Photolysis of 2-Cyclopropylcyclohexanone: a Three-carbon Photochemical Ring Expansion

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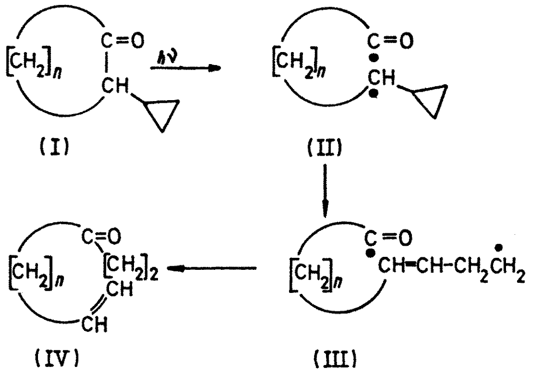
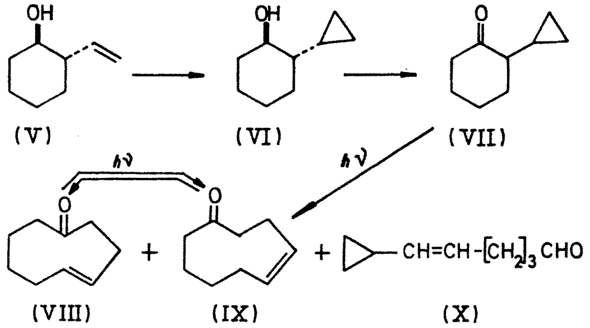
Summary Irradiation of 2-cyclopropylcyclohexanone gives a mixture of *cis*- and *trans*-cyclonon-4-enone as the major photochemical products.

FEW methods are available for the ring expansion of carbocyclic systems by three atoms.[1] Our interest in ring expansion reactions[2] and the application of photochemical methods to ring expansion reactions[3] prompted us to examine the photochemical behaviour of 2-cyclopropylcyclohexanone (VII). The ready type I cleavage of 1-cyclopropylpropan-2-one[4] to produce the cyclopropylcarbinyl radical and the ready isomerization of such radicals to the corresponding homoallyl radicals[5] suggested that the photolysis of 2-cyclopropylcycloalkanones (I) might lead to carbocyclic systems containing three additional carbon atoms by the sequence (I) → (IV). We report an initial study which demonstrates the feasibility of this novel method of ring expansion.





trans-2-Vinylcyclohexanol (V)[6] was converted into *trans*-2-cyclopropylcyclohexanol (VI)† by a Simmons–Smith reaction. Oxidation of (VI) with Jones' reagent gave 2-cyclopropylcyclohexanone (VII): u.v. (iso-octane) 294 nm. (ϵ 25). Photolysis‡ of (VII) in benzene or hexane through Vycor with 3000 Å lamps led to the formation of three new products which were readily separated by chromatography on silica gel impregnated with silver nitrate. The products were identified as *trans*-cyclonon-4-enone (VIII), 44% (i.r. 1701, 1640, and 975 cm.$^{-1}$), *cis*-cyclonon-4-enone (IX) 29%, (i.r. 1701, 1650, 758, 743, and 718 cm.$^{-1}$), and 1-cyclopropylhex-1-en-6-al (X), 21%. Other spectroscopic data are consistent with the assigned structures, and catalytic hydrogenation of (VIII) and (IX) gave cyclononanone in quantitative yield.

The photochemical rearrangement also occurs readily when Pyrex optics are used and preliminary sensitization and quenching studies indicate that the reaction is not sensitized by acetone nor quenched by di-t-butylnitroxide, results which are consistent with rearrangement by way of a singlet excited state. The two ring-expanded unsaturated ketones (VIII) and (IX) are readily interconverted by photolysis but at low conversions there is a preference for the formation of (VIII). A similar preference for the formation *trans*-allylcarbinyl radicals from the corresponding cyclopropylcarbinyl systems was recently noted in a low temperature e.s.r. study of this type of isomerization.[5] It should be noted that the cyclic $\beta\gamma$-cyclopropylketones *cis*- and *trans*-caran-4-ones have very recently been shown to undergo ring contraction *via* the cyclopropylcarbinyl–allylcarbinyl radical isomerization.[7]

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† All new compounds gave satisfactory analytical results and had the expected spectral properties.

‡ Irradiations were conducted under nitrogen in a vessel mounted in the centre of a Rayonet Photochemical Reactor equipped with RPR-3000 Å lamps.

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