The Photochemistry of Two Rigid β,γ-Cyclopropyl Ketones, *exo*- and *endo*-Tricyclo[3,2,1,$0^{2,4}$]octan-6-one

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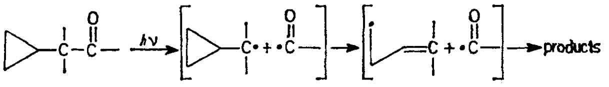
Summary Photochemical rearrangement of ketones (**3**) and (**9**) to bicyclo-octenones (**5**) and (**11**), respectively, can be explained by α-cleavage to (**12**) and (**13**), followed by stereoelectronically controlled opening to (**14**) and (**15**), and then collapse to products.

ONE of the principal paths in the photochemistry of β,γ-cyclopropyl ketones can be simply explained as an α-cleavage, rearrangement of the initially formed cyclopropylcarbinyl radical to homoallyl, and then product formation through disproportionation or coupling of the resulting radical pair or biradical, (equation 1).[1,2] If these transformations involve a discrete cyclopropylcarbinyl radical, its rearrangement should be under stereoelectronic control, with preferential cleavage of the β,γ-cyclopropane bond which can overlap the orbital on C(α) containing the odd electron.[3,4] However, previous studies[1,2] have involved only β,γ-cyclopropyl ketones that would lead to cyclopropylcarbinyl radicals in which rotation about the original C(α)–C(β) bond is unconstrained, and thus the question of stereoelectronic control in the ring opening cannot be answered. It has also been reported[1] that gas phase photolysis of 1-cyclopropyl propan-2-one (**1**) leads to



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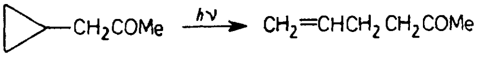
hex-5-en-2-one (**2**) by a pathway that does not include α-cleavage, so that opening of the cyclopropane does not involve cyclopropylcarbinyl radicals.



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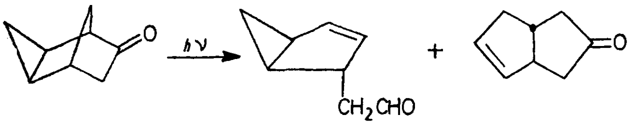

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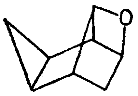

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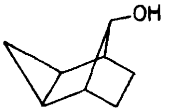

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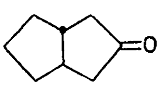

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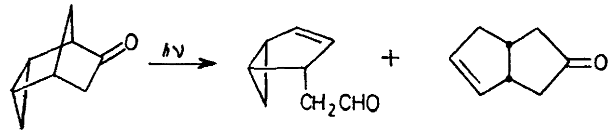
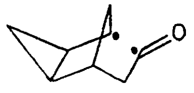


(9) (10) (11)

We have now investigated the rearrangement for stereoelectronic control by studying the photolysis of *exo*- and *endo*-tricyclo[3,2,1,0^{2,4}]octan-6-one, (**3**) and (**9**), two β,γ-cyclopropyl ketones which lead to rigid cyclopropylcarbinyl radicals on α-cleavage.

Irradiation of (**3**)[5] in benzene solution (*ca.* 0·025 M, $\lambda > 2800$ Å) gave the aldehyde (**4**), 54%, and *trans*-bicyclo[3,3,0]oct-6-en-3-one (**5**), 29%. Prolonged photolysis of (**3**), as well as direct irradiation of purified (**4**), gave the oxetan (**6**) by an intramolecular Paternò–Büchi reaction.[6] Similarly, rearrangement of the *endo* tricyclic ketone (**9**)[5] under the same conditions gave the aldehyde (**10**), 58%, and *cis*-bicyclo[3,3,0]oct-6-en-3-one (**11**), 17%. In this case no oxetan was observed, even on direct irradiation of (**10**). We attribute this difference between (**10**) and (**4**) to steric interference by the three-membered ring of (**10**), which disfavours the rotational conformation of the side chain necessary for [2 + 2] cycloaddition of olefin to carbonyl. Structures of these photoproducts are supported by i.r., 220 MHz n.m.r., and high resolution mass spectra, as well as by the following observations. Hydrogenation of (**5**) gave the saturated bicyclic ketone (**8**), which was also available in small amounts on irradiation of (**3**) in pentane as solvent. Ketones (**8**)[7] and (**11**)[8] were found to be identical with authentic samples by spectral methods and g.l.c. The oxetan (**6**) was reduced by lithium aluminium hydride to the alcohol (**7**), m.p. 74—76° (lit.[9] m.p. 75—76°), derived *p*-bromobenzenesulphonate m.p. 82—83·5° (lit.[9] m.p. 83—83·5). Careful g.l.c. examination of the reaction mixtures revealed no other significant products from these irradiations.

Formation of (**5**) and (**11**) as the only volatile products involving opening of the cyclopropane ring suggests selective cleavage of the less substituted, external cyclopropane bond. This is the stereoelectronically controlled cleavage expected[4] in cyclopropylcarbinyl radicals (**12**) and (**13**), and the results thus strongly suggest that these transformations proceed stepwise through initial α-cleavage to (**12**) and (**13**), rearrangement to homoallyl radicals (**14**) and (**15**), and finally collapse to (**5**) and (**11**). The successful coupling of biradical (**14**) to form the highly strained *trans*-bicyclooctenone (**5**) is particularly noteworthy. Hydrogen transfer in (**12**) and (**13**) to give the aldehydes (**4**) and (**10**), and formation of the oxetan (**6**) from (**4**), are reactions analogous to those of norcamphor and its photochemically derived unsaturated aldehyde.[10]



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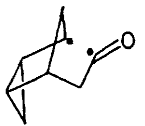

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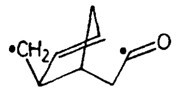

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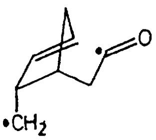

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All products are photolabile under the irradiation conditions, and the yields reported were determined by calibrated g.l.c. measurements on photolyses to low conversion.

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