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SOLUTION PHOTOCHEMISTRY. III.[1)]

INTRAMOLECULAR CYCLOADDITION OF SOME ACYCLIC 1,7-DIENES

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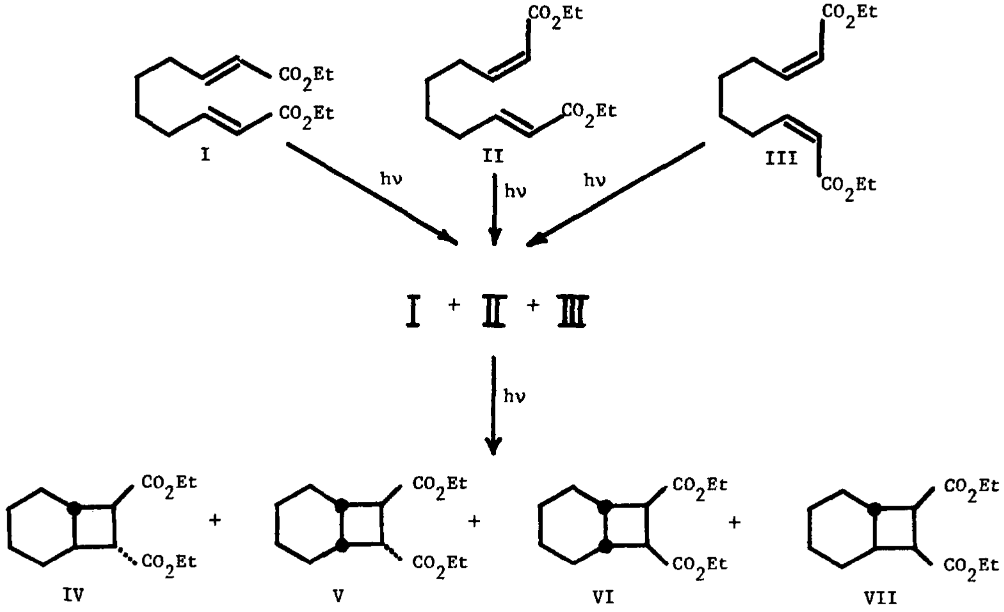
In order to determine the propensity that simple acyclic 1,7-dienes exhibit toward intramolecular cycloaddition and to ascertain their preference, if any, for either "crossed" or "straight" cycloaddition (3), we have investigated the photochemistry of diethyl-trans,trans-deca-2,8-diene-1,10-dioate (I) and its cis,trans and cis,cis geometric isomers II and III (4) (See Fig. 1).

Direct photolysis of the α,β-unsaturated diesters I-III led solely to migration of the double bonds into the β,γ-position, the details of which will be reported elsewhere. The present communication is concerned with the triplet energy sensitized reactions of I-III which ultimately led exclusively to intramolecular cyclobutane ring formation.

Photolysis (5) of 1-2% acetone solutions of diethyl-trans,trans-deca-2,8-diene-1,10-dioate (I) afforded a mixture of six products II-VII plus starting material. Following the course of the photolysis by vapor phase chromatography and isolation using preparative vpc (6) showed the initial photolysis mixture to be composed primarily of compounds I, II, and III in a ratio of approximately 3.8 : 3.5 : 1.0. Continued irradiation gave increasing amounts of products IV-VII at the expense of I, II, and III until a photostationary mixture consisting of IV (43%), V (17%), VI (33%), and VII (7%) (7) was eventually attained (8.5 hrs starting with 0.5 g of I). At this point compounds I-III had been totally consumed. The same photostationary state mixture was obtained, within experimental error, when pure diethyl-cis,trans-deca-2,8-diene-1,10-dioate (II) was photolyzed in acetone or when the photolysis of I was carried out using acetophenone (benzene solvent, Pyrex filter) as the triplet energy sensitizer. On the other hand, photolysis of diethyl-cis,cis-deca-2,8-diene-1,10-dioate (III) gave a slightly different IV-VII photostationary state mixture composed of IV (26%), V (17%), VI (49%), and VII (8%) (7).

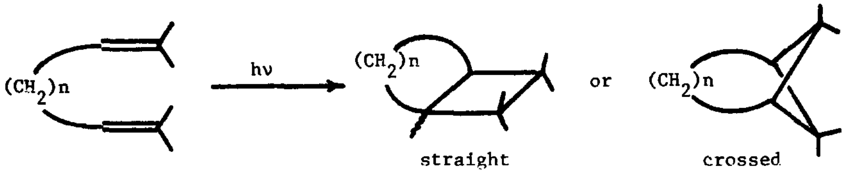
The bicyclo[4.2.0]octane adducts IV-VII were separated by preparative vpc (6). Compounds IV, V, and VI were identified by direct comparison with authentic samples prepared by the photoaddition of diethyl maleate to cyclohexene (8a) and by hydrolysis to the corresponding known (8) dicarboxylic acids. The trans,cis-diester VII, available only in minute quantities in an impure state, was characterized by its sodium ethoxide catalyzed epimerization to the more thermodynamically stable trans,anti,trans-diester IV (8b,9).

