Contrasting Photochemistry of Cyclopentenone and Cyclohexenone†

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Summary Room-temperature irradiation of 4,4-diphenyl- and 4-methyl-4-phenyl-cyclopentenone led very efficiently to keten rearrangement products [*e.g.* (**4**)] rather than bicyclic ketones [*e.g.* (**6**)] characteristic of cyclohexenone photochemistry; at low temperatures the bicyclic ketone primary product underwent further photochemical reaction to give the keten, but the bicyclic ketone was not an intermediate at room temperature.

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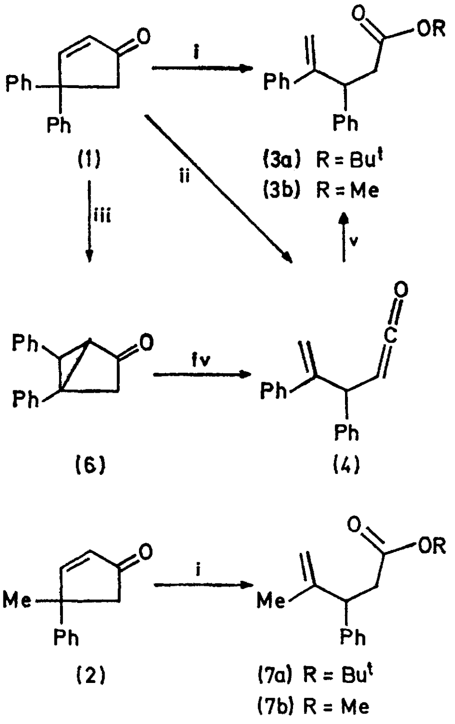
† For previous paper in series: 'Photochemistry', see: H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, 1972, **94**, 3647.

In view of the intriguing photochemistry of cyclohexenones in our previous investigations,[1] we have examined the behaviour of the related cyclopentenones (**1**) and (**2**).‡ The former was synthesized by reduction ($NaBH_4$) of the known[2] 5,5-diphenylcyclopent-2-enone to the saturated alcohol, followed by xanthate elimination and subsequent allylic oxidation with Collins' reagent.[3] The methylphenylenone (**2**) was obtained by reaction of lithium dimethylcuprate with 3-phenylcyclopent-2-enone followed by oxidation with dichlorodicyanobenzoquinone.

Photolysis of (**1**) in t-butyl alcohol[4] was different from that of the corresponding cyclohexenone,[1] giving the olefinic ester (**3a**) rather than bicyclic ketone (Scheme 1). Structure (**3a**) was proved by an independent synthesis from 3,4-diphenyl-4-oxobutanoic acid[5] by Wittig reaction of the methyl ester and conversion of the product into the t-butyl derivative, which was identical spectrally with photoproduct (**3a**).

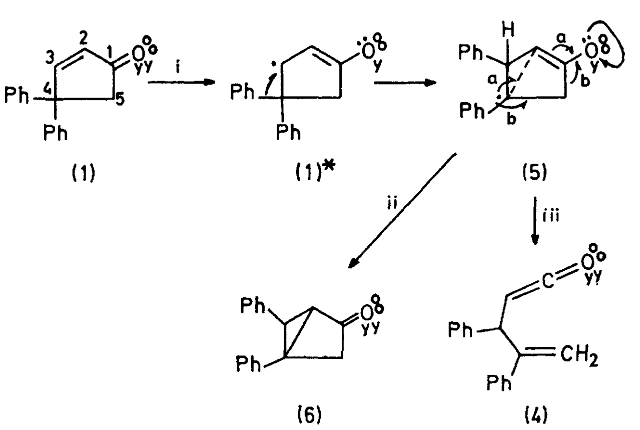


SCHEME 1. Reagents: *i*, hν, Bu^{t}OH, *room temp.*; *ii*, hν, C_6H_6, *room temp.*; *iii*, hν, −140°, 366 *nm*; *iv*, hν, −140°, 315 *nm*; *v*, *MeOH*.

Photolysis in anhydrous benzene caused appearance of an i.r. band at 4·74 μm, characteristic of ketens. Treatment of the solution with methanol gave the methyl ester (**3b**). Thus, in absence of nucleophiles, the photochemical reaction can be formulated (Scheme 2) as involving the same initial phenyl migration as suggested for the photochemistry of 4,4-diarylcyclohexenones.[1] However, the resulting biradical (**5**) undergoes fission of the 1–5 bond to give the observed keten (**4**).

Photochemistry of (**2**) followed the same course and afforded the t-butyl ester (**7a**) in t-butyl alcohol.

The process was remarkably efficient, with a quantum yield ϕ 0·31 for (**1**) and 0·56 for (**2**) in direct irradiations. Photosensitization of (**1**) in t-butyl alcohol with acetophenone (E_T 74 kcal mol^{-1}) gave ϕ 0·30. The equivalence of direct and sensitized quantum yields is evidence for a triplet excited state, in analogy to the cyclohexenone photochemistry.[1]



SCHEME 2. *i*, hν; *ii*, *path a*, −140°; *iii*, *path b*, *room temp.*

The formation of the unsaturated keten (**4**) and the failure of 2,4-bridging parallel to that of cyclohexenone photochemistry was surprising in view of the work of Plank and Floyd[6] and Matsuura and Ogura[7] where pivaloyl migration from C-4 to C-3 gave a bicyclo[2,1,0]pentan-2-one in molecules containing several t-butyl groups.

The possible formation of such strained bicyclic products was examined by low-temperature studies. Photolyses were carried out at −140° with 366 nm light and monitored by i.r. spectroscopy. Diphenylenone (**1**) absorbs at 366 nm but the potential product (**6**) should not.[7] As the CO absorption of (**1**) disappeared the 5·68 μm (*cf.* 5·67 μm reported by Matsuura and Ogura[7]) band due to intermediate (**6**) developed. When essentially all absorption due to diphenylenone (**1**) had disappeared, irradiation was begun at 315 nm where bicyclic ketone (**6**) should absorb. This led to appearance of the keten absorption due to (**4**).

Thus at low temperature closure of bond 2–4 seems to occur to the exclusion of fission of bond 1–5, but this appears not to be the mechanism at room temperature. *A priori*, bicyclic ketone (**6**) could be absent in the room temperature photolysis owing to a high efficiency of disappearance to give keten product compared with the rate of formation of (**6**). However, the overall quantum yields (0·56 and 0·31) for the two rearrangements do not allow a two-step set of photochemical processes with the second step much more efficient than the first. Present evidence does not rigorously preclude the second step being thermal and fast in room temperature photolysis but it does reveal that it may occur photochemically at low temperature (see Scheme 1).

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‡ All compounds gave satisfactory elemental analyses.

Recently the room temperature rearrangement of (**2**) to keten (**7b**) has been observed independently.[8] Our mechanistic studies will be reported in full later.

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