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THE REACTION OF SINGLET OXYGEN WITH 2-PHENYLCYCLOALKENES POSSESSING SMALL AND COMMON RINGS

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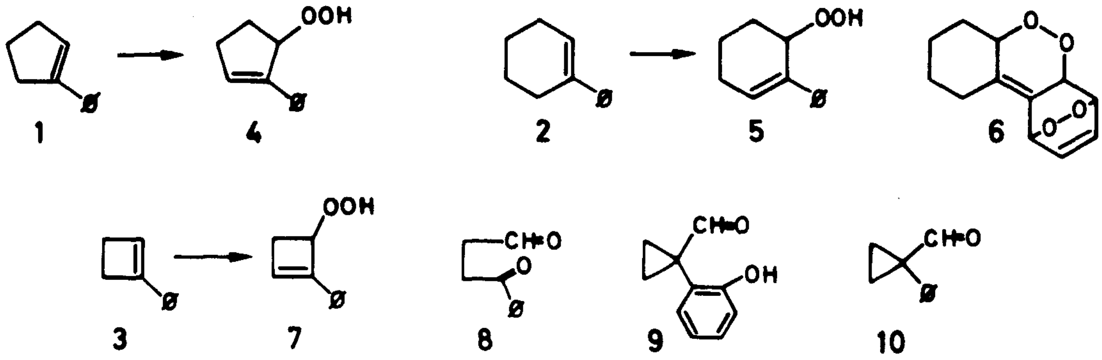
It has been recently recognized that molecules of the styrene type react with singlet oxygen to give products which can be rationalized as arising from an initially formed Diels-Alder adduct, rather than a dioxetane.[1,2] We now report our preliminary results with the 2-phenyl derivatives of cyclopentene (1), cyclohexene (2), and cyclobutene (3). All molecules react freely with singlet oxygen, giving in each case different products which appear to be a reflection of ring size.



1 4 2 5 6

3 7 8 9 10

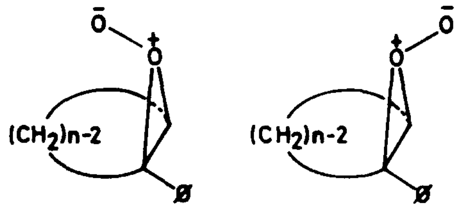
The photo-oxygenation of 1 in acetonitrile using methylene blue as sensitizer is straightforward in that the sole product obtained is the hydroperoxide 4.[3] Phenylcyclohexene (2) reacts similarly to give the homologous hydroperoxide 5, but accompanied by the double peroxide 6 in a ratio of 3:1. The behaviour of the cyclobutene 3 is dramatically different in that four products are obtained; the hydroperoxide 7, the keto-aldehyde 8, and the cyclopropyl carboxaldehydes 9 and 10. Unlike the common ring olefins 1 and 2, the product composition arising from 3 is solvent-dependent (Table).

Table. Photo-oxygenation of 1-Phenylcyclobutene (3) in Various Solvents

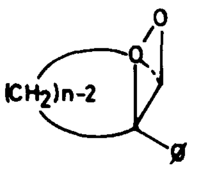
Solvent, Sensitizer	7	8	9	10	Polymer
CCl_4, TPP	0%	40%	0%	0%	60%
$CDCl_3$, TPP	20	60	0	traces	20
CH_2Cl_2, TPP	12	38	0	traces	50
CH_3CN, MB	28	47	10	traces	15
CH_3OH, RB	28	29	33	0	10

TPP = Tetraphenylporphin, MB = Methylene Blue,
RB = Rose Bengal

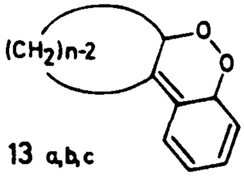
These results, diverse as they are, may be conveniently rationalized in terms of the primary formation of three intermediates, the perepoxide (11), the dioxetane (12), and the Diels-Alder adduct (13).



11 a,b,c



12 a,b,c

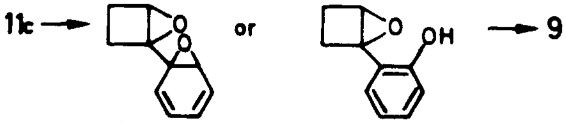


13 a,b,c

a: n=5; b: n=6; c: n=4.

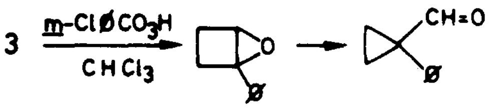
Although the sequence or simultaneity of events cannot be known for certain, it seems reasonable to suppose that the perepoxide forms first. Evidence for its intermediacy is indicated by a dominant Markovnikov effect, which would be expected in such cyclic systems where steric, stereoelectronic, and statistical factors are identical in both ene modes.[4] The C(1)-O bonds in perepoxides 11a-c are weakened by the phenyl substituent and therefore secondary allylic hydroperoxides 4, 5, and 7 are formed preferentially. Tertiary hydroperoxides are never detected. Moreover, for the strained ring olefin 3 the corresponding perepoxide 11c readily expands to the dioxetane 12c and once formed promptly snaps open to the 1,4 dicarbonyl derivative 8. However, in more polar solvents, the perepoxide enjoys longer life, thanks to solvation,[5] and consequently alternative avenues to reaction are opened up. Apart from hydroperoxidation, the phenolic cyclopropylcarboxaldehyde 9 is formed with increasing abundance in the more polar solvents.

A plausible mechanism is that intra or intermolecular oxygenation occurs since, after all, the perepoxide 11c is expected to be an oxenoid reagent. Electrophilic addition or insertion gives the areneoxide-epoxide 14 or the phenolic epoxide 15, both of which will rearrange to the same ring contracted product 9.



14 15

The traces of phenylcyclopropylcarboxaldehyde 10 in the reaction mixture could derive from the unobserved epoxide 16 arising adventitiously.[6] Indeed treatment of 3 with m-chloroperbenzoic acid gives 10.[7]



16 10

In the case of the common ring perepoxides 11a and 11b there is no propensity to expansion to dioxetanes 12a and 12b. Conformational and steric considerations favour the formation of anti 11b[8] and its conversion to the *endo* peroxide 13b as no allylic hydrogens are available. A second molecule of oxygen immediately attacks 13b to form the double peroxide 6.

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REFERENCES AND NOTES

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2) M. Matsumoto & K. Kondo, Tet. Letters, 3935 (1975).

3) Our usual procedure was followed (C.W. Jefford & A.F. Boschung, Helv. Chim. Acta 57, 2242 (1974)).

4) For a long time the absence of an observed Markovnikov effect has been used as an argument against perepoxides as intermediates. See for example:
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5) L.M. Stephenson, D.E. McClure & P.K. Sysak, J. Amer. Chem. Soc. 95, 7888 (1973).

6) It has been proposed that singlet oxygen could reduce perepoxide intermediates to form epoxides and ozone. See M.J.S. Dewar, A.C. Griffin, W. Thiel & I.J. Turchi, J. Amer. Chem. Soc. 97, 4439 (1975).

7) Cyclobutane epoxides are known to undergo thermal ring contractions. J.L. Ripoll & J.M. Conia, Bull. Soc. Chim. France, 2755 (1965).

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