

PHOTOOXIDATION OF SOME MESOIONIC AND RELATED SYSTEMS

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Photooxidation of several mesoionic compounds gave ring cleavage products, some of which were apparently formed via the endoperoxides of the mesoionic rings. Photooxidation of a Δ^2 -oxazolin-4-one and a Δ^2 -thiazolin-4-one gave the corresponding 4,4'-bisoxa- and bisthiazolinone in dichloromethane, whereas the former gave benzamide in dimethylformamide.

Investigations of photooxidation of 1,3-dipolar species are relatively few¹⁾ by comparison with those on electronically equivalent 1,3-dienes.²⁾ As part of our studies of the photochemistry and cycloaddition reactions of mesoionic compounds, we have been surveying the photooxidation reactions of these ring systems, which may be regarded as resonance-stabilized 1,3-dipoles. The recent reports³⁻⁵⁾ on the photooxidation of sydnone and some other mesoionic compounds prompt us to report our results on photooxidation of some mesoionic and related ring systems.⁶⁾

When a solution of the mesoionic 2,5-diphenyl-1,3-dithiol-4-one 1a (λ_{\max} 540 nm) in dichloromethane was irradiated with a tungsten-halogen lamp while a slow stream of oxygen was bubbled, dibenzoyl disulfide 2 (35 or 70% depending on the source of the benzoyl group) and a compound assigned as the dimer 3 (10%; mp 186-188 °C dec) were isolated.⁷⁾ The dimer 3 had a correct elemental analysis, showed a strained thiol lactone carbonyl band at 1690 cm^{-1} corresponding to the dimers of this type,⁸⁾ and its electron impact mass spectrum, while lacking the molecular ion peak, was virtually identical to that of the dithiolone 1a with an extra peak at m/e 178 corresponding to $\text{PhC}\equiv\text{CPh}^+$. This shows that the compound still retains the dithiolone framework with formation of an intermolecular carbon-to-carbon bond. The dimer regenerated the characteristic deep violet color of the dithiolone 1a on warming, which was identified by conversion into dimethyl 2,5-diphenylthiophene-3,4-dicarboxylate 4 (68%) by the reaction with dimethyl acetylenedicarboxylate.

