

The Photosensitized Cyclisation of the Geometrical Isomers of Dimethyl Octa-2,6-diene-1,8-dioate

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Summary Photolysis of acetone solutions of the 1,5-dienes (VIIa—c) leads to *cis,trans*-isomerization with concomitant formation of the cyclised products (VIII) and (IX).

TRIPLET-SENSITIZED photolysis of the 1,6-diene (I)¹ and of the three 1,7-dienes (IVa—c)² has been shown to give cyclised products with gross structures (III) and (VI), respectively.^{1,2} These results may be rationalized on the basis that the direction of bond formation leading to the bicyclo[*n*,2,0] systems (III) and (VI) rather than to

bicyclo[*n*,1,1] systems is determined by preferential formation of the presumed most stable diradicals (II) and (V) in each case.

That such an argument does *not* serve to predict the course of reaction for the geometrical isomers of the 1,5-diene system (VII) is shown by the fact that (VIIa—c) undergo photosensitized cyclisation to give exclusively the bicyclo[2,1,1]hexane isomers (VIII) and (IX).

Thus typically, photolysis[†] of 250 mg of dimethyl octa-*trans*-2,*trans*-6-diene-1,8-dioate (VIIa)³ in 200 ml of acetone for 1.25 h afforded a photostationary 65:35 mixture of (VIII):(IX) in high yield. The reaction was followed

[†] Photolyses were performed in a water-cooled immersion well apparatus using a 450w Hanovia Type L lamp and a Corex filter. Only the acetone absorbed light under these conditions. Solutions were thoroughly degassed with argon (<5 p.p.m. oxygen) prior to photolysis.

quantitatively by g.l.c.† which showed the formation and decay of the *cis,trans*- and *cis,cis*-isomers (VIIb) and (VIIc), as well as the disappearance of (VIIa) and the build-up of (VIII) and (IX) during the course of the photolysis.

Interruption of the photolysis while appreciable amounts of *cis,trans*-isomer (VIIb) were still present permitted its isolation by preparative g.l.c. Its n.m.r. spectrum was identical with that reported⁴ (J_{trans} 15.5 Hz and J_{cis} 11.2 Hz), and its other spectral and physical properties were completely in accord with its structure.

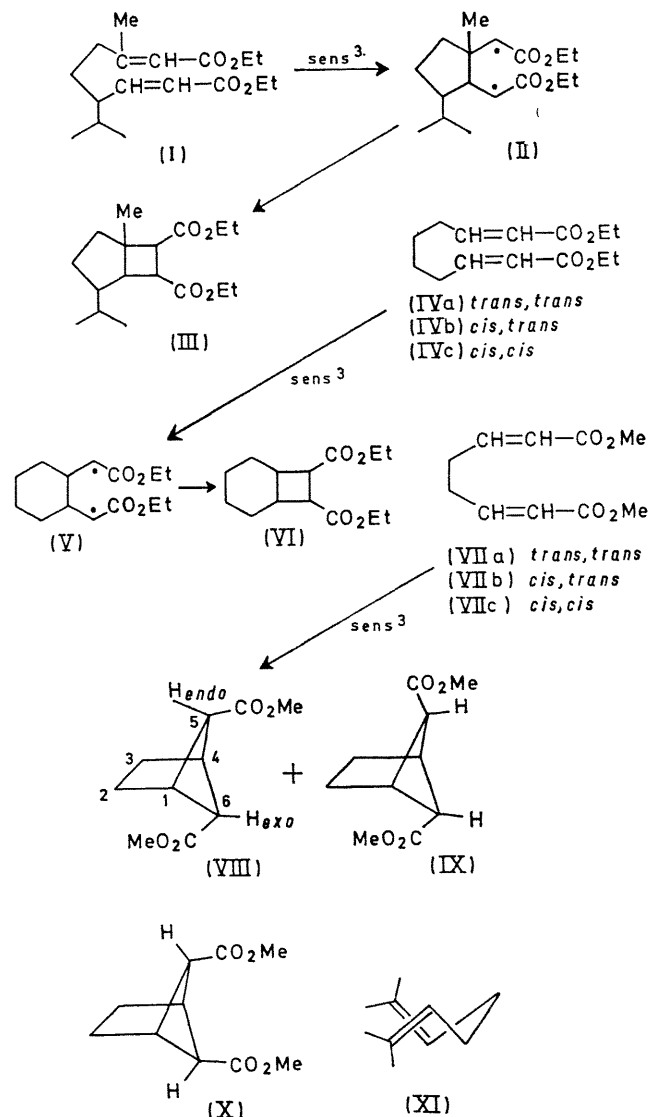
Photolysis of (VIIa) as above led to the formation and disappearance of diesters (VIIa) and (VIIc), as determined by quantitative g.l.c., and to the eventual sole production of the saturated diesters (VIII) and (IX) in the same 65:35 ratio.

