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Tetrahedron

Tetrahedron Vol. 62, No. 46, 2006

Tetrahedron Symposium-in-Print Number 126

Organic chemistry of singlet oxygen

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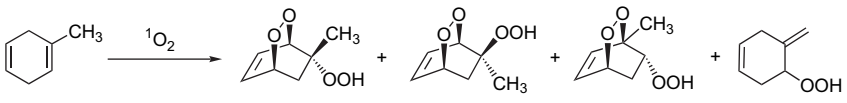
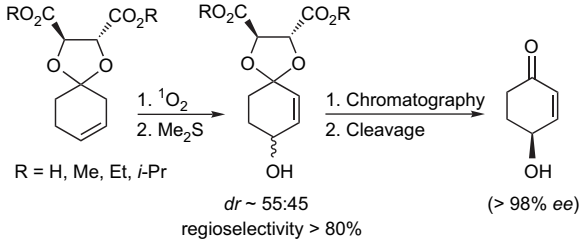
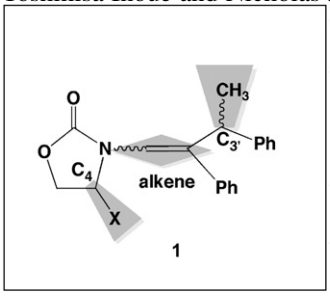
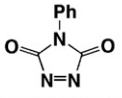
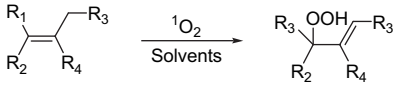


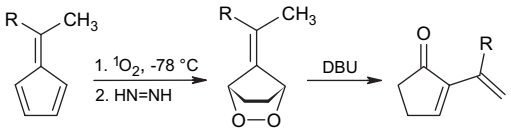
The photooxygenation of methyl-substituted cyclohexa-1,4-diene derivatives has been searched. The substituent effect is discussed.

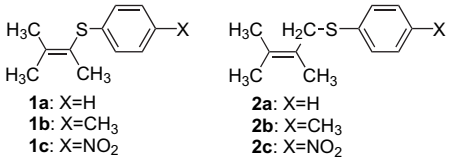




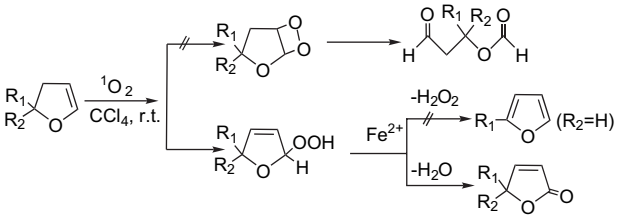
Reactive species	Stereo-differentiating structural factor	Stereoselectivity
	C_4	Low
O_3	C_4 + alkene	Low to Moderate
$^1O_2$	C_4 + alkene + $C_{3'}$	High





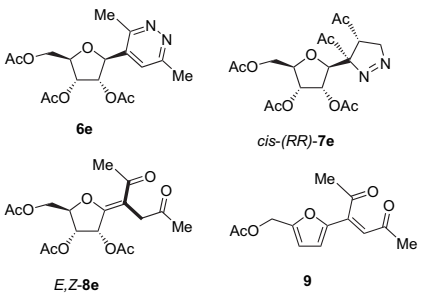


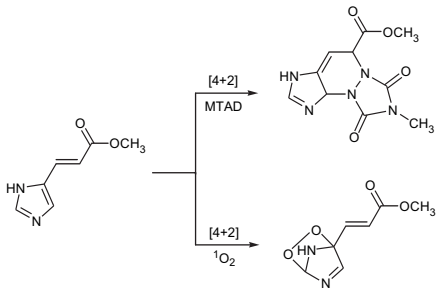
The singlet oxygen photooxidation of several allyl and vinyl sulfides, sulfoxides, and sulfones were conducted in deuterated solvents. The results indicate that only vinyl sulfides are suspectible to hydrogen bonding solvent effects.

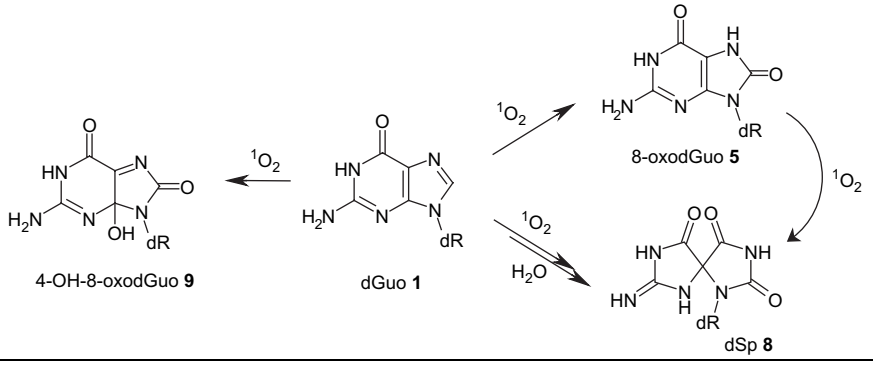


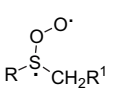
Photooxygenation of 2,3-dihydrofurans in CCl_4 at ambient temperature followed by ferrous ion-catalyzed *gem*-dehydration of the yielded allylic hydroperoxides afford the corresponding α,β-unsaturated γ-lactones in good to excellent yields.