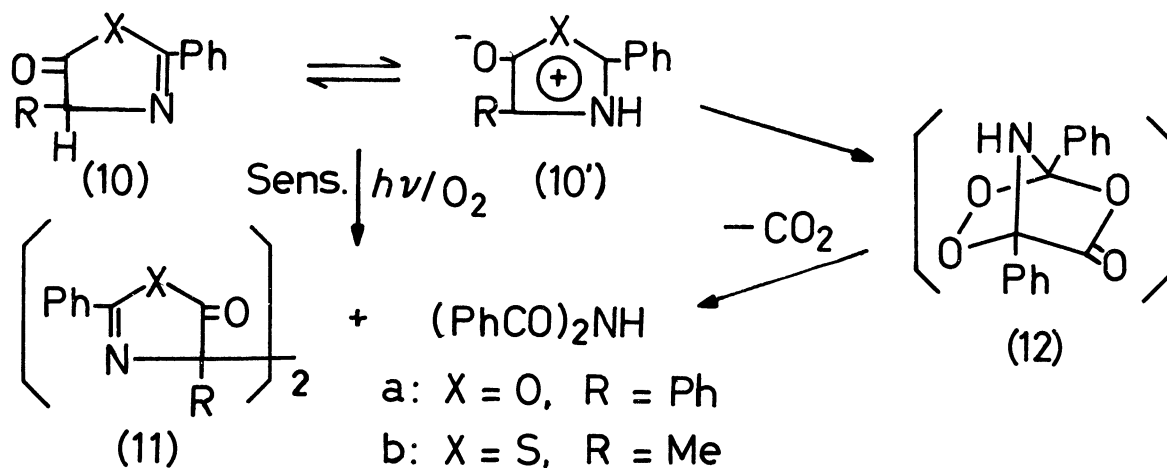
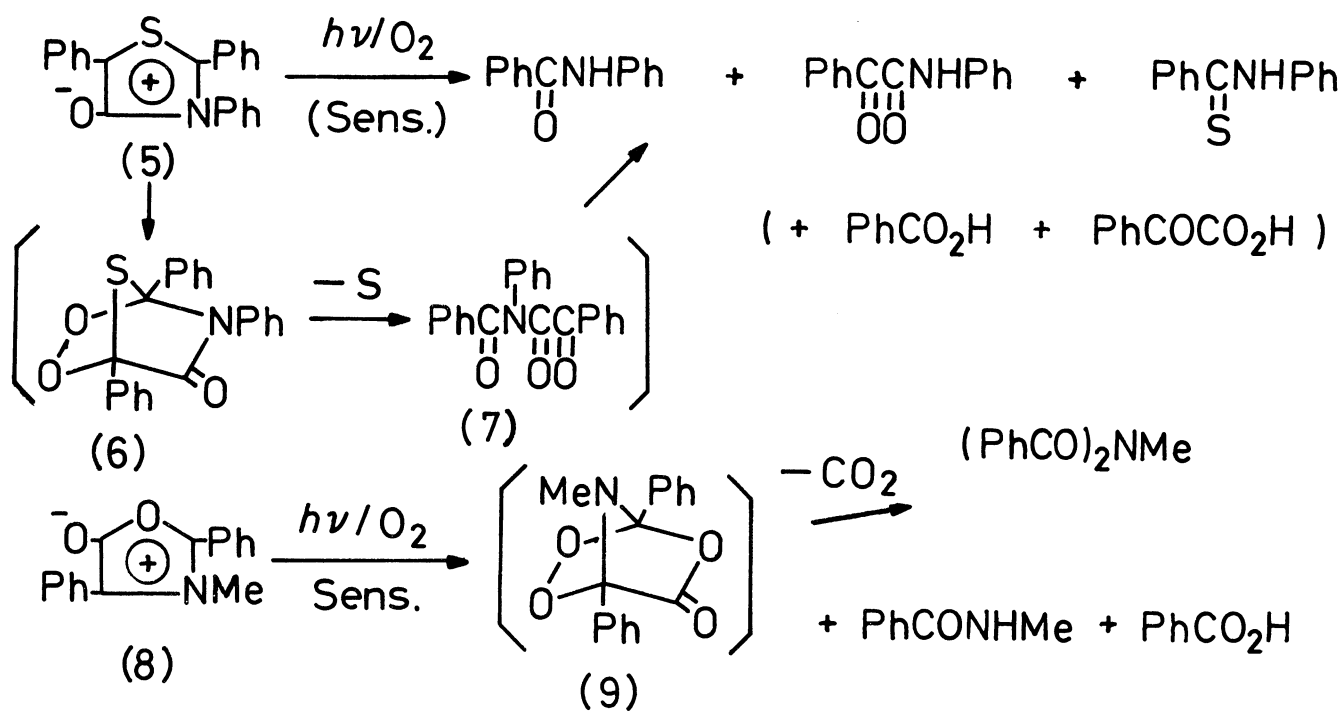
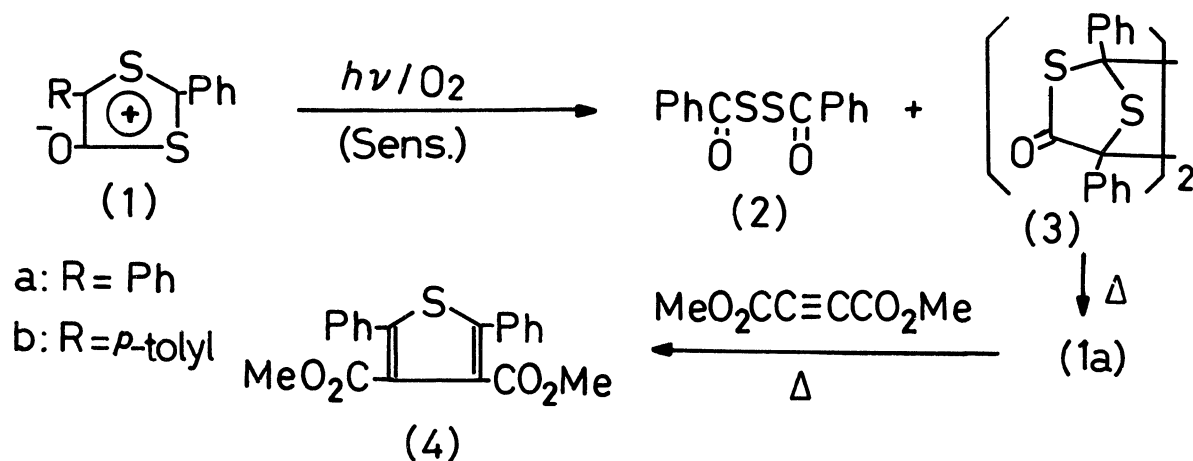
Similar photooxidation of a dichloromethane solution of the mesoionic 2,3,5-triphenyl-4-thiazolone 5 (λ_{\max} 422 nm) and t.l.c. separation of the product mixture gave benzanilide (52%), phenylglyoxylanilide (3.3%), and thio-benzanilide (0.6%), and a mixture of benzoic and phenylglyoxylic acid, which could not be separated efficiently, and were detected by g.l.p.c. after conversion into the corresponding methyl esters with diazomethane. The photooxidations of these highly colored compounds 1 and 5 proceeded in the presence or absence

