

Solvent effect on the sensitized photooxygenation of cyclic and acyclic

?-diimines

Lemp, Else

Zanocco, Antonio L.

Günther, German

Pizarro, Nancy

The reaction of singlet molecular oxygen with a series of cyclic and acyclic ?-diimines was studied. Time-resolved methods were used to measure total reaction rate constants and steady-state methods were used to determine chemical reaction rate constants. GC-MS was used to tentatively assign the reaction products. 5,6-Disubstituted cyclic ?-diimines are singlet oxygen quenchers, but become more effective in polar solvents. A reaction mechanism involving a perepoxide intermediate or transition state leading to a hydroperoxide seems to be a key reaction path for product formation. A replacement of the phenyl substituent for a methyl substituent opens up an additional reaction involving a perepoxide-like exciplex, which increases singlet oxygen quenching of the cyclic ?-diimines. The reactivity of 5,6-disubstituted cyclic ?-diimines towards singlet oxygen is highly dependent on steric interactions arising from vicinal phenyl rings and from electronic effects.

1,4-Disubstituted acyclic ?-d