo compounds. Our previous work suggests that these oxidations are proceeding through the intermediate carbonyl oxides, 1 and 3[21,24].



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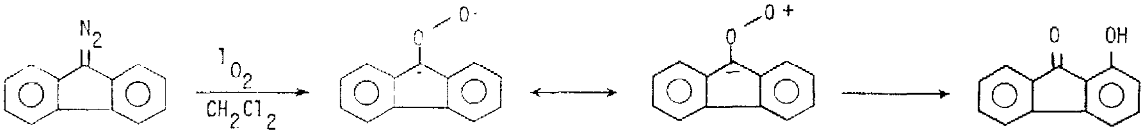

3 5 4

Oxidations *via* carbonyl oxide oxenoids have been considered[26] to be electrophilic in character. Such character implies a large contribution from canonical forms of type **5**. The larger yield of intramolecular oxidation product in the 9-diazofluorene case lends support to this view. Recently Ando *et al*[27] have presented evidence that the oxenoid produced by photooxidation of phenylbenzoyldiazomethane also exhibits electrophilic character. We are now investigating further the question of the electrophilic character of carbonyl oxides as well as the details of the oxygen atom transfer step by using suitably substituted derivatives of **1**.

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17. The photooxidations were carried out at ~5° in a pyrex vessel using a General Electric DWY 650 watt lamp. A typical reaction mixture using diphenyldiazomethane contains **2** plus benzophenone (69.8%), benzophenone azine (11.76%), and benzophenone diperoxide (4%).
18. E. C. Blossey, D. C. Neckers, A. L. Thayer, and A. P. Schaap, *J. Am. Chem. Soc.*, **95**, 5820 (1973).
19. The yields are corrected taking into account the further reaction of the hydroxy compounds as measured in separate experiments, e.g. exposure of 55 mg of **2** to the photooxidation conditions and workup leads to recovery of 40 mg of **2**.
20. The products were identified by comparing TLC Rf, IR, mass spectral, and, for **4**, m.p. data with those of the authentic compounds.
21. The electronic structure of the carbonyl oxides is in doubt. We show both the usual zwitterionic structure as well as the diradical structures suggested by the earlier work of Hamilton and Giacin[1] and the theoretical calculation of Goddard et al [22,23].
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24. A remotely possible alternative path to **2** and **4** has been ruled out. Rearrangement of **1** to phenyl benzoate followed by a Photo Fries[25] rearrangement could lead to **2**. We have shown that no phenyl benzoate is present in our reaction mixture and that phenyl benzoate is not converted to **2** under our photolysis conditions.
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