of a dye sensitizer, and were retarded by addition of diazabicyclo(2.2.2)octane. Both compounds were inert to oxygen in the dark.

Similar irradiation of the mesoionic 3-methyl-2,4-diphenyl-5-oxazolone 8 in dichloromethane in the presence of methylene blue and oxygen, and fractional sublimation of the products afforded N-methyldibenzamide (29%), N-methylbenzamide (2%), and benzoic acid (4.1%). The product distribution in this case is thus considerably different from that of the autooxidation of the oxazolone 8.⁹⁾ Notably, α -methyliminophenylglyoxylic acid, one of the major autooxidation products, could not be detected among the products.

The photooxidation of 2,4-diphenyl- Δ^2 -oxazolin-5-one 10a in dichloromethane in the presence of a polymer-supported rose bengal sensitizer gave 4,4'-bis-(2,4-diphenyl- Δ^2 -oxazolin-5-one) 11a (12%) while that in dimethylformamide gave dibenzamide (13%) with only a trace amount (0.6%) of the bisoxazolinone 11a. It is known that the oxazolinone exists as the oxazolinone form 10a in nonpolar solvent whereas in dimethylformamide, it exists predominantly as the mesoionic tautomer 10'a.¹⁰⁾ Although the isolated yields of the products were low, the above results suggest that the photooxidation of the oxazolinone form and the mesoionic form mainly afford the bisoxazolinone and the amide respectively. After the completion of these works,⁶⁾ Dixit et al.⁴⁾ reported the same conclusion from photooxidation studies of some oxazolinones under different conditions (medium pressure mercury lamp/quartz filter/methanol or methanol--benzene). In support of this interpretation, methylene blue-sensitized photooxidation of 4-methyl-2-phenyl- Δ^2 -thiazolin-5-one 10b in dichloromethane, in which the thiazolinone exists entirely as the keto form 10b,¹¹⁾ gave the bis-thiazolinone 11b (54%). A mesoionic 5-thiazolone is recently reported to give products, one of which was probably formed by fragmentation of the 1,3-cycloadduct of singlet oxygen across the mesoionic ring.⁵⁾

The dibenzamides from the oxazolones 8 and 10a are most probably formed by decarboxylative fragmentation of the endoperoxide intermediates 9 and 12, and the products from the thiazolone 5 may well be the hydrolysis products (during chromatographic work up) of N-glyoxalylbenzanilide 7, which is expected to be formed from the endoperoxide 6. However, the photooxidation of 2-phenyl-5-p-tolyl-1,3-dithiol-4-one 1b gave dibenzoyl disulfide 2 as one of the products showing that the formation of the disulfide from the dithiolone is, at least in part, the result of an intermolecular reaction.¹²⁾ A possible route to the disulfide may be the cleavage of the endoperoxide intermediate to carbon monoxide and two arylthio radicals and their recombination.



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- 7) All the yields reported are based on isolated products with sufficient purity.
- 8) For the isolation of similar dithiolone dimers by non-photochemical reactions, see, H. Gotthardt, C. W. Weissshuhn, O. M. Huss, and D. J. Brauer, *Tetrahedron Lett.*, 1978, 671; H. Gotthardt, O. M. Huss, and C. M. Weissshuhn, *Chem. Ber.*, 112, 1650 (1979).
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- 12) This reaction gave a dimer of 1b (11%) and a crude disulfide mixture, from which the disulfide 2 (20%) was isolated. H.p.l.c. of the crude mixture showed the presence of small amounts of di-p-toluoyl disulfide and another unknown component, but they have not been isolated. This experiment was performed by Mr. Nobuo Aoki, to whom the authors' thanks are due.

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