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PHOTOSENSITIZED OXYGENATION OF 2-PHENYL-1,3-OXAZEPINE[1]

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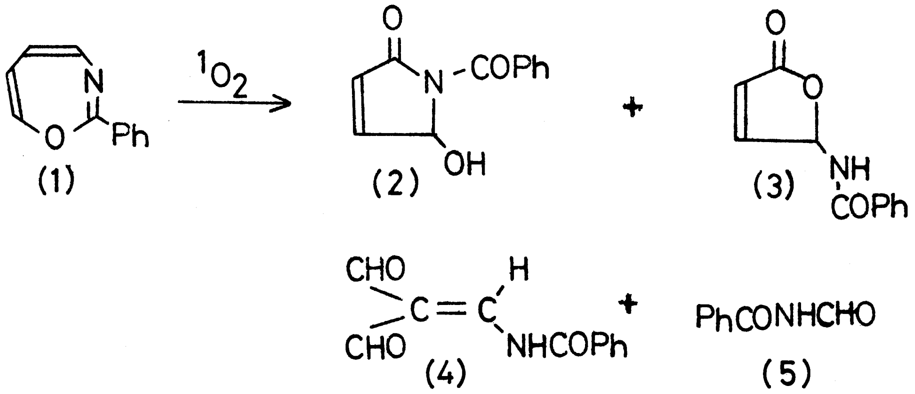
The dye-sensitized photooxygenation of 2-phenyl-1,3-oxazepine (1) in methylene chloride yields fragment products, 2, 3, 4, and 5. Among them, pyrrolinone (2) and butenolide (3) are assumed to originate from the 1,4-epidioxide (6), and ethylidene malonaldehyde (4) from dioxetane (10) or 1,6-epidioxide (11).

Although the photo-sensitized oxygenation of the unsaturated five-membered heterocycles has extensively been investigated,[3] that of the seven-membered heterocyclic compounds is little known,[4] except for a recent paper on 1,2-diazepines.[5] In connection with this, we wish to report the first example of the photooxygenation of a 1,3-oxazepine. The photo-oxidation of 2-phenyl-1,3-oxazepine (1) in the presence of methylene blue afforded several oxidized fragments arising from the 1,2- (or 1,6) and 1,4-additions of singlet oxygen.

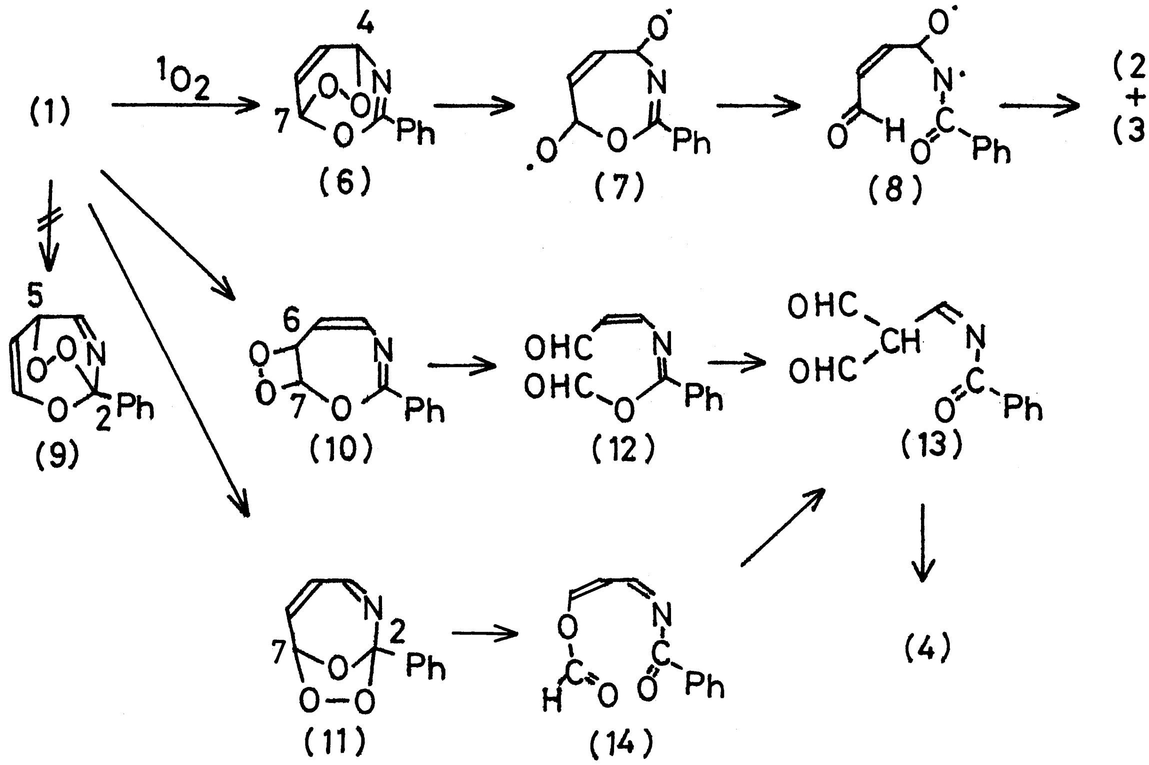
A solution of 1 (300 mg) in dry methylene chloride (200 ml) containing methylene blue (20 mg) was photolyzed (tungsten lamps, Pyrex vessel) for 12 hr while a stream of oxygen was bubbled through the solution. Separation of the photolysate was achieved by silica gel t.l.c. (benzene : ether, 4 : 1) to give pyrrolinone (2), mp 104-106°, butenolide (3), mp 150-150.5°, ethylidene malonaldehyde (4), mp 126-128°, and N-formylbenzamide (5), mp 108°, in 7, 18, 15, and 13 % yields, respectively,[6] in addition to a small amount of 2-phenyl-3-hydroxypyridine and benzamide. The structures of products were characterized by the following spectral properties as well as by chemical evidence. For 2, m/e, 203 (9 %), 105 (100 %); ν_{max}(KBr), 3400, 1750, 1665 cm^{-1}; λ_{max}(EtOH), 239.5 nm (log ε, 3.99); δ (CCl_4), 5.0 (1H, broad), 6.08 (1H, J=6.0 and 1.2 Hz), 6.33 (1H, J=2.0 and 1.2 Hz), 7.10 (1H, J=6.0 and 2.0 Hz) and 7.25-7.70 (5H). For 3, m/e, 203 (18 %), 105 (100 %); ν_{max}(KBr), 3350, 1775 cm^{-1}; λ_{max}(EtOH), 227 nm (log ε, 3.18) and 272 (1.91); δ (acetone-d_6), 6.26 (1H, J=5.5 and

