

Photolysis at 185 nm of saturated cyclic ethers in the liquid state

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Saturated ethers start to absorb near 200 nm. Their first absorption band is attributed to an $n \rightarrow$ Rydberg transition. Excitation at 185 nm leads to the scission of a C–O bond and in cyclic ethers to the formation of alkyl oxyl biradicals. Reclosure, disproportionation and intramolecular hydrogen atom abstraction by the oxyl end of the molecule are considered to be the major processes for these biradicals. However, in some cyclic ethers fragmentation products (e.g. cyclopropane plus formaldehyde from tetrahydrofuran) are observed. Evidence is given that these products arise from true molecular fragmentation processes.

Photochemistry of cyclic 1,2-diketones: dependence of the photoproducts on the ring size and excited state geometry

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The photochemistry of a homologous series of 3,3, ω,ω -tetramethylcycloalkane-1,2-diones ($1, n = 0, 1, 2, 3, 4$) was studied in isopropanol and benzene as solvents. In benzene the photochemistry of the substrates ($\lambda \geq 420$ nm) was found to depend markedly on the ring size. For example, $1(n = 0)$ yielded CO and 2,3-dimethyl-2-butene, $1(n = 1, 2, 3)$ afforded products resulting from initial α cleavage but also acyloins as a result of intermolecular hydrogen abstraction from other ground state substrate molecules or primary photoproducts and $1(n = 4)$ underwent intramolecular hydrogen abstraction and subsequent cyclization in addition.

In order to explain the variation in the photochemistry with the ring size of the cycloalkane-1,2-dione, the geometry of the 1,2-diketo chromophore was determined for both the ground state and the S_1 and T_1 states.

