## Independent Generation of Triplet 1,4-Biradical Intermediates Implicated in the Photochemical Cycloaddition Reaction Between 2-Cyclopentenone and Acrylonitrile<sup>1</sup>

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Abstract: Norrish Type I photochemistry of 3-cyanobicyclo[3.3.0]octane-2,6-dione and 3-cyanobicyclo[3.3.0]octane-2,8-dione is used to generate triplet 1,4-biradicals implicated in the photochemical cycloaddition reaction of 2-cyclopentenone with acrylonitrile. The fates of these biradicals have been determined and they suggest that the photocycloaddition reaction regiochemistry is governed by competition between closure of the biradicals to product and their reversion to ground state starting materials. This provides further evidence against the long-held view that the relative rates of formation of the biradicals due to the triplet exciplex governs the reaction regiochemistry. It is also found that the regiochemistry of the photochemical cycloaddition reaction between cyclopentenone and acrylonitrile is reversed from that obtained in the addition of acrylonitrile to 2-cyclohextenone.

The photochemical cycloaddition of mono-substituted alkenes to five- or six-membered cyclic  $\alpha,\beta$ unsaturated ketones yields cyclobutane adducts which can have head-to-head or head-to-tail regiochemistry (Scheme 1).<sup>24</sup> The reaction is known to proceed from the triplet excited state of the enone which reacts with alkenes to form triplet 1,4-biradical intermediates; following spin inversion these close to product in competition with fragmentation to their ground state precursors.<sup>2b</sup> In principle, the biradical intermediates



could have any or all of the structures 1-4 shown in Scheme 1 and the reaction regiochemistry could be controlled by the relative amount of each biradical formed, or by the relative efficiencies with which they close to products in competition with collapse to starting materials. For many years it has been assumed that the regiochemistry is determined by the relative orientation of the dipoles of the enone and the alkene in an exciplex intermediate that precedes biradical formation. In part, this exciplex mechanism was proposed on the basis of the observation that reaction of 2-cyclohexenone with electron rich alkenes such as ethyl vinyl ether shows a preference for formation of the head-to-tail regioisomers 5 while the electron poor alkene acrylonitrile yields mainly the head-to-head regioisomer  $6.^3$  As shown in Scheme 1, the electrostatically more stable alignment of the dipole of the alkenes with the enone triplet excited state leads to the observed regiochemistry if it is assumed that the dipole moment of the enone triplet excited state is reversed from that in the ground state. Implicit in the exciplex mechanism is the assumption that the alignment in the exciplex accelerates the rate of formation of some biradical intermediates over others and that this is the origin of the regioselectivity; it does not take into account the possibility that the isomeric biradicals could partition between products and starting materials with different efficiencies.

New evidence has called into question the existence of the exciplex intermediate in this reaction. For example, several instances have been found in which electron poor alkenes add to cyclohexenones to give mainly the head-to-tail regioisomers.<sup>4-6</sup> In addition, the rate constant for interaction of the enone triplet excited state with alkenes does not vary with alkene substituent in the manner expected for the formation of an excited complex possessing charge transfer character.<sup>7</sup> Furthermore, for the reaction of ethoxy- and alkyl-substituted alkenes with cyclopentenone we have quantitatively trapped the biradical intermediates with hydrogen selenide. For these alkenes we find that approximately equal amounts of the biradicals 2 and 3 are formed and that biradicals 1 and 4 are not important intermediates in the photocycloaddition reaction.<sup>8,9</sup> This means that in the photocycloaddition reactions where one of 5 and 6 is the favoured product the regioselectivity does not arise from faster formation of one of the biradicals 2 and 3 as the exciplex mechanism requires. Instead, it implies that the reaction regiochemistry depends on the relative efficiencies with which biradicals 2 and 3 close to products in competition with reversion to enone and alkene.

In order to confirm this conclusion we have now attempted to generate the biradicals by an independent route so that the manner in which they partition between cyclisation to 5 and 6 and collapse to enone and alkene could be monitored. The approach chosen is shown in Scheme 2. It was anticipated that triplet sensitised Norrish Type I cleavage of diketones 7 and 8 could be followed by decarbonylation to yield the triplet 1,4-biradicals 2 and 3 implicated in the cycloaddition reaction. Measurement of the relative amounts



of 5 and 6 and cyclopentenone formed in the photolysis of each diketone would then give a direct quantitative measure of the modes of decay of the biradicals 2 and 3 if biradicals 1 and 4 are not important intermediates.<sup>8</sup>

The diketone 8 was prepared with the substituent X equal to H, Me, OEt, OBu<sup>t</sup>, and CN.<sup>10</sup> Sensitised and direct photolysis of diketone 8 (X=H) in benzene solution gave products of intramolecular disproportionation of the Norrish Type I biradical 9. Similarly, photolysis of diketones 8 (X=Me, OBu<sup>t</sup>, single diastereomer) gave products derived from intramolecular disproportionation of the Norrish Type I biradical 10. The major primary product of photolysis of diketone \$ (X=OEt) was diketone \$ (X=H); the ethoxy group is presumable lost by a Norrish Type II fragmentation pathway. In all four cases no traces of cyclopentenone or the corresponding cyclobutanes 5 were found indicating that the decarbonylation of the Norrish type I biradicals is too slow to compete with their alternative decay pathways. Performing the photolyses at elevated temperature did not alter this situation. It was concluded therefore that these diketones are not useful for the independent generation of the 1,4-biradicals implicated in the photocycloaddtion reaction of 2-cyclopentenone with monosubstituted alkenes. With diketone \$ (X=CN) direct and sensitised photolysis also gave mainly products arising from intramolecular disproportionation of the Norrish Type I biradical initially formed; however, some decarbonylation did occur to give 2-cyclopentenone and both diastereomers of 5. The molar ratio of cyclopentenone to the diastereomers of 5 was 1:1.09.<sup>11</sup> This indicates that the rate of fragmentation of biradical 2 (X=CN) to cyclopentenone and alkene is similar to the rate of closure to 5.



