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PHOTOCYCLISATION OF α-BROMOMETHYL-1,2-DIKETONES

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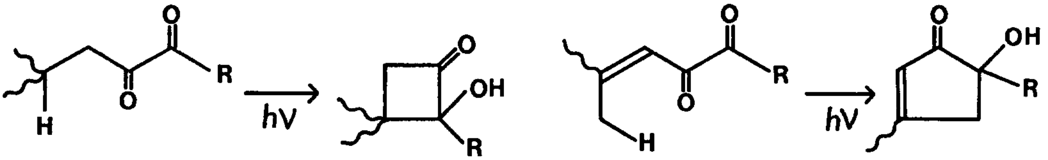
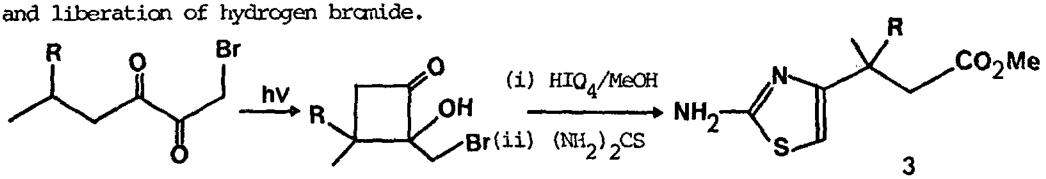
Summary: Appropriately substituted α-bromomethyl-1,2-diketones undergo photocyclisation in solution to hydroxycyclobutanone and hydroxycyclopentenone derivatives without loss of bromine.

The photocyclisation of 1,2 diketones bearing abstractable γ hydrogens to give hydroxycyclobutanones[1] or hydroxycyclopentenones,[2] depending on the structure of the starting ketone, is often a clean and efficient process ($\phi \sim 0.5 - 1$)[1,3].



Unfortunately, depending on the neature of R, competition from other intramolecular H abstractions or intramolecular Paterno Buchi reactions[4] may occur and thus, except in the case of symmetrical diketones, it is generally necessary to restrict R to methyl or aryl - the latter not bearing an o-alkyl substituent. Since these groups are not readily elaborated or removed this restriction is a sèrious limitation on the synthetic potential of the reaction. We report here that α-bromomethyl-1,2 diketones,[5] unlike simple α-haloketones in which the primary photochemical process is cleavage of the C-Halogen bond,[6] undergo clean photocyclisation with retention of the bromine.

Irradiation of 1 a,b in methyl acetate (c ~ 3%) at 20° under N_2 with pyrex filtered light gave rapid and essentially quantitative conversion to 2 a,b. These hydroxycyclobutanones are oils which are known to dimerise readily and undergo rearrangement by 1,2 shift in the α-hydroxy ketone system[7] but their structures follow from the spectra and the products from periodic acid oxidation[8] (characterised as the amino thiazoles 3 a,b after reaction with thiourea). Under similar irradiation 4 cyclised to 5 and 6 to 7 in 80 - 90% yield but in these cases it was essential to use light λ > 360 nm otherwise secondary photolysis occurred with darkening of the solution and liberation of hydrogen bromide.



1a R = H
1b R = Me

2

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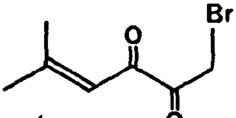

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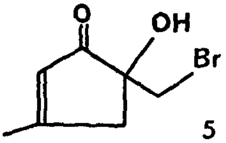

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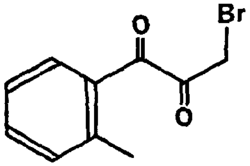

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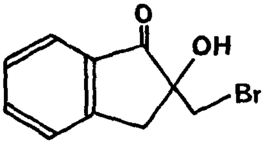

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These photoproducts show the expected reactions (e.g. epoxide formation on base treatment and reductive elimination with Zn/HOAc) and with their diversity of functional groups and the accessibility of the starting diketones are potentially attractive intermediates for organic synthesis.

References and Notes

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6. J. C. Anderson and C. B. Reese, Tetrahedron Letters 1, 1962; W. R. Bergmark, J. Amer. Chem. Soc., 100, 61 (1978)
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8. 2a IR 3450, 1775 cm^{-1}; M^+ 208/206; δ (CCl_4) 1.25 (s, 3), 1.35 (s, 3), 2.65, 2.9 (ABq, s, J 17 Hz), 3.65 (s, 2), 3.9 (brs, 1, exchanges D_2O). 3a m.p. 116°. 2b IR 3440, 1775 cm^{-1}; M^+ 194/192 n.m.r. consistent with mixture of diastereoisomers; 3b m.p. 81°.
9. 5 m.p. 49° IR 3380, 1710 cm^{-1} M^+ 206/204, δ (CCl_4) 2.2 (s, 3), 2.5,2.6 (ABq, 2, J 17 Hz), 3.55 (s, 2), 3.6 (brs, 1 exchanges D_2O); 7 m.p. 88-89° IR 3385, 1715 cm^{-1} M^+ 242/240, δ (CCl_4) 3.3,3.5 (ABq, 2, J 18 Hz), 3.45 (br s, 1, exchanges D_2O), 3.6 (s, 2), 7.3 - 7.5 (m, 4).

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