FIG. 1 - PHOTOLYSIS RESULTS



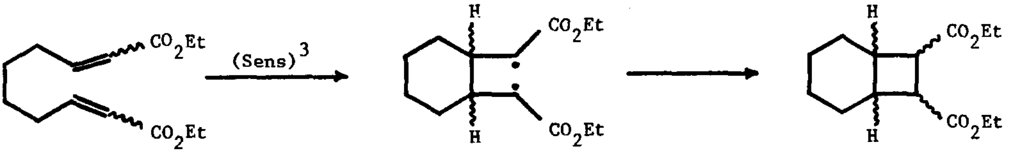
DISCUSSION

The results presented above are striking in that only straight cycloaddition is observed for the three possible geometric isomers of diethyl deca-2,8-diene-1,10-dioate for which n = 4.



As has been noted (10), crossed cycloaddition usually predominates (in the absence of prohibitive steric constraints) for dienes in which n = 2, and straight cycloaddition is favored for dienes with n values of 3, no n = 4 systems having been previously investigated to the best of our knowledge. It was of particular interest for us to observe this specificity in a 1,7-diene system since the "rule of five" (10), a mnemonic which correctly predicts the major cycloaddition paths taken by 1,5 and 1,6-dienes, is inapplicable in this case.

The present results with the deca-2,8-diene-1,10-dioates are probably most straightforwardly rationalized on the grounds that formation of the most stable diradical intermediate through a cyclic six-membered transition state determines the crossed *vs* straight nature of the cycloaddition.



VIII

The steric course followed in these cyclizations is difficult to explain for two reasons, a) *cis,trans double bond isomerization in I - III is faster than cycloaddition*, and b) photoproduct VI is invariably formed in greater amounts than V even though V has been shown (11) to be thermodynamically more stable than VI. On the other hand IV is always formed in preference to VII which *is* compatible with their observed relative thermodynamic stabilities (11). Evidently, factors other than thermodynamic stability govern the closure of the putative diradical intermediate VIII, at least in the case of formation of V and VI, or else one or more of the cycloadditions is concerted. It should be noted that the products IV - VII can in theory arise from concerted $\pi_2^s + \pi_2^s$ internal cycloaddition (12) of I and II (i.e., I → IV + VI and II → V + VII).

Nevertheless, the postulate of diradical intermediates is supported by a) the initiation of the cycloadditions from triplet excited states, and b) the failure to observe products derived from concerted $\pi_2^s + \pi_2^s$ cycloaddition of the *cis,cis*-diene III, even when III is used as the starting material.

Since the direction (i.e., straight or crossed) of light induced intramolecular cycloaddition reactions of non-conjugated dienes cannot always be rationalized on the basis of radical stability, most notably in the case of 1,5-hexadiene and its derivatives, we are currently investigating the possibility that certain reactions of this type, regardless of the stability of the diradicals involved, may be explicable in terms of conformational effects coupled with consideration of the nodal properties of the dienes' excited state highest occupied molecular orbitals.

ACKNOWLEDGEMENT

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REFERENCES

1. Part II: J.R. Scheffer and B.A. Boire, *Tetrahedron Lett.*, 4005 (1969).

2. National Research Council 1967 Science Scholarship Fellow, 1967 - present.

3. J.R. Scheffer and M.L. Lungle, *Tetrahedron Lett.*, 845 (1969).

4. Diethyl *trans,trans*-deca-2,8-diene-1,10-dioate (I) was prepared by the method of J.D. Anderson, *et. al.*, *J. Org. Chem.*, *31*, 3890 (1966). The geometric isomers II and III were fully characterized by elemental analysis and spectral data. Details will be presented in the next paper in this series on the direct photolysis of I, J.R. Scheffer and B.A. Boire, in preparation.

5. Photolyses were carried out in a water cooled immersion well apparatus using a 450 Watt Hanovia lamp and a Corex filter.

6. Analytical vapor phase chromatography was performed using a 5' x ¼" stainless steel column packed with 20% DEGS on 60/80 Chromosorb W at a temperature of 160° and a helium flow of 180 ml/min. Preparative vpc was carried out at the same temperature and flow rate on a 20' x 3/8" aluminum column packed with 30% DEGS on 45/60 Chromosorb W.

7. Vpc analysis good to approximately ±2%.

8. a) P. deMayo, S.T. Reid, and R.W. Yip, *Can. J. Chem.*, *42*, 2828 (1964).
   b) R. Robson, P.W. Grubb, and J.A. Barltrop, *J. Chem. Soc.*, 2153 (1964).

9. Experimental details of the characterization of compounds IV - VII will be given in the full paper.

10. R. Srinivasan and K.H. Carlough, *J. Amer. Chem. Soc.*, *89*, 4932 (1967).

11. Robson, Grubb and Barltrop (8b) concluded from base-catalyzed epimerization experiments that *dimethyl* V was thermodynamically more stable than dimethyl VI and that dimethyl IV was thermodynamically more stable than dimethyl VII. We have come to the same conclusion for the *diethyl* esters IV-VII on the basis of base-catalyzed and thermal equilibration studies. Thus for example, thermolysis of either pure V or pure VI at 250° in a sealed tube for anywhere from 28 to 88 hrs gives an 81 : 19 mixture of V : VI with only a trace (< 1%) of any other products observable.

12. R.B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, *8*, 781 (1969).