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PHOTOCHEMICALLY-INDUCED BOND-SWITCHING REARRANGEMENTS OF CONJUGATED CIS-BICYCLO[5.1.0]OCTENONES[1]

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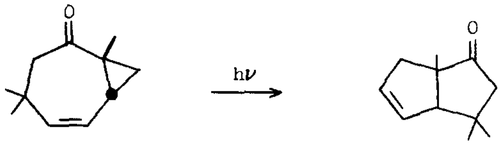
Earlier studies have demonstrated that many conjugated cyclopropyl ketones are converted to α,β-unsaturated ketones when subjected to ultraviolet irradiation.[3] Considerable mechanistic rationale is currently being applied to an understanding of the factors which control the direction of cyclopropyl ring cleavage under these conditions.[4] We have now extended our study of the photochemical behavior of unsaturated medium-sized ring ketones[3,5] to include cis-bicyclo[5.1.0]cyclooctenones 1 and 7 in order to gain added information about the role of stereoelectronic and stereochemical factors in these photorearrangements.

1,4,4-Trimethyl-cis-bicyclo[5.1.0]oct-5-en-2-one (1) was prepared by reaction of dimethyloxosulfonium methylide with eucarvone.[6] When an ether solution of 1 [λ_{max}^{EtOH} 207 (ε 3710) and 272 mμ (ε 266)] was irradiated directly (λ > 250 mμ, Corex filter), starting material (1) was observed to be transformed gradually into a single monomeric photoproduct (8% yield after 5 hr); extensive polymer formation was also noted. Preparative scale gas chromatographic purification gave a colorless isomeric ketone, semicarbazone, mp 202-204°,[7] which was identified as 1,4,4-trimethylbicyclo[3.3.0]oct-6-en-2-one (2) on the basis of its spectral properties, particularly its unequivocal nmr spectrum: ν_{max}^{neat} 1745 and 1680 cm^{-1}; λ_{max}^{EtOH} 286 mμ (ε 40); $\delta_{TMS}^{CDCl_3}$ 1.10 (singlet, 6H, overlapping CH_3 groups at C_4), 1.29 (singlet, 3H, CH_3 group at C_1), 2.12 (AB quartet, J_{AB} = 16 Hz, Δ_{AB} = 19.5 Hz, 2H, $-COCH_2-$), 2.40 (multiplet, 2H, $-CH_2-$ at C_8), 2.72 (multiplet, 1H, allylic proton at C_5), and 5.68 (broadened singlet, 2H, vinyl protons). When the irradiation was repeated using methanol as solvent, the rate of production of 2 was significantly enhanced (20% complete after 1 hr). The photorearrangement was found not to be quenchable with varying concentrations of piperylene (E_T^{trans} = 59 kcal/mole,



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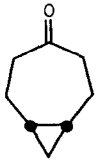
$E_T^{\underline{cis}}$ = 57 kcal/mole) or naphthalene (E_T = 61 kcal/mole) in ether. Neither was the photoreaction subject to sensitization with benzophenone (E_T = 68.5 kcal/mole) or acetone (E_T = 82 kcal/mole) under conditions where the sensitizer absorbed the major portion of the incident radiation.

Bromination in ether at room temperature of ketal 4,[7] obtained in 92% yield from *cis*-bicyclo[5.1.0]octan-4-one (3),[8] gave monobromide 5 which without purification was dehydrohalogenated by means of potassium *t*-butoxide in dry dimethylsulfoxide at room temperature (50% overall yield). The resulting monounsaturated ketal 6[7] was hydrolyzed with 3% sulfuric acid to give 7[7] in 95% yield; bp 55-57° (1.2 mm); $\nu_{max}^{CCl_4}$ 1665 cm^{-1}; $\lambda_{max}^{isooctane}$ 237 (ε 7,700), 322 (ε 50), and 337 sh mμ (ε 40); $\delta_{TMS}^{CCl_4}$ 0.57 (multiplet, 1H, C_8-H), 0.9-3.05 (broad absorption, 7H), 5.83 (doublet, J = 12.5 Hz, 1H, vinyl proton at C_3), and 6.83 (doublet with additional coupling, J = 12.5 Hz, vinyl proton at C_2).

