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OXIDATION OF NAPHTHALENE BY AN INTERMEDIATE IN THE SINGLET OXYGEN OXIDATION OF DIPHENYLDIAZOMETHANE: A CHEMICAL MODEL FOR THE MONOOXYGENASE ENZYMES

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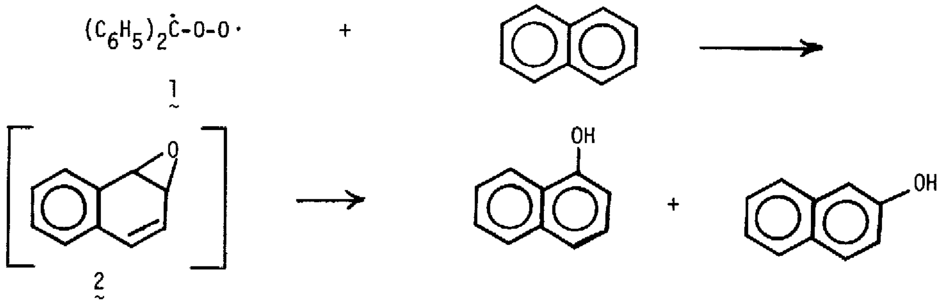
Hamilton has suggested[1] that the oxygen atom transfer which occurs in many monooxygenase - catalyzed reactions proceeds <u>via</u> an oxenoid reagent. One of the oxenoid reagents which has been examined as a model for the oxygen transfer step in these reactions is a carbonyl oxide. Hamilton and Giacin[2] had earlier found that carbonyl oxides produced in the photooxidation of diazo compounds can oxidize saturated hydrocarbons. Additional support for the suggestion that carbonyl oxides can react as oxenoids came from the observation[3] that the carbonyl oxide produced by photooxidation of 9-diazofluorene can effect an NIH shift[4] in anisole-4-D. More recently Keay and Hamilton[5] have shown that an intermediate produced in the oxonization of alkyne, probably an α-carbonyl carbonyl oxide, is a powerful oxenoid which can epoxidize alkenes

We have shown[6-9] that singlet oxygen oxidation of diazo compounds produces carbonyl oxides which can be trapped by aldehydes to give ozonides. Because the conditions used in these oxidations are less strenuous then those associated with the ozonolysis reaction, we felt that they offered a better opportunity to study the oxenoid properties of carbonyl oxides.

We have now found that an intermediate produced in the photosensitized oxidation[10,11] of diphenyldiazomethane, most likely the carbonyl oxide **1**, is capable of oxidizing naphthalene to a mixture of α and β-naphthols.[12] The total yield of naphthols obtained (~14%) suggests that the oxenoid reagent produced under these conditions is a relatively powerful oxygen atom transfer reagent.

Our previous work indicates that the singlet oxygen oxidation of diazo compounds produces carbonyl oxides. Two possibilities for naphthol formation then need to be considered, namely, 1) direct insertion of an oxygen atom into a C-H bond of naphthalene or 2) formation and subsequent rearrangement of naphthalene 1,2-oxide, **2**. Some support for the second possible mechanism comes from the observed ratio of α to β naphthol (85/15) which is to be compared to the 88/12 ratio produced[13] by isomerization of 1,2-naphthalene oxide in methylene chloride saturated with acetamide.[14] We tentatively suggest that the reaction involves attack of the naphthalene by carbonyl oxide, **1**,[15] to give oxide, **2**, which subsequently rearranges to the naphthols.



Further investigations are in progress including an attempt to determine whether the reaction leads to the NIH shift in suitably-substituted naphthalenes.

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10. The photooxidations were carried out at ~5° in a pyrex vessel in acetonitrile solvent, us rose bengal sensitizer and a General Electric DWY 650 watt lamp.
11. Control reactions indicated that no naphthols are formed when the same reaction condition are used without diphenyldiazomethane or when the reagents are exposed to oxygen without irradiation.
12. The naphthols were identified by comparing infrared, nmr, mass spectral,tlc and m.p. data with those of the authentic materials. Naphthalene: Diphenyldiazomethane ratio used was 6
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14. Reference 13 describes a range (98/2-88/12) of naphthol ratios obtained from isomerizing the oxide under a variety of conditions. The value referenced is that obtained under conditions most closely approximating those used here.
15. While a zwitterionic form for the carbonyl oxide cannot be ruled out we have written the diradical form based on the earlier evidence[2] of Hamilton and Giacin, and the recent theoretical considerations presented by Wadt and Goddard.[16]
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