Photochemical Rearrangement of 4-Methyl-4-arylcyclopentenones

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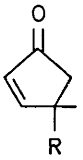
Summary Upon photolysis cyclopentenones (**1a**) and (**1b**) are rapidly converted into the isomeric ketens (**4a**) and (**4b**) respectively.

We describe here the preparation and photolysis of 4-methyl-4-phenylcyclopentenone (**1a**) and the related *o*-tolyl compound (**1b**). Saturated ketones (**2a**) and (**2b**) were prepared in 72 and 20% yield respectively by conjugate addition of phenyl-lithium and *o*-tolyl-lithium[1] to 3-methylcyclopent-2-enone (**3**) in the presence of CuBr under conditions such that the reactive species is expected[2] to be lithium diarylcuprate. Each cyclopentanone was then brominated in acetic acid and directly dehydrobrominated[3] in dimethylformamide containing lithium bromide and lithium carbonate to furnish (**1a**) and (**1b**).

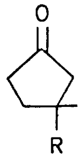
Irradiation of (**1a**) in benzene solution (1 mg/ml) for 30 min using a medium-pressure mercury arc and a uranium glass filter ($\lambda > 3300$ Å) caused virtually quantitative rearrangement to the keten (**4a**). I.r. spectra of aliquot portions taken during reaction showed progressive replacement of the original carbonyl absorption at 1720 cm^{-1} by a new sharp band at 2115 cm^{-1}. After irradiation the reaction mixture was treated with methanol, and subsequent isolation by preparative v.p.c. yielded methyl ester (**5a**). The structure of this ester was assigned from its i.r. and n.m.r. spectra and confirmed by independent synthesis. Reaction[4] of 4-oxo-3-phenylpentanoic acid[5] with methylenetriphenylphosphine in dimethyl sulphoxide followed by esterification with ethereal diazomethane gave authentic (**5a**) identical in all respects with the ester described above.

Similarly, irradiation of (**1b**) led to (**4b**), isolated as ester (**5b**), the structure of which was apparent from its spectroscopic properties. In particular, the i.r. absorption of (**5b**) at 745 cm^{-1} indicated[6] that this ester was a 1,2-disubstituted benzene, and that, therefore, no unexpected rearrangement on the benzene ring had occurred. (**1b**) has a similar absorption at 748 cm^{-1}.

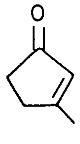
The deuteriated ketone (**6**), which was prepared by treatment of (**1a**) with potassium carbonate in EtOD and D_2O, was also photolysed under the conditions described above. In the isolated product the deuterium label was clearly as shown in (**7**) from the absence in its n.m.r. spectrum of the CH_2 signal present in (**5a**) at δ 4·84 br p.p.m. (2H). This result confirms that, as expected, this methylene carbon atom of (**5a**) is derived from C(5) in starting ketone (**1a**).



(1)



(2)



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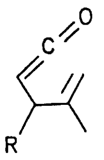

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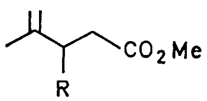
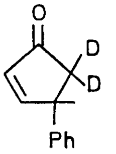
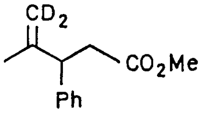


(5)

a ; R = Ph
b ; R = *o*-MeC_6H_4
c ; R = Me



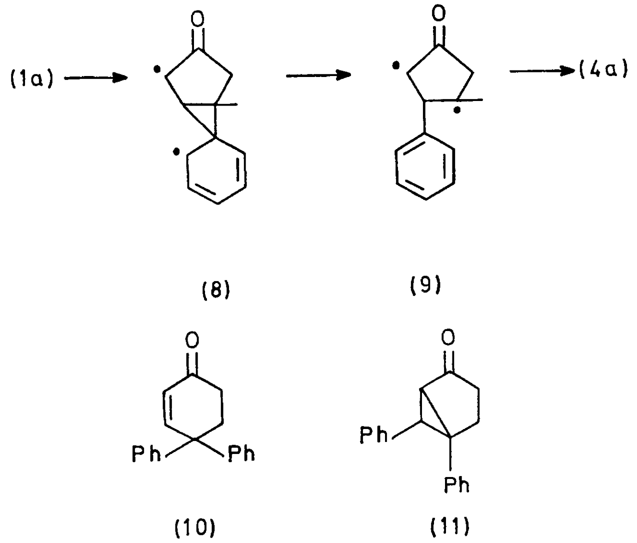
(6)



(7)

The rearrangement was completely quenched in the presence of 2,3-dimethylbuta-1,3-diene (E_T *ca.* 60 kcal/mol[7]) and could be efficiently sensitized by propiophenone (E_T *ca.*

74·6 kcal/mol[8]). The straightforward conclusion that the transformation occurs solely from the ketone triplet state must be regarded as tentative, however, because of the small singlet-triplet splitting (1—2 kcal/mol) in cyclopentenones.[9]



Scheme

This rapid rearrangement is most readily accounted for by the pathway in the Scheme in which the bridging step leading to (**8**) and the cleavage leading to (**9**) are simply the first two formal steps of a di-π-methane rearrangement.[10] Fragmentation of the 1,4-diradical (**9**) yields the observed keten directly. On this basis the transformation is analogous to the well studied di-π-methane rearrangement of (**10**) to (**11**). The gross difference in structure of the products is directly attributable to the fact that in the present five-membered ring examples, the rearranged diradical (**9**) is a 1,4-diradical which suffers preferential fragmentation rather than collapse to a bicyclic system. This suggested pathway provides an explanation for the fact that phenyl (and *o*-tolyl) but not methyl may undergo this rearrangement; no parallel reaction occurs with 4,4-dimethylcyclopentenone (**1c**).[9] This scheme also readily justifies the apparent rapid α-cleavage of (**1a**) and (**1b**). It is known[9] that cyclopentenones unsubstituted at C(5) are resistant to direct photochemical α-cleavage.

Finally, related photochemical transformations, which now may be regarded as oxadi-π-methane rearrangements,[12] have been noted[13] in 4-acylcyclopent-2-enones. The present direct observation of a ketene product lends experimental support to the suggested[13] intermediacy of ketens in these earlier, more complicated reactions.

All new compounds isolated gave satisfactory elemental analysis for carbon and hydrogen. We acknowledge with pleasure the partial support of this research by the donors of The Petroleum Research Fund, administered by the American Chemical Society.

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