NEW PHOTOCHEMICAL REACTIONS OF α-DIKETONES T. L. Burkoth and Edwin F. Ullman Contribution No. 12 from Synvar Research Institute 3221 Porter Drive, Palo Alto, California (Received in USA 4 November 1969; received in UK for publication 9 December 1969)

The most general known photochemical reaction of alkyl α -diketones is 2-hydroxycyclobutanone formation.¹ Recent reports² of alternative photochemical. pathways of α -diketones prompts us to describe our studies of three new reactions that take place in suitably designed molecules.

Formation of hydroxycyclobutanones from α -diketones probably proceeds by β -hydrogen abstraction through a pseudo six-membered ring transition state. Although γ -hydrogen abstraction should proceed through an equally strain-free pseudo six-membered ring, evidence for this process has not heretofore been obtained. The absence of γ -hydrogen abstraction suggests a statistical preference for a transition state incorporating an sp² hybridized carbon in the pseudo ring. To determine if γ -hydrogen abstraction could occur in a favorably substituted α -diketone, I³ was prepared by acyloin condensation of ethyl γ phenylpropionate followed by oxidation with bismuth oxide in acetic acid.⁴



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Irradiation of I in methanol (> 400 mµ light) gave 90% of the normal product ${\rm II}^5$ and 10% of an abnormal product, the hydroxycyclopentanone III.⁶ Confirmation of structure III was obtained by phosphorous oxychloride dehydration to the cyclopentenone IV.⁷

The formation of III suggests γ -hydrogen abstraction followed by hydrogen migration and cyclization as depicted in equation 1. The occurrence of γ hydrogen abstraction in I is consistent with the 9.2-fold greater reactivity of benzyl than of methylene hydrogens toward triplet ketones.⁸ Based on this reactivity difference a minimum statistical preference for β - over γ -hydrogen abstraction of $\Delta\Delta S = 8.7$ e.u. is estimated.⁹ Thus, only in α -diketones with very strong activating groups in the γ -position can cyclopentanones be expected to be significant photo-products.

Further elucidation of the scope of α -diketone photo-processes was obtained from the cyclohexenyl diketone V.¹⁰ The preparation of V was achieved by the α -diketone synthesis of Cuvigny and Normant¹¹ (equation 2). This compound has sterically accessible and reactive β -hydrogens, but the biradical resulting from intramolecular hydrogen abstraction would cyclize to give a highly strained product. Nevertheless V in cyclohexane underwent rapid photochemical reaction (> 400 mµ light) to give the furanone VII¹² in 50% yield.



This product probably does not result from hydrogen abstraction. Rather the diketone V may be pictured as an analog of cross conjugated dienones which frequently undergo light-induced bonding between their terminal carbon atoms.¹³ Rearrangement of intermediate VI, possibly by way of two 1,2-hydrogen shifts, would not be unexpected.

Extension of this reaction to α -ketopropiophenone (VIII, R=H) was unsuccessful. Hydrogen abstraction from solvent competed with cyclization even in benzene to give the corresponding pinacol, 3,4-dihydroxy-3,4-diphenyl-2,5hexanedione.¹⁴ On the other hand 2-methyl- α -ketopropiophenone (VIII, R=CH₃) reacted rapidly to give the indanone X (see also ref. 2). Similar but slower reactions occurred with 2,2'-dimethylbenzil and 2,2'-dimethyl-4-methoxybenzil. In the latter case equal amounts of the two possible products were formed.



Like Hamer 2 we observed no deuterium incorporation into X or recovered VIII (R=CH₃) on irradiation in methanol-d₁. Nevertheless we believe this does not exclude photo-enolization as the primary process. Photo-enolization reactions probably yield directly both possible sterioisomeric enols¹⁵ (eg; IX and XI). Enol XI is expected to revert very rapidly to VIII by an intramolecular 1,5-hydrogen shift, and cyclization of enol IX could occur by a fast concerted process requiring little atomic reorganization. Rapid cyclization of IX to X finds excellent analogy in the known photo-rearrangement



XII

XII ---> XIII.¹⁶ Hence the reactions of enols IX and XI might both compete with deuterium exchange.

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- 3. I: mp 72-3°; <u>m/e</u> 294 (M); λ_{max} CH₃OH 260 mµ (@ 600), 415 mµ (@ 12).
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- II: <u>m/e</u> 294; ν_{max}neat 1775, 3440 cm⁻¹; nmr (CCl₄) 1.7 and 2.5δ (broad, 11 H), 3.8δ (1 OH) and 7.1δ (10 ArH).
- 6. III: $\underline{m/e}$ 294 (M); v_{max} neat 1740, 3460 cm⁻¹; nmr (CCl₄) 1.5, 1.3, and 2.36 (broad, 11 H), 3.06 (1 OH), 7.26 (10 ArH).
- 7. IV: m/e 276 (M); ν_{max}neat 1690, 1620; λ_{max}CH₃OH 275 mµ (€ 13,300); nmr (CCl₄) 1.86 (M, 2H), 2.2-3.06 (broad, 8H), 7.26 (5 ArH), 7.46 (5 ArH).
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