The methylene blue-sensitized photooxygenation of β-ribofuranosyl furan **1e** followed by in situ Et_2S treatment afforded the conformationally stable β-ribofuranoside **4e** almost quantitatively. The latter was converted to pyridazine C-nucleoside **6e** by cyclization with NH_2NH_2 and to pyrazoline **7e** through a 1,3-dipolar cycloaddition with diazomethane. Attempts to epoxidize the double bond failed both by dimethyldioxirane (DMDO), which left **4e** unchanged, and by NEt_3/*t*-BuOOH or NaOO-*t*-Bu which respectively afforded the new and unexpected *exo*-glycals *E*,*Z*-**8e** and the novel furan derivative **9**.

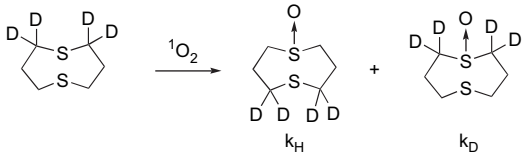


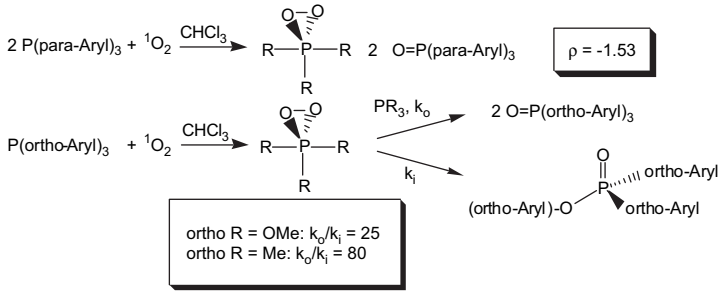




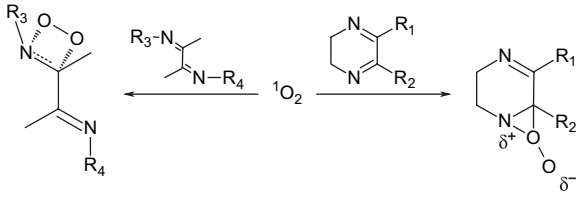


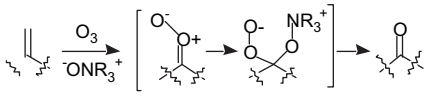
Effect of R and R^1 (alkyl, phenyl) on the chemistry of the persulfoxide

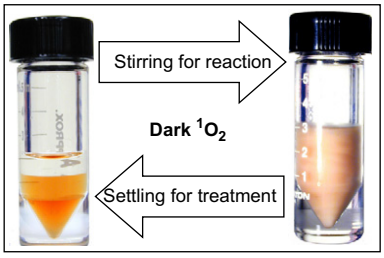




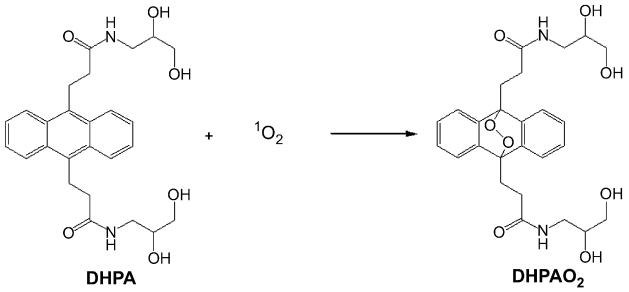
Steric and electronic effects on the reactivity of arylphosphines with singlet oxygen are reported.

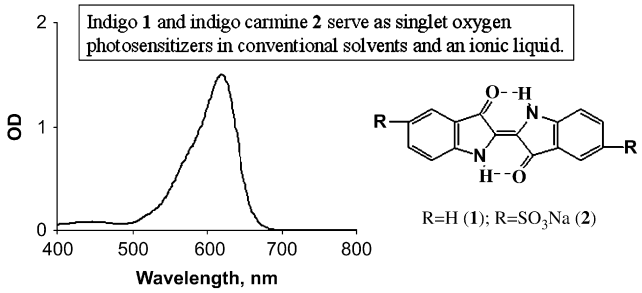






The chemical source of singlet oxygen H_2O_2/MoO_4^{2-} can oxidize labile and hydrophobic substrates in microemulsion. The respective advantages and limitations of single-phase and multiphase microemulsion systems are shortly reviewed and discussed.





*Corresponding author
Supplementary data available via ScienceDirect

COVER

The cover figure shows the reaction of homochiral cyclohexene ketals with $^1O_2$, which gives hydroperoxides and after reduction the corresponding allylic alcohols with excellent regioselectivity. Mechanistic considerations were used to rationalize the regioselectivity. The work was conducted by Torsten Linker and co-workers.

Abstracted/indexed in: AGRICOLA, Beilstein, BIOSIS Previews, CAB Abstracts, Chemical Abstracts. Current Contents: Life Sciences, Current Contents: Physical, Chemical and Earth Sciences, Current Contents Search, Derwent Drug File, Ei compendex, EMBASE/Excerpta Medica, Medline, PASCAL, Research Alert, Science Citation Index, SciSearch. Also covered in the abstract and citation database SCOPUS®. Full text available on ScienceDirect®

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ISSN 0040-4020