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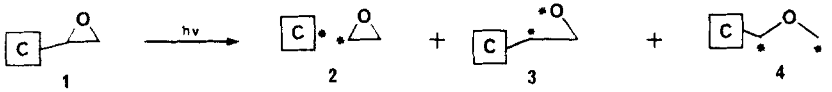
PHOTOCHEMICAL ACTIVATION OF α-β EPOXYKETONES. FORMATION OF BENZANNELATED PERHYDROAZULENES BY INTRAMOLECULAR TRAPPING OF A REACTIVE INTERMEDIATE

Ken S. Feldman[†]
Chemistry Department, Stanford University, Stanford, California 94305

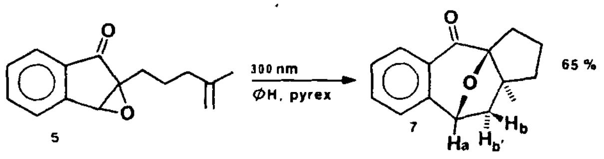
Summary: Linear and angular benzannelated perhydroazulenes can be efficiently prepared by intramolecular cycloaddition of unactivated olefins to reactive intermediates generated by irradiation of α-β epoxyketones.

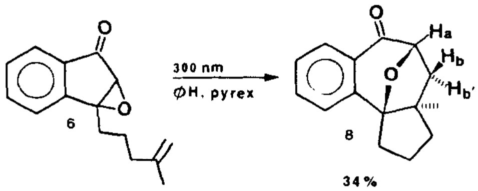
Excitation of chromophores containing adjacent oxiranes 1 are known to produce several types of high energy reactive intermediates corresponding to the different modes of σ-bond cleavage.[1]



The reactive intermediate 4 has been shown to undergo addition reactions with suitably activated olefins or carbonyl compounds to generate tetrahydrofurans or 1,3 dioxolanes.[1] However, the electronic nature of 4 (triplet diradical ** = •,• or carbonyl ylid ** = +, -) remains an unsettled issue.

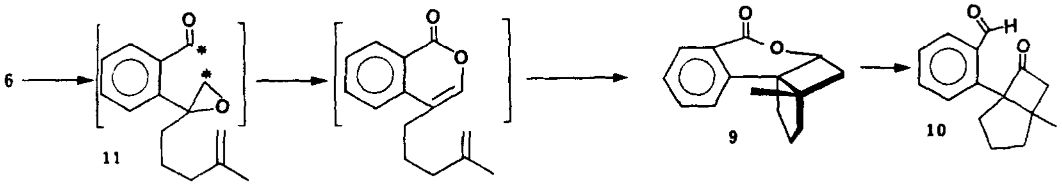
Herein we report that irradiation of aromatic epoxy ketones [3] 5 and 6 produce intermediates (such as 4) than can be efficiently trapped in an intramolecular manner by unactivated olefins. The assignment of gross structure 7 and 8 depend upon comparison of their spectral data with that of carbonyl ylid adducts of known structure.[4] The stereochemical assignment of 7 is based on the observed coupling constants (7, J_{ab} = 7.0 Hz, $J_{ab'}$ = 0 Hz). The stereochemical assignment of 8 is again based on the observed coupling constants (8 , J_{ab} = 8.7 Hz, $J_{ab'}$ = 1.3 Hz) and the position of the angular methyl signal (8, δ 0.65, compare 7, δ 0.84). Examination of molecular models suggests that the methyl group in 8 is positioned almost directly over the aromatic ring and should be shielded relative to that in 7. In addition, when the methyl signal of 8 is irradiated an 11% nuclear Overhauser enhancement of $H_{b'}$ (and also small enhancements of the aromatic protons) is observed.





In addition to 8, irradiation of 6 also produces another compound in equal amounts (35%) which is assigned the structure 9 based on spectral data: (IR:

1717 cm^{-1}; irradiation of the angular methyl induces a nuclear Overhauser enhancement of a cyclobutane proton and an aromatic proton (δ7.15, d, J = 7.88 Hz)).



Further, reduction of 9 (LAH) leads to a diol (ms:m/e 232, NMR ($CDCl_3$,D_2O) δ4.59 (d, J = 11.5 Hz, ArC(H)HOD), 4.39 (d, J = 11.5 Hz, ArCH(H)OD), 4.29 (dd, J = 6.4, 1.2 Hz, C(H)OD)) which can be oxidized under Swern's conditions to yield the ketoaldehyde 10 (IR: 1770 cm^{-1}, cyclobutanone; NMR ($CDCl_3$) δ 10.18 (s, ArCHO)). A similar reduction/oxidation cycle with 8 simply regenerates 8.

The obtention of 8 and 9 suggests a mechanistic rationale in which irradiation of 6 leads to roughly equal partitioning through intermediates of types 2 (cf. 11) and 4. 11 then undergoes rearrangement to an isocoumarin[1f], the direct precursor of 9 in a second photochemical process. Irrespective of the mechanistic course of these reactions, the tetracycles 7 and 8 embody the gross skeletal structures of diterpenes of the dolastane[5] and daphnane[6] classes. These transformations may serve as useful routes to these complex natural products.

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† Address correspondence to: Chemistry Department, 152 Davey Laboratory,
Pennsylvania State University, University Park, PA 16802

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3) 5 was derived from 2-(4-methylpent-4-enyl)indane-1,3-dione, while 6 was prepared from the adduct of 4-methylpent-4-enyl magnesium bromide and 3-methoxy inden-1-one. All new compounds exhibited satisfactory spectral data.

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