Photochemistry of α-Methylene Ketones; Competitive β and γ Hydrogen Abstraction

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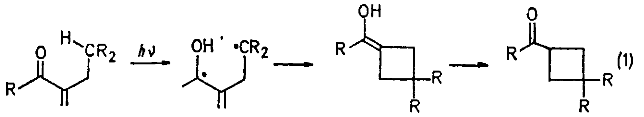
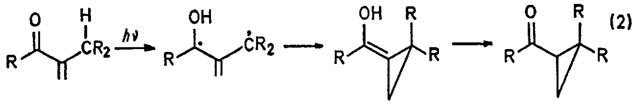
Summary Upon photolysis α-methylene ketones (**1**), (**4**), and (**7**) are isomerized to cyclopropyl ketones (**3a**), (**6**), and (**8**), respectively, as well as to the expected cyclobutyl ketones.

IN a recent publication[1] we reported the photochemical isomerization of several α-methylene ketones into related cyclobutanes and explained these reactions as the result of formation and collapse of a type II biradical intermediate,[2] equation (1). We now describe experiments demonstrating that in certain cases this transformation is accompanied by an alternative photochemical process leading to cyclopropyl ketones. As the pathway suggested in equation (2) indicates, this process differs from that reported earlier in that hydrogen is abstracted from the β carbon atom through a five-membered ring intermediate rather than from the γ-position typical of type II reactions. While a small number of reactions believed to involve such β hydrogen abstraction by carbonyl oxygen have been observed[3] previously, the examples recorded below are noteworthy in the structural simplicity of the substrates employed and are novel in exemplifying competitive β and γ abstraction in single molecules.





Irradiation of (**1**) leads[1] to (**2**) in only 31% yield, although the three other enones investigated gave 64—68% of the isomeric cyclobutyl ketones. We now find that the lower yield of (**2**) is largely due to concomitant formation of 24% of the spiroketone (**3a**),† presumably according to equation (2). This photoproduct could be isolated by preparative g.l.c. at 95°, and it was conclusively identified by comparison with a sample of (**3a**) prepared in the following manner. Reaction[4] of ethyl diazoacetate with methylenecycloheptane[5] in the presence of copper bronze yielded 79% of ester (**3b**). Saponification of this ester in methanolic alkali gave 89% of the corresponding acid (**3c**), which reacted[6] with methyl-lithium in ether to form (**3a**) in 95% yield.

Similar irradiation of (**4**)[7] led to (**5**) (23%) and (**6**)[8] (31%), while (**7**) gave the expected[1] cyclobutyl ketones (17%) and (**8**) (38%). The structure of (**8**) was confirmed by inde-

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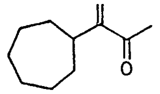
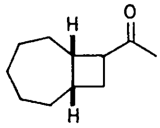
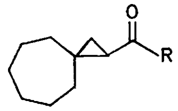
† All new compounds were fully characterized by appropriate i.r. and n.m.r. spectra and elemental analysis after purification by preparative g.l.c.



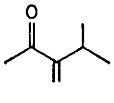
(1)



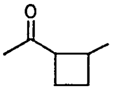
(2)



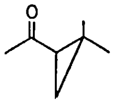
(3)
a; R=Me b; R=OEt
c; R=OH



(4)



(5)



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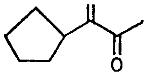

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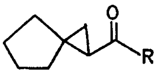
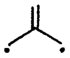


(8) R=Me (9) R=OH



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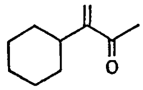
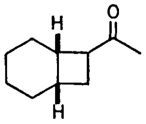


(11)



(12)

pendent synthesis through addition of methyl-lithium to (**9**).[4]

In these unsaturated ketones (**1**), (**4**), and (**7**) the occurrence of β abstraction is favoured by the α-methylene group. Rates of hydrogen abstraction by excited carbonyl oxygen are known[2] to reflect the stability of the resulting radicals, and an α-methylene group should provide considerable stabilization to a β radical centre. The biradical of equation (2) is at least formally a derivative of trimethylenemethane (**10**), a ground state triplet species with a theoretically estimated delocalization energy of approximately 34 kcal mol^{-1}.[10] The reaction is, however, sensitive to the specific structure of the ketone. The cyclohexyl-substituted ketone (**11**), although related to (**1**), (**4**), and (**7**), furnishes on photolysis a 64% yield of cyclobutyl ketones (**12**)[1] and little or no ($\leqslant$4%) cyclopropyl ketone. It is not yet clear whether this is the result of simple ground state steric factors or due to more subtle effects of structure on properties of the intermediates involved in these reactions.

Observation of these β abstractions in α-methylene ketones supports the suggestion[11] that the photo-enolization of α-diketones[12] may proceed by a similar process.

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