The Mechanism of the Photochemical Cyclisation of Non-conjugated Dienes: Dimethyl Nona-2,7-diene-1,9-dioate

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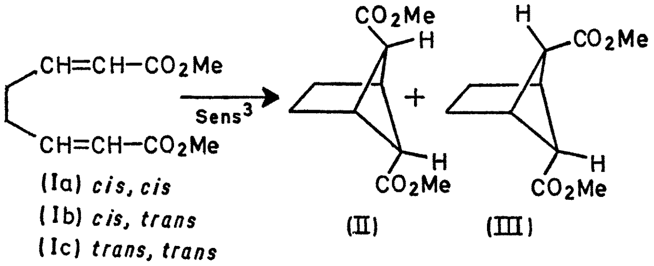
Summary Photolysis of acetone solutions of the *cis,cis*-, the *cis,trans*-, and the *trans,trans*-1,6-dienes (VIa—c) leads in each case to *cis–trans*-isomerization and, at a comparable rate, to formation of the cyclised products (VII) and (VIII).

PREVIOUSLY we showed[1-3] that the triplet-sensitized photolysis of the isomeric 1,5-dienes (Ia—c) leads to the "crossed" internal adducts (II) and (III)[1] and that similar excitation of the 1,7-dienes (IVa—c) gives exclusively "straight" cycloadducts of gross structure (V).[2,3] Despite the fact that these internal cycloadditions are photochemically allowed to proceed in a concerted $\pi_{2}^{s} + \pi_{2}^{s}$ manner,[4] convincing evidence was presented[1-3] which indicated that these cyclisations are in fact two-step processes involving biradical intermediates. This evidence was based primarily on the observation that the stereochemistry of the adducts differed from that expected if the cyclisations were concerted.

In order to complete this study, we have investigated the triplet-sensitized irradiation of the three isomeric 1,6-dienes (VIa—c) and report here that (a) cycloaddition occurs in an exclusively straight manner from all three geometric isomers to give the epimeric dimethyl bicyclo[3,2,0]heptane-2,3-dicarboxylates (VII) and (VIII), and (b) the cyclisations are again very likely non-concerted.

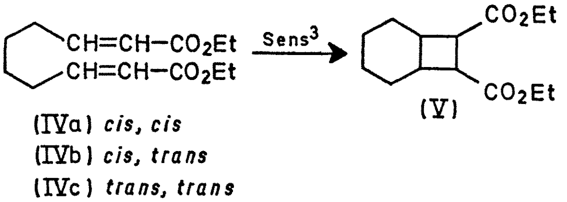
The *trans,trans*-diene (VIc) was prepared as described[5] and photolysed anaerobically as a 1% solution in acetone as triplet-energy sensitizer and solvent. The photoylsis was monitored by quantitative g.l.c. which showed the formation of the geometrical isomers (VIa) and (VIb) and, at a similar rate, the production of two photo-stable products subsequently shown to have structures (VII) and (VIII). After 6 h, starting with 0·10 g of (VIc), g.l.c. peaks corresponding to (VIa—c) were absent, and only photoproducts (VII) and (VIII) were present in a photostationary state ratio of *ca.* 3:1 in approximately 90% yield. A typical plot of the percentages of the various photoproducts against time is shown in the Figure.

Photolysis as above of either the pure *cis,trans*-isomer (VIb) [obtained by preparative g.l.c. of the initial (VIc) photolysis mixture] or of pure *cis,cis*-isomer (VIa)† gave results which were virtually identical to each other and to the results of the photolysis of (VIc); both gave (VII) : (VIII) ratios of 3:1 and differed only in the speed with which this photostationary state was attained: 3 h starting



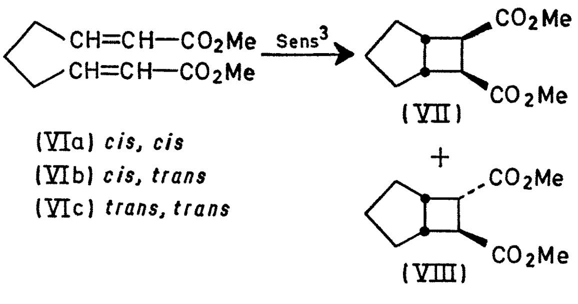
(Ia) *cis, cis*
(Ib) *cis, trans*
(Ic) *trans, trans*

(II) (III)



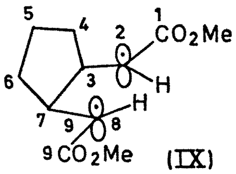
(IVa) *cis, cis*
(IVb) *cis, trans*
(IVc) *trans, trans*

(V)

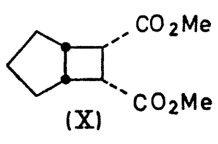


(VIa) *cis, cis*
(VIb) *cis, trans*
(VIc) *trans, trans*

(VII) (VIII)



(IX)



(X)

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† *cis,cis*-Diene-diester (VIa) was prepared by carbonation of the di-lithio-derivative of hepta-1,7-diyne followed by esterification and hydrogenation over palladium on barium sulphate catalyst poisoned by synthetic quinoline.

