Tetrahedron Letters No.53, pp. 5601-5604, 1968. Pergamon Press. Printed in Great Britain.

ORGANIC PHOTOCHEMISTRY. V. THE PHOTOSENSITIZED AND THERMAL CYCLOADDITION REACTIONS OF CYCLOPENTADIENE AND α-ACETOXYACRYLONITRILE (1)

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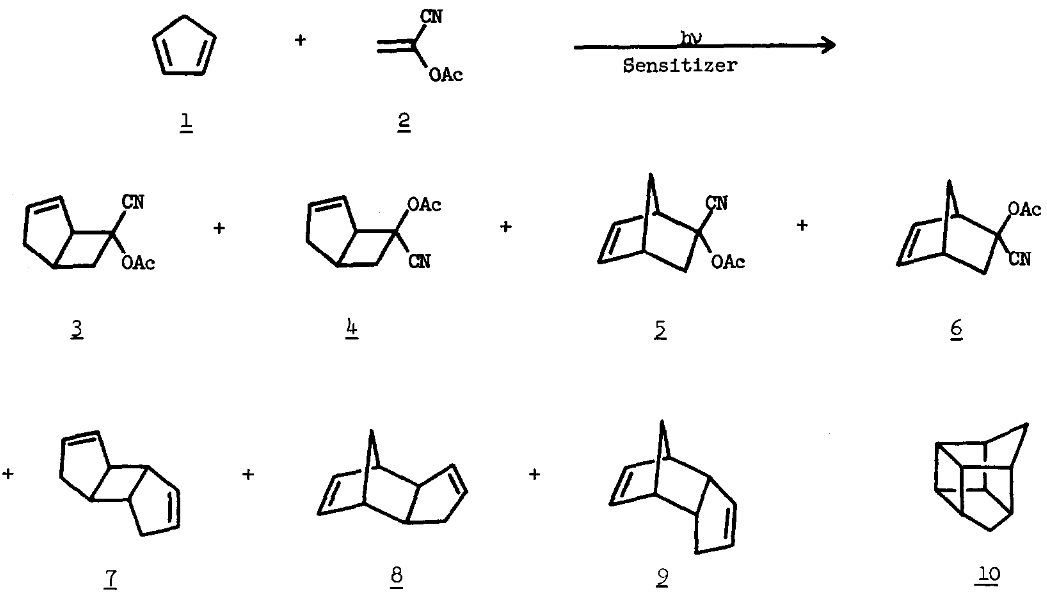
(Received in USA 1 August 1968; received in UK for publication 4 October 1968)

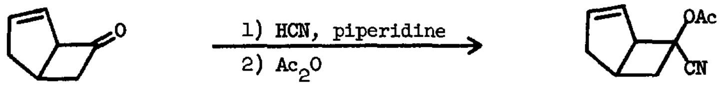
We would like to report the results of the photosensitized crossed-cycloaddition reaction between cyclopentadiene 1 and α-acetoxyacrylonitrile 2 in which the structure of the intermediate diradical can be inferred by a rigorous structure proof of the products. The product distribution in the thermal (Diels-Alder) cycloaddition of these olefins was determined. A linear free energy relationship for predicting *endo* - *exo* ratios in thermal cycloadditions of 1,1-disubstituted ethylenes is proposed.

Irradiation (2) of the olefins 1 and 2 with either acetophenone $\left[E_T\ 73.6\ \text{kcal./mole}\ (3)\right]$ or benzil $\left[E_T\ 53.7\ \text{kcal./mole}\ (3)\right]$ gave four cross-adducts 3-6 and the three diene dimers 7-9 previously reported by Hammond and co-workers (4). With acetophenone a fourth dimer 10 was formed



at high conversions of the diene 1, probably due to the photosensitized ring closure of the dimer 9 (5). We have found that acetophenone will sensitize this reaction (6). The products were separated by preparative g.c. and identified by their n.m.r., infrared, and mass spectra (7).

