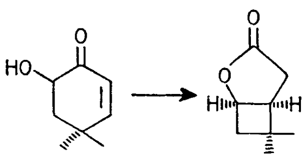
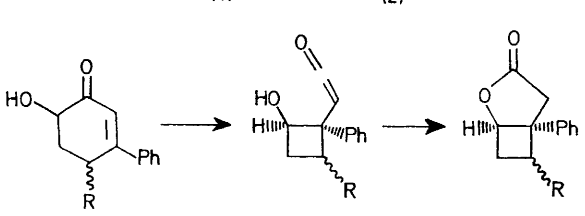
First Examples of α-Cleavage during Photolysis of Cyclohexenones: Photochemical Rearrangement of 6-Hydroxycyclohexenones

By Mark Jeffares and T. Brian H. McMurry*
(*Chemistry Department, Trinity College, Dublin 2, Ireland*)

Summary We report the first examples of products derived *via* α-cleavage on photolysis of cyclohexenones; 6-hydroxycyclohexenones afford 2-hydroxycyclobutane-acetic acid lactones (2-oxabicyclo[3.2.0]heptan-3-ones) *via* a singlet excited state.



(1) (2)



(3) (5) (4)

a, R = H
b, R = β-Me
c, R = α-Me

While photolysis of cyclopentenones frequently affords products which are derived from α-cleavage of the cyclopentenone ring,[1,2] no example has been reported to date of a similar pathway for cyclohexenones.[3] In particular, photolysis of 6-n-propylcyclohexenone[4] and 6,6-dimethylcyclohexenone,[5] systems that were examined for this route and which might be expected to favour α-cleavage, gave no identifiable products derived from α-cleavage. This behaviour is believed to result from the geometry of the excited state which affords a rapid radiationless return to the ground state.[3,6] We report that photolysis of 6-hydroxycyclohexenones affords products which are derived from an α-cleavage mechanism.

Photolysis (through quartz) of 6-hydroxy-4,4-dimethylcyclohexenone[7] (**1**) affords the cyclobutane lactone (**2**) in 7·8% yield. (All yields based on recovered starting material). The product was characterised by its i.r. and n.m.r. spectra. The reaction proceeds *via* the singlet excited state, as the lactone is not formed in the presence of the sensitiser, acetophenone, but is formed in the presence of the quencher, ferrocene.[8]

Similar photolysis (Pyrex) of 6-hydroxy-3-phenylcyclohexenone (**3a**) affords traces of the lactone (**4a**). (**4a**) was isolated in 15% yield from prolonged photolysis in the presence of ferrocene. In the presence of CH_3OD, deuterium is incorporated into the 4α-position.

Photolysis (Pyrex) of a mixture of the *cis*- and *trans*-4-methylcyclohexenones (**3b**) and (**3c**) affords only one lactone (**4c**) in low yield. We were unable to separate the isomeric ketones completely, but fractions rich in (**3c**) in the presence of ferrocene afforded (**4c**) in 33% yield. In all cases the unchanged starting material is enriched in (**3b**). This shows that the isomer (**3b**) which in the ground state has an 'equatorial' hydroxy-group is less reactive than the isomer (**3c**) which can adopt a conformation with an 'axial' hydroxy-group.†

The assignment of stereochemistry to (**4c**) with the methyl and phenyl groups *cis* follows from europium shift measurements and also from the absence of long range coupling of the 1α-proton with the 6-proton. Such a coupling is found in the lactone (**4a**) where a favourable W-conformation of the 1α- and 6-hydrogen atoms obtains. This stereochemistry implies that the reaction proceeds in the same manner and with the same stereochemical control as suggested in the hydroxycyclopentenone case.[2] A hydroxy-keten (**5**) is a probable intermediate.

Our success can probably be attributed to two factors. In the first place, the hydroxy-group stabilises the diradical formed during α-cleavage, and secondly the 6-hydroxy-group (axial or equatorial) would be expected to hydrogen bond to the carbonyl group thereby imparting some rigidity to the excited state.

α-Cleavage products were not found in all the 6-hydroxycyclohexenones studied. For example, we were unable to detect products from α-cleavage with 6-hydroxy-3,5-dimethylcyclohexenone or 6-hydroxy-3,5,5-trimethylcyclohexenone.[9] The 6-hydroxycyclohexenones were prepared by hydrolysis of the corresponding acetoxy compounds,[9] themselves prepared by oxidation [$Pb(OAc)_4$] of the corresponding cyclohexenones.[10]

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† N. m. r. measurements show that the predominant (ground state) conformations of both (**3b**) and (**3c**) possess 'equatorial' hydroxy-groups. The 4-methyl group is 'equatorial' in (**3b**) and 'axial' in (**3c**). However there should be some contribution from a second conformation of (**3c**) in which the hydroxy-group is 'axial' and the methyl 'equatorial.'

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