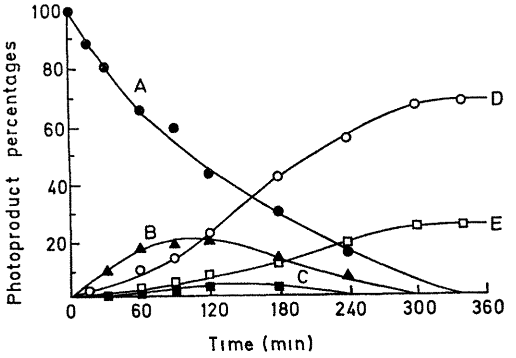

FIGURE *Photoproduct percentages as a function of time in the photolysis of* (VIc) (A) *Disappearance of* (VIc), (B) *formation and disappearance of* (VIb) (C) *formation and disappearance of* (VIa), (D) *formation of* (VII), (E) *formation of* (VIII)

with 0 10 g of (VIb) and 2 h starting with the same amount of (VIa)

Photoproducts (VII) and (VIII) were easily isolated in pure form by preparative g l c and were identified by hydrolysis to the corresponding known[6] dicarboxylic acids as well as by direct comparison with authentic samples independently prepared by the photochemical addition of dimethyl maleate to cyclopentene [6]

The fact that all three geometrical isomers (VIa—c) give, within experimental error, the same (VII) · (VIII) = 3 1 ratio coupled with the observation that cyclisation is nearly as fast as *cis trans*-isomerization, argues strongly for a non-concerted mechanism involving a common intermediate A likely candidate for this common intermediate is the vibrationally deactivated[7] triplet 1,4-biradical (IX) formed through initial 1,5-bonding, spin inversion and closure of (IX) then completes the cyclisation Apparently the closure of (IX) is kinetically controlled since the major product of the cycloaddition, (VII), is thermodynamically less stable than (VIII) This is shown by the fact that sealed-tube thermolysis (250°, 24 h) of either (VII) or (VIII) leads to an equilibrium (VII) : (VIII) ratio of *ca* 1 : 7 The source of this kinetic control is presumably the avoidance of *syn* non-bonded C-1—C-4 and C-6—C-9 interactions in the transition state for closure of diradical (IX) Indeed, the *cis,syn cis*-cycloadduct (X) is not formed at all The observation that (VIII), not (VII), is the major cyclisation product formed in the dimethyl maleate–cyclopentene photolysis[6] is in accord with this picture

The triplet, and hence non-concerted, nature of these cyclisations[5] is further shown by the direct photolysis results Photolysis of methanol solutions of *trans,trans*-diene (VIc) leads to geometrical isomerism, internal cyclisation, and to α,β to $\beta\gamma$ double-bond migration [8] The final photostationary state mixture consisted of *ca* 60% of (VII) and (VIII) (ratio 3 : 1) and 40% of dimethyl *trans,trans*-nona-3,6-diene-1,9-dioate, the double deconjugation product The question of whether the cycloaddition observed upon direct irradiation is singlet or triplet in nature will have to await quenching studies which are in progress Unsaturated ester deconjugation is characteristically a singlet-state reaction [3,8]

The direction of cyclisation found in the present work (straight) is the same as that observed in the photolysis of a number of other cyclic and acyclic 1,6-dienes [9] While the formation of photoproducts (VII) and (VIII) is in accord with traditional concepts of product control through radical stability,[10] we have been intrigued for some time by the possibility that the internal photocyclisations of non-conjugated dienes may be controlled by orbital symmetry effects This approach has been outlined for the 1,7-diene cyclisations[3] and can also be applied to the 1,6-diene cycloadditions described here Its application to 1,5- and 1,4-diene cyclisations will be discussed in a forthcoming full paper

The 1,8- and 1,9-dienes in this homologous series do not undergo triplet-sensitized cyclisation The sole reaction of these dienes upon prolonged irradiation in acetone was geometrical isomerism, both gave rise to identical *cis,cis cis,trans* . *trans,trans* ratios of 1 . 2 5 1 5

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