Structural Requirements for the Photochemical Ring Expansion of Cyclic Ketones to Cyclic Acetals

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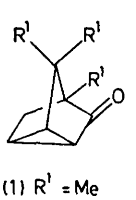
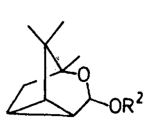
Summary Evidence is presented that photochemical ring expansion of bicyclo[2,2,1]heptan-2-ones to cyclic acetals occurs when structural features inhibit enal formation and/or facilitate oxacarbene formation from the biradical formed by α-cleavage.

Following the discovery of the photochemical ring expansion of cyclocamphanone (**1**) in alcoholic solution to acetals of type (**2**) and the proposal that this proceeds *via* the biradical (**3**) and the cyclic oxacarbene (**4**),[1,2] many analogous reactions have been observed.[2,3] Most of these have involved cyclobutanones, and it has been postulated[4] that the latter differ from other cycloalkanones in undergoing concerted ring expansion to oxacarbenes. Reports of the formation of ring-expanded cyclic acetals from carbocyclic ketones other than cyclobutanones are limited to the tricyclic ketones (**1**) and (**5**),[1] the cyclopentanones (**6**)[5] and (**7**),[6] and certain bicyclo[2,2,1]heptan-2-ones, *e.g.*, camphor (**8**),[7] camphenilone (**9**), and fenchone (**10**),[8] but not others, *e.g.*, 2-norbornanone (**11**).[2,8,9] Turro and Morton[5b] have concluded that in the case of (**6**) the cyclopropane ring facilitates ring expansion by stabilization of the corresponding oxacarbene. However, no such factor is discernible in the cases of (**8**)—(**10**), and it has been proposed[8] that here oxacarbene formation, which is normally an unfavourable process, occurs as a minor pathway, because competing processes, in particular enal formation, are unfavourable. It follows that a bicyclo[2,2,1]heptan-2-one in which enal formation is completely inhibited should give oxacarbene-derived compounds as the major products. We have tested this prediction in the case of 6-*endo*-methoxycarbonylcamphor (**12**).†



(1) R¹ = Me
(5) R¹ = H



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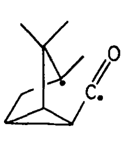
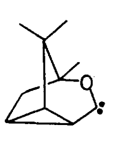
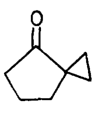


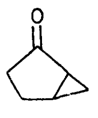
(3)



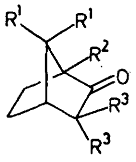
(4)



(6)

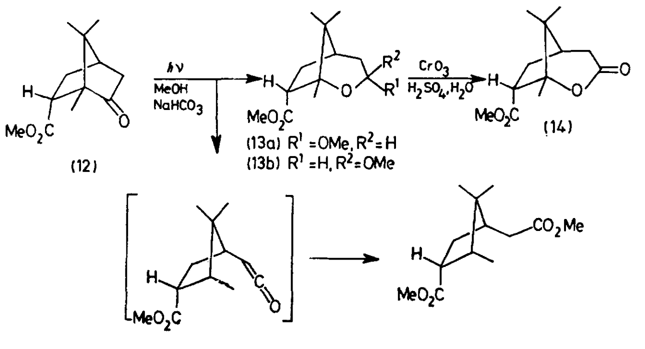


(7)



(8) R¹ = R² = Me, R³ = H
(9) R¹ = R² = H, R³ = Me
(10) R¹ = H, R² = R³ = Me
(11) R¹ = R² = R³ = H

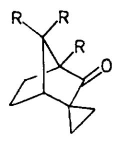
Irradiation of a 6% solution of (**12**) in MeOH in a quartz tube in the presence of $NaHCO_3$[10] with a 450 W Hanovia medium-pressure Hg lamp for 22 h gave, as the major products, the epimeric acetals (**13a**) and (**13b**). These structural assignments were corroborated by the oxidation of a mixture of (**13a**) and (**13b**) to the lactone (**14**). The acetals (**13**) were accompanied by the diester (**15**); the ratio of (**13**):(**15**), as estimated by ^{1}H n.m.r. spectroscopy, was 94:6. Thus, the formation of oxacarbene-derived products becomes the major pathway for (**12**). The minor product (**15**) must be derived from the ketene (**16**). While the formation of such ketene-derived products is common for cyclopentanones and cyclohexanones,[11] it is normally insignificant in the case of bicyclo[2,2,1]heptan-2-ones.[8,12] The formation of (**15**), like that of (**13**), can be attributed to suppression of the normally predominant enal formation.



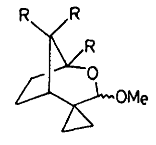
(12) (13a) R¹ = OMe, R² = H
(13b) R¹ = H, R² = OMe
(14) (16) (15)

If (**13**) is formed as the major product from (**12**) because structural features prohibit enal formation, the quantum yield should be low compared with that for enal formation in related systems. This we have shown to be the case. The quantum yield for the formation of (**13**) in MeOH is 0·03 at 313 nm, significantly lower than the quantum yields for the formation of enal from cyclopentanone [0·23 (MeOH), 0·11 (C_6H_6)],[5b,13] (**8**) [0·12 (C_6H_6), 0·12 n-C_7H_{16})],[7,13] (**11**) [0·28 (C_6H_6)],[13] and (**6**) [0·12 (MeOH)].[5b]

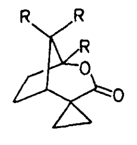
The formation of oxacarbene-derived products from (**1**) and (**5**) can now be attributed to a combination of two factors (a) inhibition of enal formation and (b) facilitation of oxacarbene formation. This is in accord with the photochemistry of the ketones (**17**) and (**18**). Irradiation of (**17**) in MeOH in the presence of $NaHCO_3$ gave a mixture of the acetals (**19**), together with a small amount of other products; this was oxidized to the lactone (**20**). Irradiation of (**18**) at −78 °C gave, as the major product, the enal (**21**), together with the acetal (**22**) (*ca.* 20%). The mixture was oxidized to compounds including the lactone (**23**), also obtained by the oxidation of (**18**) with peracetic acid.



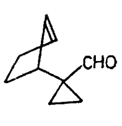
(17) R = Me
(18) R = H



(19) R = Me
(22) R = H



(20) R = Me
(23) R = H



(21)

These results may be compared with the previous observations that camphor (**8**) gives mainly an enal together with a small amount of oxacarbene-derived products,[7] and that 2-norbornanone (**11**) gives only an enal.[2,8,9] Thus the cyclopropyl ring adjacent to the carbonyl group facilitates the formation of oxacarbene-derived products as in the cases of (**6**) and (**7**). The structural requirements for such reactions can therefore be interpreted in terms of such facilitation and the inhibition of competing reactions.

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† New compounds were characterized by elemental analysis and i.r., ^{1}H n.m.r., and mass spectroscopy.

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