Photochemical Formation of 5-Oxabicyclo[2,1,1]hexan-2-ones from Unsaturated 1,2-Diketones

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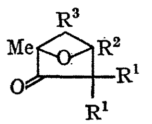
Summary 5-Oxabicyclo[2,1,1]hexan-2-ones are formed on photolysis of both $\beta\gamma$- and $\gamma\delta$-unsaturated acyclic 1,2-diketones, the formation from the latter involving an initial migration of the double bond *via* a cyclobutanol intermediate.

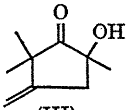
WHEN 4,4,5-trimethylhex-5-ene-2,3-dione (the *gem*-dimethyl group was chosen to prevent the double bond moving into conjugation during preparation) is irradiated in pentane solution under N_2 with light ($\lambda > 380$ nm.), it is quantitatively converted into a single isomeric compound to which we assign the 1,3,3,4-tetramethyl-5-oxabicyclo[2,1,1]-hexan-2-one structure (Ia). The compound showed strong absorptions at 1770 and 1790 cm.$^{-1}$ (the double absorption being attributable to Fermi resonance of 890 cm.$^{-1}$ overtone with the C=O band) and the ^{1}H n.m.r. spectrum showed four sharp singlets τ 8·65—8·95 (each 3H) and an AB quartet τ 7·50 and 7·74 (J_{AB} 8 c./sec. (2H). On g.l.c. below 90° it gave a single symmetrical peak but at higher temperatures decomposition occurred to a mixture of the starting diketone and the four compounds (II—V). The latter three products were also obtained by treatment of (Ia) with a trace of toluene-*p*-sulphonic acid in ether. From the reported behaviour of the related monoketones 5-methylhex-5-en-2-one[1] and 4-methylpent-4-en-2-one,[2] the formation of products (VI) and (VII) might be expected but no trace of either was detected.



(I)a; R^1=R^2=Me, R^3=H
b; R^1=R^2=H, R^3=Me
c; R^1=R^3=Me, R^2=H

CH_2:CMe CO·CMe$_2$·COMe

(II)



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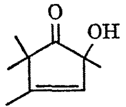

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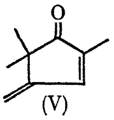

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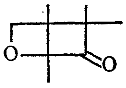
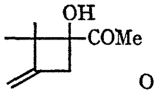
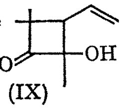


(VI)



(VII)



(IX)

CH_2:CHCH$_2$CR$_2$COCOMe

(VIII)a; R=H
b; R=Me

MeCH:CHCMe$_2$COCOMe

(X)

Unexpectedly, similar products (Ib,c) were formed in substantial quantities from irradiation of the hept-6-ene-2,3-diones (VIIIa,b) at room temperature. In the latter case we have established that the sole primary photoproduct is a mixture of isomers of the 2-hydroxycyclobutanone (IX) the *cis*-isomer of which undergoes a rapid thermal rearrangement at room temperature (the *trans* more slowly) to the hept-5-ene-2,3-dione (X) (with incorporation of one deuterium atom at C-7 in the presence of D_2O) which undergoes a further photocyclisation.

The starting diketones were prepared by standard methods. All new compounds gave satisfactory elemental analysis (IX not isolated) and spectra in accord with their postulated structures.

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[1] N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Letters*, 1965, 1525.

[2] N. C. Yang, D.-M. Thap, E. F. Kiefer, and D. A. Carlson, *Tetrahedron Letters*, 1966, 3671; 1967, 1617.