Irradiation of 7 in pentane with a Pyrex filter (λ > 280 mμ) led to the formation of a lone photoproduct (60% yield after 1 hr). Spectral data on a purified (vpc) sample of this material [ν_{max}^{neat} 1740 cm^{-1}; $\lambda_{max}^{isooctane}$ 302.5 mμ (ε 70); $\delta_{TMS}^{CCl_4}$ 1.2-3.45 (broad multiplet, 8H) and 5.58 (symmetrical 14 line multiplet, 2H, vinyl protons)] suggested that it was *cis*-bicyclo[3.3.0]oct-7-en-2-one (8). Final confirmation of structure 8 was achieved by direct comparison of spectra and vpc retention times with those of an authentic sample.[9] In contrast to 1, when the photorearrangement of 7 was conducted in acetone solvent, the yield of 8 (82% after one hr) was greater than that in the direct irradiation; however, sensitization by benzophenone in concentrations sufficient to absorb greater than 90% of the available light was found not to enhance the rate of formation of 8 (33% after one hr). Also, the reaction was not quenched by concentrations of naphthalene and piperylene as high as 1 *M*.



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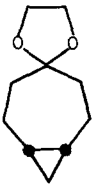

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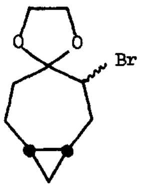

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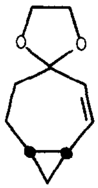

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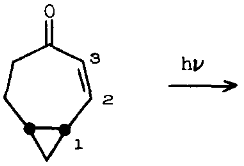

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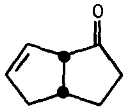

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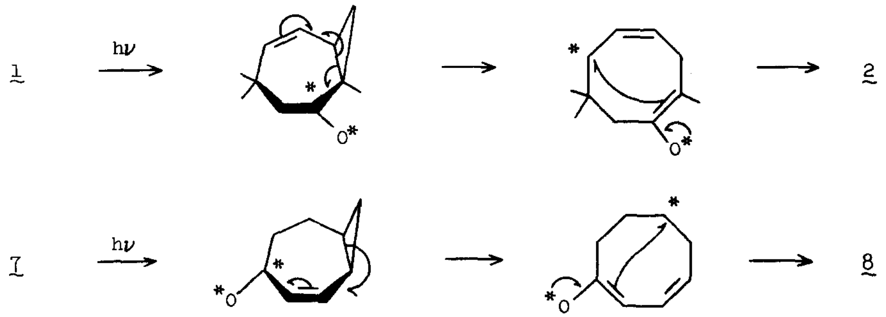
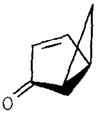
With regard to the multiplicity of these photorearrangements, the inability of piperylene and naphthalene to quench the reactions denotes that under conditions of direct irradiation either n → π* singlet states are primarily involved or rates of intramolecular rearrangement of the corresponding triplet states are faster than diffusion control. Whatever the case, the formation of the same product (8) with the preformed triplet of 7 shows that rearrangement by the respective triplet state is possible in this instance.

Scheme I



Interestingly, exclusive cleavage of the cyclopropyl bond internal to the seven-membered ring obtains in both examples to afford products ultimately derived from rebonding via 5-centered transition states (Scheme I). The proclivity for light-induced rearrangement shared by 1 and 7 is likely founded (1) in the capability of the internal bent bond of the cyclopropyl ring to maintain continuous overlap with both the carbonyl group and the double bond and (2) the possibility of rebonding by way of a relatively strain-free cyclic pathway. The first characteristic appears to be shared by the lower homologous systems 9[10] and 10;[11]



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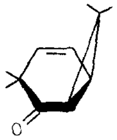

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in contrast, the second property is presently unique within the isomeric cis-bicyclo[5.1.0] octenone series.

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(1) Appreciation is expressed to the Army Research Office (Durham) for partial financial support of this research.

(2) Ohio State University Postdoctoral Fellow, 1967-69.

(3) For a summary of leading references, see L. A. Paquette, R. F. Eizember, and O. Cox, J. Am. Chem. Soc., 90, 5153 (1968).

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