The diene-diester (VIIc) was isolated with difficulty in very small amounts by preparative g.l.c. and shown from spectral data to have *cis,cis*-geometry; its n.m.r. spectrum was identical with that reported⁴ (J_{cis} 11.2 Hz). We tentatively conclude that (VIIc) also leads to cyclised products (VIII) and/or (IX) upon photolysis since it is unequivocally present during photolysis of (VIIa) (max. 7%) and VIIb (max. 11%) and no final products other than (VIII) and (IX) were detectable by g.l.c.

The structures of bicyclic esters (VIII) and (IX) were proved by spectral data and by their non-identity with the three known⁴ dimethyl bicyclo[2,2,0]hexane-2,3-dicarboxylates. Photoproduct (VIII), m.p. 65–66°, and (IX), m.p. 83–85°, were shown to be isomeric with starting material by elemental analysis and mass spectrometry. The n.m.r. spectra (100 MHz) of (VIII) and (IX) were particularly revealing; neither showed signals attributable to vinyl hydrogens. For (VIII), n.m.r. (CCl₄) showed δ 1.73 (m, 4, 2- and 3-H₂), 2.04 (s, 1, 5-H *endo*), 2.98 (d, 2, J 3 Hz, 1- and 4-H), 3.25 (m, 1, 6-H *exo* deshielded by 5-*exo*-CO₂CH₃), 3.60 (s, 3, 6-*endo*-CO₂CH₃), and 3.68 (s, 3, 5-*exo*-CO₂CH₃). For (IX), the n.m.r. (CCl₄) showed δ 1.68 (s, 4, 2- and 3-H₂), 2.24 (t, 2, J 2.5 Hz, *exo* 5-H and 6-H), 2.89 (t, 2, J 2.5 Hz, 1-H and 4-H), and 3.58 (s, 6, *endo*-CO₂CH₃). Structure (IX) is preferred to (X) for the symmetrical cyclo-adduct for the following reasons: (a) The experimental coupling $J_{1,6} = J_{4,6} = J_{1,5} = J_{4,5} = 2.5$ Hz found for this isomer is typical of *exo*-proton-bridgehead coupling in bicyclo[2,1,1]-hexane systems;⁵ *endo*-proton-bridgehead coupling in bicyclo[2,1,1]hexane systems is zero⁶ as typified in (VIII) ($J_{1,5} = J_{4,5} = 0$ Hz causing 5-H to appear as a singlet and 1-H and 4-H to appear as a doublet), and (b) the equivalent 5- and 6- protons of the symmetrical cyclised product appear at lower field (δ 2.24) than would be expected for the *endo*-protons in (X). For example, the *endo*-proton in isomer (VIII) appears at δ 2.04. Attempted epimerization of either (VIII) or (IX) under a variety of conditions was unsuccessful. Similar behaviour has been observed for the methyl bicyclo[2,1,1]hexane-5-carboxylate system.⁶

For steric reasons, concerted formation of the bicyclo[2,1,1]hexane ring is most likely to occur from the "opposed" 1,5-diene conformation (XI). With this in mind, it can be seen that concerted cycloaddition of the *trans,trans*-diene (VIIa) should lead to (X), (VIIb) should give (VIII), and

(VIIc) should afford (IX). The fact that (X) is *not* formed, even when pure (VIIa) is used as starting material, we take as evidence that these cycloadditions, at least in the case of (VIIa), are occurring *via* non-concerted mechanisms. This



argument is supported by the triplet nature of the cyclisations. Direct photolysis of (VIIa–c) in hexane gives approximately 20% of the cyclised products (VIII) and (IX) (ratio 65:35) plus a host of new products whose structures are currently being elucidated.

The present results are in agreement with the well known tendency of 1,5-dienes to undergo "crossed" photo-cyclisation.⁷ While the reasons for this preference remain obscure, it is clear from this and other work⁸ that effects other than radical stability predominate; it may be that an important factor is the nodal character (symmetry) of the excited

† Analytical g.l.c. as well as isolation of the dienes (VIIb) and (VIIc) was carried out using a 5ft. \times $\frac{1}{4}$ in. stainless-steel column packed with 10% FFAP on 60/80 Chromosorb W at a temperature of 150° and a helium flow rate of 120 ml/min. Photoisomers (VIII) and (IX) were separated and collected using a 20ft. \times $\frac{3}{8}$ in. aluminium column packed with 30% Carbowax 20M on 45/60 Chromosorb W at 200° and a flow of 90 ml/min.

state highest occupied molecular orbital which is different from that of 1,6- and 1,7-dienes due to through-bond coupling⁹ in the 1,5-diene system.

We thank the National Research Council, the Research

Corporation, and the University of British Columbia for financial support.

(Received, November 23rd, 1970; Com.2024.)

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