PHOTOCHEMICAL REARRANGEMENT OF 8-OXABICYCLO[3.2.1]OCT-6-EN-2-ONES

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Abstract: Irradiation of 8-oxabicyclo[3.2.1]oct-6-en-2-ones results in a 1,3-acyl rearrangement. The initial photoproduct undergoes a subsequent reaction involving hydrogen transfer followed by intramolecular cycloaddition of a ketene intermediate.

The diverse photochemistry exhibited by β , γ -enones has attracted much attention over the past two decades and has been the subject of several reviews.¹⁻⁴ Photoreactions involving β , γ -unsaturated ketones have been characterized as either 1,3-acyl or oxa-di- π -methane rearrangements. A number of studies have shown that the former occurs from the n, π^* singlet state whereas the oxa-di- π -methane rearrangement proceeds from the triplet state which is primarily π , π^* in character.⁵⁻⁸ During the course of our investigations dealing with 8-oxabicyclo[3.2.1]oct-6-en-2-ones,⁹ we had the occasion to examine the photochemical behavior of these interesting bicyclic enones. This communication documents the results of these studies.

Each of the oxabicyclooctenones employed in this study was prepared by the rhodium (II) acetate tandem cyclization-cycloaddition reaction of the appropriate diazoketone precursor.⁹ Irradiation of a benzene solution of 1 for 12 h through Pyrex cleanly afforded oxatricyclo[3.2.1.0^{3,7}]octanone 4 in 85% yield. The structure of this material was deduced on the basis of its spectral data.¹⁰ Subsequent studies showed that 4 is not a primary reaction product but is formed by a subsequent photoreaction of a oxabicyclo[3.3.0]oct-3-ene-6-one intermediate (i.e. 3). With short exposures, oxabicyclooctenone 3 accounts for nearly all of the product produced. At longer exposures, owing to a secondary photoreaction of 3, the amount of 4 substantially increased. This was independently demonstrated by the conversion of 3 to 4 under the photolytic conditions used.

The formation of **3** is readily accounted for by Norrish Type I cleavage of the carbonylbridgehead C-C bond to afford the stabilized allyl-acyl diradical **2**. This is followed by recombination of the diradical at the opposite allylic terminus (i.e. a 1,3-acyl shift). Due to the geometric requirements of the resulting 5,5-fused system, recombination of the diradical results in the expected *cis*-ring junction. As is typically observed in 1,3-acyl shift rearrangments, the reaction is actually a photoequilibrium, the position of which is dictated by the relative UV absorptions of the two isomers. The same products were also obtained upon triplet sensitization (acetophenone) and no evidence was found suggesting an oxa-di- π -methane rearrangement. In a related manner, brief irradiation of enone **5** afforded the *cis*-fused bicycle **6** as the primary photoproduct. Once



again, triplet sensitization provided similar results. When the direct irradiation was carried out for a total of 12 h, cyclobutanone 7 was isolated in 85% yield.¹⁰

A reasonable mechanism to account for the formation of the oxatricyclo[3.2.1.0^{3,7}]octanone system involves a sequence consisting of Norrish type I cleavage of either enone 1 or 3 to give diradical 2 which subsequently undergoes an internal hydrogen transfer to produce a ketene





intermediate (i.e. 8).¹¹ Intramolecular [2+2]-cycloaddition of the cyclic enol ether with the reactive ketene nicely rationalizes the formation of the products.¹² In support of this interpretation, we have carried out the irradiation of enones 1 and 3 (as well as 5 and 6) in methanol and find that the major product produced (88%) corresponds to dihydrofuran 9 (or 10). The formation of these esters clearly implicates a ketene intermediate in the secondary photochemistry of these systems.

Recent years have seen a number of elegant methods for the stereospecific preparation of triquinanes.¹³ We felt that this combined tandem cyclization-cycloaddition-photorearrangement methodology should provide a convenient access to the oxa analogs of these fascinating carbocycles. With this goal in mind, diazodione 11 was prepared and allowed to undergo rhodium catalyzed cycloaddition with dimethyl acetylenedicarboxylate. Irradiation of the resulting cycloadduct 12 for 2 h cleanly afforded the linear oxatriquinane 13 in 79% yield. Encouraged with this success, the related diazodione 14 was prepared and subjected to the usual conditions. Photolysis of the resulting cycloadduct 15 in benzene for 2 h cleanly afforded the bent oxatriquinane 16 in 96% yield. Note that in both 13 and 16 adjacent quaternary centers are introduced efficiently and stereospecifically.



The above two examples establish the viability of this approach as a convenient and rapid entry into the oxatriquinane ring system. Other aspects dealing with the photochemistry of 8-oxabicyclo[3.2.1]oct-6-en-4-ones will appear in forthcoming papers.

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References and Notes

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