In order to establish firmly the position of the double bond in the bicyclo[3.2.0]heptene isomers 3 and 4, one of them was synthesized by the addition of hydrogen cyanide to the ketone 11 (8), followed by acetylation. Comparison of 4 from each reaction was made by infrared and n.m.r. spectra and g.c. retention time. Only one isomer was detected in this reaction, probably due to kinetic control with the attack by cyanide ion being from the less hindered *exo* face of the ketone 11. One double bond position isomer 13 was synthesized by the analogous reaction of the ketone 12 as reported by Roberts and Gorham (9). In this reaction also, only one cyanohydrin acetate was formed, probably the isomer shown based on the analogous ketone 11 reaction. No trace of 13 could be detected in the photoreaction. Since only two cyclobutyl derivatives were formed in the photoreaction we assume that 3 is the enantiomer of 4, not of 13. These results are consistent with the expectation (4b,10) that, of the several possible diradical intermediates, the photosensitized products would result from the presumed more stable diradical 14. Several



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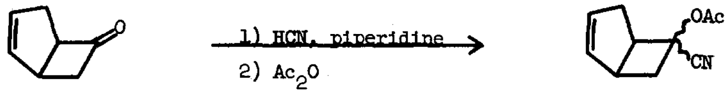

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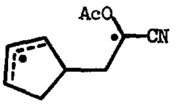

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related reactions have been reported, but the position of the double bond was not established rigorously (1,10,11).

There were no appreciable differences in the product distributions from the two photosensitized reactions. Approximately equal amounts of the four cross-adducts 3-6 were formed when the thermal reaction between 1 and 2 was minimized. This non-dependence on the sensitizer is in agreement with the explanation offered for the variation in product distributions observed with the acyclic dienes, since the cyclic diene 1 cannot assume the *s-trans* conformation (1,12,13).

The thermal (Diels-Alder) reaction of the olefins 1 and 2 has been reported previously by Bartlett and Tate (14); no stereochemical assignments or product separations were made. We found that at 150° without solvent 1 and 2 gave only products of 1,4-addition 5 and 6. It is estimated that 2% (relative to 5 and 6) of the cyclobutanes 3 and 4 could have been detected. The absence of 3 and 4 in the thermal reaction establishes the absence of a triplet diradical as an intermediate in the thermal reaction, but does not eliminate a singlet diradical as an intermediate.

The product distribution for the thermal addition was 75% *endo*-acetoxy 5 and 25% *endo*-cyano 6. The *endo*:*exo* isomer ratio for the reactions of the diene 1 with vinyl acetate and acrylonitrile are 81:19 (15) and 60:40 (16) respectively. Kinetic control is assumed for all of these additions. A quantitative estimate can be made of the isomer ratio expected from the reaction of the 1,1-disubstituted olefin 2 by assuming a linear free energy relationship for each of the substituents (OAc and CN) on the ethylene:

$$\log k_{\underline{\text{endo}}\text{-X},\ \underline{\text{exo}}\text{-Y}} = \log k_{\underline{\text{endo}}\text{-X}} + \log k_{\underline{\text{exo}}\text{-Y}} + \log \frac{2}{k_E}$$

$$\log k_{\underline{\text{endo}}\text{-Y},\ \underline{\text{exo}}\text{-X}} = \log k_{\underline{\text{endo}}\text{-Y}} + \log k_{\underline{\text{exo}}\text{-X}} + \log \frac{2}{k_E}$$

where $k_{\underline{\text{endo}}\text{-X},\ \underline{\text{exo}}\text{-Y}}$, $k_{\underline{\text{endo}}\text{-X}}$, $k_{\underline{\text{exo}}\text{-Y}}$, and k_E are the rate constants for the formation of the disubstituted *endo*-X, *exo*-Y adduct, the monosubstituted *endo*-X and *exo*-Y adducts, and the unsubstituted ethylene adduct respectively, etc. Using the product distributions cited above for the monosubstituted olefins, one calculates an isomer distribution of 74% *endo*-acetoxy 5 and 26% *endo*-cyano 6 in excellent agreement with the experimental results.

Examination of the literature reveals few cases where this free energy relationship can be tested. Two examples which predict the major isomer correctly are the additions of methacrylic acid and isopropenyl acetate (17). However the quantitative correlation is poor for both cases. Possible sources of error are non-kinetic control and poor accuracy in the isomer ratios. For a linear free energy relationship of this type to be valid the electronic and steric interactions between the two substituents on ethylene should be minimal. These conditions are probably met reasonably well for non-bulky groups since these are cross-conjugated systems.

Acknowledgment. The authors wish to thank Drs. J. C. Little and M. J. Mintz and Prof. M. Stiles for many helpful discussions during this work.

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