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# PHOTOCHEMISTRY OF AN OXASPIROPENTANE DERIVATIVE[1a]

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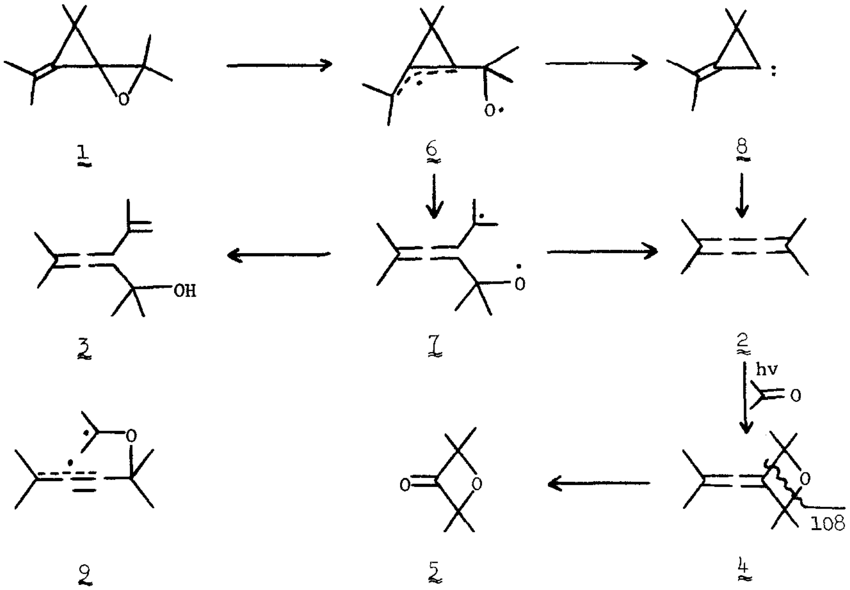
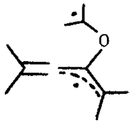
In conjunction with studies on the chemistry of oxaspiropentane 1,[2] we have examined the photochemical decomposition of this strained epoxide. Irradiation of a benzene solution of 1 with 2537 Å light resulted in the formation of three volatile products identified as cumulene 2,[3] allene alcohol 3,[2] and alleneoxetane 4. The latter compound displays nmr singlets at τ 8.62 and 8.28 in a 2:1 ratio and weak allene absorption at 5.04 μ in the infrared. A mass spectrum (70 *e*V) confirmed its isomeric relationship with 1 ($M^+$ at *m/e* 166) and showed an odd-electron fragment at *m/e* 108 as the base peak. This corresponds to cleavage to the butatriene radical-cation as indicated, a process which finds analogy in the mass spectrum of oxetane itself.[4] Chemical assurance of the assigned structure is provided by its clean degradation to tetramethyloxetanone 5[5] by ozone in pyridine/methylene chloride.

Careful glpc monitoring of the photolysis demonstrated that the yields of 2 and 3 increased to a maximum (19% and 13%, respectively) and then decreased upon further irradiation. In contrast, oxetane 4 was not evident during the initial phases of reaction, but thereafter its yield increased monotonically as a function of photolysis time to a maximum of *ca.* 10%. This behavior suggested that 4 was a secondary photoproduct. Ready confirmation of this proposal was provided when irradiation of a benzene solution containing equimolar amounts of acetone and 2 gave 4 in good yield.

Mechanistic possibilities are illustrated below. Energy transfer from the benzene photosensitizer yields an excited oxaspiropentane species which is capable of bond rupture of the indicated C—O linkage to produce delocalized biradical 6. Structural reorganization of this species in a fashion analogous to that of the related cation[3] gives biradical 7. This second intermediate provides a ready pathway to 3 by intramolecular radical disproportionation through a favorable six-center process. It may also account for 2 by elimination of acetone. Recent studies on the photodecomposition of phenyl epoxides,[6] however, provide analogy for a second pathway to 2, involving carbene intermediate 8. This species could arise by loss of acetone from 6 and would be expected to collapse to 2 readily.[7] Attempts to demonstrate the presence of carbene 8 by interception with added olefins were unsuccessful. The significance of this result is not certain, however, since the isomerization of 8 to the cumulene could easily be too rapid for olefin trapping to compete.



The orientational preference for the addition of acetone to butatriene 2 in the elimination-addition pathway to 4 is of interest in that it is opposite to the favored mode of ketone photoadditions to allenes.[8] Attack of the n-$\pi^*$ excited carbonyl oxygen at the terminal end of the cumulene system generates biradical intermediate 9 by way of a transition state in which there is substantial delocalization of the incipient radical. Alternate attack at a central carbon would also produce a delocalized biradical intermediate (10), but inspection of atomic orbital representation 11 shows that a 90° rotation about the π bond undergoing attack is necessary to achieve maximum overlap, and accordingly, the transition state for this mode of attack should enjoy less stabilization than that leading to 9.



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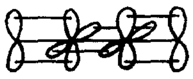

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