Photochemistry of βγ-Epoxy Ketones: Photoisomerization of 2,2,4,4-Tetramethyl-7-oxabicyclo[4,1,0]heptan-3-one

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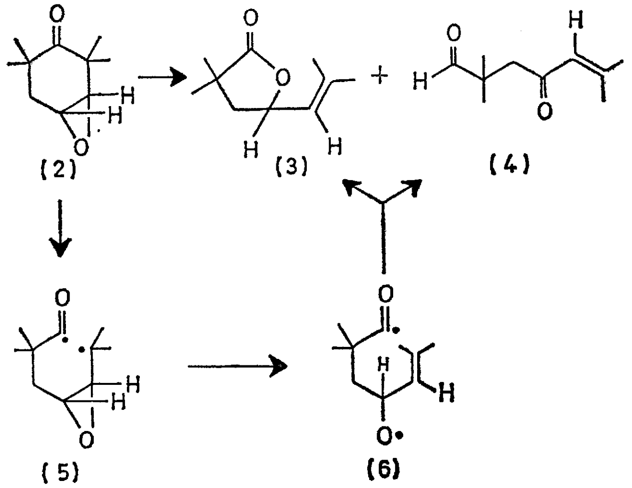
Summary Irradiation of 2,2,4,4-tetramethyl-7-oxabicyclo-[4,1,0]heptan-3-one does not lead to photodecarbonylation, but rather photoisomerization occurs to give 2,2-dimethyl-4-(2-methylpropenyl)butanolide and 2,2,6-trimethyl-4-oxohept-5-enal.

Two reports have recently appeared concerning the photochemistry of compounds which contain the 7-oxabicyclo-[4,1,0]heptan-3-one skeletal framework.[1,2] Although in both studies photodecarbonylation occurs to give unsaturated epoxides, product formation in the one case involves a formal 1,4-hydrogen shift in the intermediate biradical,[1] whereas in the other case a formal 1,6-hydrogen shift occurs.[2] Since the substituents in these compounds permit only one of the two alternative photodecarbonylation routes to be operative in each case, we have examined the photochemistry of a 7-oxabicyclo[4,1,0]heptan-3-one, the βγ-epoxy ketone (**2**), in which both routes could be competitive. However, in striking contrast to earlier reports,[1,2] irradiation of (**2**) leads to photoisomerization and not photodecarbonylation.

2,2,4,4-Tetramethyl-7-oxabicyclo[4,1,0]heptan-3-one (**2**)† [ν_{max} (CCl_4) 1710 cm^{-1}; δ ($CDCl_3$) 1·11 (3H, s), 1·16 (6H, s), 1·29 (3H, s), 2·22 (2H, d, *J* 2 Hz), 3·06 (1H, d, *J* 4 Hz), 3·38 (1H, dt, *J* 4 and 2 Hz)] was prepared by epoxidation of 2,2,6,6-tetramethylcyclohex-3-enone (**1**) with *m*-chloroperbenzoic acid. The enone (**1**) was obtained in *ca.* 20% yield by treatment of 2-methylcyclohex-2-enone[3] with a ten-fold excess of methyl iodide and sodium t-pentoxide in anhydrous ether under reflux.[4]‡



Scheme.

Irradiation of an ether solution of the βγ-epoxy ketone (**2**) [λ_{max} (C_6H_{12}) 284 nm, ε 17] through a Corex filter with a Hanovia L 450-W lamp to 95% conversion provided 2,2-dimethyl-4-(2-methylpropenyl)butanolide (**3**) [ν_{max} (CCl_4) 1770 cm^{-1}; δ (C_6D_6) 0·94 (3H, s), 1·07 (3H, s), 1·44 (3H,d, *J* 1 Hz), 1·53 (3H, d, *J* 1 Hz), 4·68—5·09 (1H, m); *m/e* 168 (*P*), 124 (*P* — 44)[5]] in *ca.* 50% yield and 2,2,6-trimethyl-4-oxohept-5-enal (**4**) [ν_{max} (CCl_4) 1730, 1690, and 1620 cm^{-1}; δ ($CDCl_3$) 1·11 (6H, s), 1·89 (3H, d, *J* 1 Hz), 2·14 (3H, d, *J* 1 Hz), 2·72 (2H, s), 6·04 (1H, m), 9·58 (1H, s)] in *ca.* 20% yield.§ The epoxy ketone (**2**) was photochemically inert when irradiated in acetone solution through a Pyrex filter.

The photoproducts are readily accounted for by initial Norrish Type I bond cleavage of (**2**) to give the diradical (**5**) (Scheme), which undergoes subsequent ring-opening to provide the diradical (**6**). Ring closure of (**6**) affords (**3**), and a 1,4-hydrogen shift in (**6**) gives (**4**).

The photo-products resulting from irradiation of (**2**) are analogous to those obtained in the photoisomerizations of 2-(oxiranyl)cycloalkanones.[6] Indeed, these results suggest that such photoisomerizations are the characteristic reactions of 7-oxabicyclo[4,1,0]heptan-3-ones and that photodecarbonylation only becomes a major process in such systems when specific skeletal constraints prevent similar photoisomerizations from occurring.

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† Satisfactory elemental analyses and spectral data consistent with the structural assignments have been obtained for all new compounds.

‡ 2,6,6-Trimethylcyclohex-2-enone was also isolated from the reaction mixture in *ca.* 5% yield.

§ The aldehyde (**4**) proved to be photolabile and continued irradiation led to its disappearance.

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[4] For other examples of the synthesis of 2,2,6,6-tetrasubstituted cyclohex-3-enones by the exhaustive alkylation of 2-substituted cyclohex-2-enones see: J. M. Conia and A. Le Craz, *Bull. Soc. chim. France*, 1960, 1934; J. D. McChesney and A. F. Wycpalek, *Chem. Comm.*, 1971, 542.

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