Unusual Photochemical Loss of a Methylene Group

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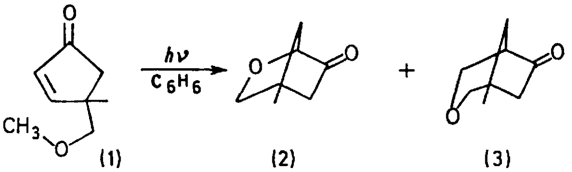
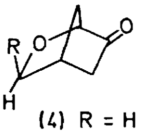
Summary Photolysis of the cyclopentenone (**1**) leads to loss of the methoxy methylene group and formation of the bicyclic ketone (**2**).

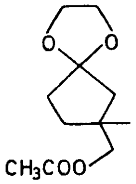
We describe here the transformation of cyclopentenone (**1**) upon irradiation ($\lambda > 3400$ Å) in benzene solution into the bicyclic ketone (**2**), a reaction unusual in that it requires loss of a methylene group.



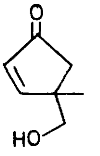
(1) (2) (3)



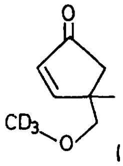
(4) R = H
(5) R = Me



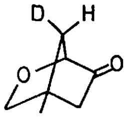
(6)



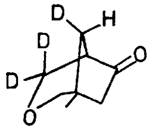
(7)



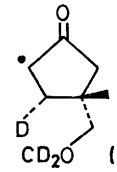
(1D)



(2D)



(3D)



(8)

Previously we reported[1] the photochemical isomerization of (**1**) to (**3**) and noted the concomitant formation of a second product. The yields of these products are variable and temperature dependent, with the second compound disfavoured at higher temperature. At 20° the yield of each photoproduct from (**1**) is about 20%. N.m.r. data, together with a carbonyl absorption at 1768 cm^{-1} in the i.r., support structure (**2**). The signal for each proton is assignable at 220 MHz, and the spectrum is also in good general agreement with data[2] recorded earlier for the closely related compounds (**4**) and (**5**). Furthermore, we have independently prepared (**2**)† from (**6**) and shown this material to be identical with the photoproduct.

In exploring the photolytic conversion of (**1**) into (**2**) we have made these observations. (i) Neither (**3**) nor (**7**)† is an intermediate in the reaction. Irradiation of each of these ketones under the conditions used for (**1**) gave no trace of (**2**). Photolysis of (**3**) at shorter wavelengths ($\lambda > 2800$ Å) is already known[1] to give products other than (**2**). (ii) The apparent loss of the methoxymethylene group was confirmed by photolysis of the deuteriated analogue (**1D**) to form (**2D**) and (**3D**). The n.m.r. spectra of these products require the labelling patterns shown. The distribution of deuterium in (**3D**) is consistent with the intermediacy of the previously implicated[1] biradical (**8**) (or the analogous protium species), while the stereospecific labelling in (**2D**) indicates that a similar hydrogen transfer occurs in the novel

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† This new compound gave satisfactory elemental analysis for carbon and hydrogen and showed i.r. and n.m.r. spectra compatible with the assigned structure, after purification by preparative g.l.c.

demethylation reaction. (iii) Formation of both (**2**) and (**3**) is quenched by low concentrations of 2,3-dimethylbuta-1,3-diene (E_T *ca.* 60 kcal/mol[4]). Stern–Volmer plots of the data (0·0—0·04 M-quencher) are linear and show that the two processes are quenched at different rates, implying that each product is associated with a kinetically distinguishable quenchable species. From the slopes (which equal $k_q\tau$) of the curves, and with the usual assumption[5] that $k_q = 5 \times 10^9$ l/mol s in benzene at 25°, we calculate $\tau(\mathbf{2}) = 2$ ns and $\tau(\mathbf{3}) = 16$ ns as the apparent lifetimes of these two species. (iv) Formation of both (**2**) and (**3**) may be sensitized by propiophenone (E_T *ca.* 72 kcal/mol in benzene at 25°[6]), and under these conditions the relative efficiency of formation of (**2**) is lower than in direct irradiation.

Controls established the stability of (**2**) and (**3**) under the conditions of these experiments. More quantitative data are needed before the two intermediate species identified kinetically can be defined more precisely. Further insight may also come from recognition of the ultimate fate of the expelled methylene fragment as well as from discovery of additional examples of the reaction. At present the only possibly related transformation of which we are aware is the photolysis of two *o*-methoxybenzophenones to give 3% of the related *o*-hydroxy-compounds.[7]

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