2.0 Hz), 6.90 (1H, J=9.0, 2.0, and 1.8 Hz), 7.57 (1H, J=5.5 and 1.8 Hz) and 8.56 (1H, broad J=9.0 Hz). For 4, m/e, 203 (30 %), 105 (100 %); $\nu_{max}(CHCl_3)$, 1720, 1665, and 1593 cm^{-1}; λ_{max}(EtOH), 228 nm (log ε, 4.01), 267 (4.14) and 312 (4.03); δ (DMSO-d_6), 8.62 (1H, J=12.0 and 3.3 Hz), 9.79 (1H, singlet), 10.06 (1H, J=3.3 Hz), and 12.6 (1H, broad with J=12.0 Hz). Independently, 2 was also synthesized by the photooxidation of N-benzoylpyrrole in methanol under the same conditions used for 1, where, however, N-benzoyl-5-methoxy-Δ^3-pyrroline-2-one, mp 91-92°, was the main product.[7] Catalytic hydrogenation of butenolide (3) on Pd-C gave 4-benzoylaminobutanolide, mp 159-160°. Compound 5 was identified by comparison with an authentic sample. In addition products 2 - 5 were all readily hydrolyzed with aqueous sodium hydroxide solution to give benzamide in good yields, suggesting that benzamide is not a primary photo-product. 2-Phenyl-3-hydroxypyridine is considered not to be a photo-product but a product originating from the vibrationally excited state.[8]



The pyrrolinone and butenolide products, 2 and 3, could arise through 1,4-addition of singlet oxygen to the diene portion of 1, leading to the 4,7-endo-peroxide (6). Successive O-O bond cleavage of 6 affords diradical (7), which then undergoes cleavage of the allylic C-O bond to form diradical (8). It is then possible to derive both lactone and lactam type products, 2 and 3, from the same intermediate (8) through hydrogen abstraction by the N- or O-radical and subsequent recombination of the resulting diradicals. It should be noted here that no products from the 2,5-endo-peroxide (9) have been detected, and therefore 1,4-addition of singlet oxygen did not occur in the diene portion containing a nitrogen atom. This observation coincides with the case of 1,2-diazepines.[5]

A plausible explanation for the formation of ethylidene malonaldehyde (4) is outlined in the following reaction scheme passing through either dioxetane (10) or 2,7-endo-peroxide (11). The former could arise from 1,2-addition of the oxygen to the C_6-C_7 position of 1, and the latter from 1,6-addition to the C_2-C_7 position. The oxetane ring opening of 10 leads to formate (12), which in turn converts into the product (4) via N-benzoyl dialdehyde (13) by 1,5-formyl migration and subsequent proton transfer. On the other hand, the other epidioxide (11) could lead to the intermediate (13) by Baeyer-Villiger type rearrangement followed by 1,3-formyl migration of the resulting formate (14). A precedent example[9] suggests the further oxidation of the carbon-carbon double bond of 4 giving N-formylbenzamide (5).



Contrary to the case of 1,2-diazepines,[5] we were not able to isolate any initial adducts of 2-phenyl-1,3-oxazepine (1) and singlet oxygen. Accordingly the mechanistic considerations are speculative at present. However, the proposed reaction paths such as O-O bond cleavage, formyl migration and Baeyer-Villiger type rearrangement have been confirmed in the photooxygenation of the corresponding five-membered analogs, i.e., isoxazole derivatives.[10] In connection with the photooxygenation of electron-rich olefins such as enamines[11] and vinyl ethers,[12] there is possibility that peroxiranes or zwitterion intermediates would be the precursors of epidioxides (6), (10), and (11). To clarify the reaction mechanism further studies are in progress.

References and notes

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