Photolysis of diketone 7 (X=CN) also yielded products of intramolecular disproportionation of the initially produced Norrish Type I biradicals as well as cyclopentenone and both diastereomers of the adduct 6. The molar ratio of cyclopentenone to 6 was 1:3.67.<sup>11</sup> This indicates that closure of biradical 3 to 6 occurs at a rate more than three times greater than the rate of cleavage to cyclopentenone and acrylonitrile.

The regiochemical outcome of the photocycloaddition reaction of cyclopentenone with acrylonitrile was also determined. Direct UV light irradiation of cyclopentenone with acrylonitrile in benzene yielded four cycloadducts in a ratio 15:25:45:15. The cycloadducts were separated and characterised.<sup>10</sup> Much to our surprise, the first two of these were found to be diastereomers of **6** and the latter pair were diastereomers of **5** so that the ratio **5:6** was 60:40, indicating that the head-to-tail regioisomer is the favoured product. This is very different from the result reported by Corey et al<sup>3</sup> for the addition of acrylonitrile to cyclohexenone in pentane where formation of the head-to-head product is favoured. We have repeated this reaction in order to confirm the identity of the products; we find six products in the ratio 37:39:7:7:5:5. The first two are diastereomers of the head-to-head adduct 11, the second two are diastereomers of the head-to-tail adduct 12 and the last two are diastereomers of the *trans* fused head-to-tail regioisomer 13.<sup>10</sup> Thus the ratio of head-to-head to head-to-head to head-to-tail adducts is 76:24.

Combination of the ratio 5:6 (X=CN) formed in the cyclopentenone/acrylonitrile photocycloaddition reaction with the ratios of fragmentation *versus* closure for biradicals 2 and 3 determined from photolysis of diketones 7 and 8 it is possible to calculate that biradicals 2 and 3 are formed in the ratio 1:1.54 in the photocycloaddition reaction. This is equal to their relative rate constants of formation, k. The relative rates of formation of biradicals 2 and 3, and their fates are summarised in Scheme 3. This treatment assumes that biradicals 1 and 4 are unimportant and that biradicals 2 and 3 are conformationally equilibrated so that their fates are independent of their mode of generation.



The following conclusions can be drawn from this work:

- 1. The fates of the intermediate biradicals rather than their rates of formation control the regiochemistry of the photocycloaddition reaction between acrylonitrile and cyclopentenone. This is in agreement with recent findings for other alkenes using hydrogen selenide to trap the biradicals.<sup>3,9</sup>
- The preferential formation of head-to-head cycloadducts from the reaction of cyclic enones with electron poor alkenes is the exception rather than the rule since the number of examples of preferential formation of head-to-tail isomers now exceeds those in which head-to-head isomers dominate.
- 3. The above two conclusions imply that it is unnecessary to introduce an exciplex into the mechanism of the photocycloaddition reaction of alkenes with cyclic enones in order to explain the reaction regiochemistry.
- 4 The ring size of an enone can affect the regiochemical outcome of the cycloaddition reaction. This complements earlier results<sup>4,5</sup> which suggest that the ring size of 1-methoxycarbonylcycloalkenes can also affect the regiochemical outcome of their photocycloaddition reactions with cyclic enones.

## References

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- 10. Diketone 8 (X=H) was prepared by the method of A.A. Hagedorn and D.G. Farnum, J. Org. Chem., 1977, 42, 3765. The methyldiketone 8 (X=Me) was prepared by treatment of 3,7-bis(methoxycarbonyl)bicyclo[3.3.0]octane-2,6-dione (a synthetic precursor of 8 (X=H)) with MeI/NaH and subsequent hydrolysis and decarboxylation. Diketones 8 (X=OEt, OBu') were prepared by treatment of the silyl enol ether of the mono ketal of diketone 8 (X=H) with iodosobenzene in the presence of boron trifluoride etherate and either ethanol or Bu'OH. Diketone 8 (X=CN) was prepared by treatment of the mono ketal of diketone 8 (X=H) with lithium diisopropylamide followed by tosylcyanide. Diketone 7 was prepared by the method of R.O. Duthaler and P. Maienfisch, Helv. Chim. Acta, 1984, 67, 856. It was converted to 7 (X=CN) by treatment of its dianion (generated using two equivalents of lithium diisopropylamide) with benzylthiocyanate. Details of the syntheses and of the characterisation of the cycloadducts will be described in a full paper.
- 11. The ratio of cyclopentenone to adducts 5 or 6 was measured at low and varying conversions in order to ensure that secondary photochemistry of cyclopentenone or the adducts did not perturb the product distribution. The ratio was measured by gas chromatography using calibrated internal standards. The adducts 5 and 6 and cyclopentenone in the photolysis mixtures were identified by g.c. co-injection with authentic samples and by comparison of their mass spectra (from g.c.-m.s.) with those of authentic samples. The relative amounts of the diastereomers of 5 and 6 obtained by photolysis of diketones 7 and 8 (X=CN) were the same as observed in the mixture of 5 and 6 produced by photocycloaddition between cyclopentenone and acrylonitrile.