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THE PHOTOCHEMISTRY OF CRYSTALLINE DIMETHYL ALL-TRANS-HEXATRIENE-1,6-DICARBOXYLATE

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Following our study of the solid-state photochemistry of muconic-acid derivatives (1) we have analysed the photo-products of the dimethylester of all-trans-hexatriene-1,6-dicarboxylic acid (I) in order to test the solid-state behaviour of trans-triene systems. Since (I) and its lower homologue dimethyl trans-trans-muconate crystallise in closely related packing arrangements (2) differences in their photochemistry could yield useful information on the role of crystal structure on reactions in the solid state. It has now been found that (I) gives a cyclobutane dimer as well as polymer, whereas dimethyl trans-trans-muconate is lightstable under identical conditions.

(I), m.p. 172° (3), after recrystallisation from ethanol, was irradiated under "pyrex" for 6 days in sunlight ($\lambda > 290$ mμ); powder photographs of the irradiated sample showed new lines while some lines of the monomer pattern had become diffuse. The reaction was interrupted after a low degree of conversion (dimer yield 22%) in order to avoid secondary reactions either of the dimer itself or of the monomer in its partially destroyed crystalline phase. Thin-layer chromatography (chloroform) and exposure to iodine vapour showed three peaks of R_F = 0 (polymer), 0.9 (monomer) and 0.5 (dimer). The mixture was dissolved in the minimum amount of chloroform and chromatographed on a silicic-acid column; the monomer and dimer were eluted with benzene and benzene/chloroform (9:1) respectively; the polymer remained on the column.

The structure of the dimer (II), m.p. 139-140°, as *dimethyl 1,3-trans-di-[4-(1-carbomethoxy)buta-1,3-trans-trans-dienyl] cyclobutane-2,4-trans-dicarboxylate*, was established as follows: the molecular weight M of $C_{20}H_{24}O_8$ is 392 (mass spectrum); the strongest peak at 196 $(\frac{m}{e} = \frac{M}{2})$ supports the cyclobutane structure in view of Mandelbaum's work (4) on the mass spectrometry of cyclobutanes. The NMR spectrum ($CDCl_3$) of (II) has maxima at τ = 2.90 (multiplet, β-hydrogen of the $C{=}C{-}CO_2Me$ system, at low field due to deshielding by the C=O group), 3.85 (multiplet), 4.20 (doublet, centered at 4.20 and separated by 15 cps), 6.30 (multiplet, overlapped with two sharp peaks at 6.30 and 6.38), 6.59 (multiplet), in the ratio 1:2:1:7:1. The spectrum shows the presence of a cyclobutane ring, of only two types of $-OCH_3$ groups (whose absorption overlaps that of one of the cyclobutane hydrogens), and of the *trans*-configuration of the α,β-double bond. The τ value of the β-hydrogen corresponds well to that of Hβ in dimethyl *trans*-*trans*-muconate (5); the *cis*oid conformation of the $C{=}C{-}CO_2Me$ system, which may account for this deshielding effect (6) has already been postulated as characteristic of such groups from a consideration of non-bonded interactions (7) and recently been demonstrated in (III) by an X-ray structure analysis (8).

The infrared spectrum (in KBr) with maxima at 1700 and 1725 $cm.^{-1}$ indicates two carbomethoxy groups of which one is conjugated to a double bond; the maxima at 1640(s), 1612(s), 1005(s) and 945(m) $cm.^{-1}$ support the argument for the presence of an all-trans-diene system; the absence of bands at 820 and 830 $cm.^{-1}$ rules out the α,β-cis-configuration (9). The ultraviolet system (EtOH) with a maximum at 266 mμ (log ε = 4.31) suggests the presence of a diene system attached to a cyclobutane; the bathochromic effect of the four-ring on the diene system has been noted by Wren (10).

Ozonolysis of the dimer in acetic acid (2 hrs.) and treatment of the reaction mixture with 20% hydrogen peroxide gave 1,3-trans-dicarbomethoxy-cyclobutane-2,4-trans-dicarboxylic acid, m.p. 179-180° from acetone, identical (powder photography) with the ozonolysis product obtained in 33% yield from the dimethylester of 2,2'-dimethoxy-α-truxillic acid (IV) of m.p. 132°. Since the centrosymmetric configuration of this truxillic acid ester had been established by NMR (11) and by crystallographic (12) methods the ozonolysis product must have the structure (V) which is supported by the appearance of two bands of equal intensity at 1725 and 1755 $cm.^{-1}$. It is not identical with the solid-state photodimer (VI) of monomethyl fumarate (13) but gives on methylation with diazomethane the solid-state dimer (VII) of dimethyl fumarate (14).

In the triclinic crystal structure of the monomer (a = 7.60, b = 5.99, c = 13.06 Å, α = 81.4°, β = 107.7°, γ = 105.9°; space group $P\bar{1}$; n = 2) all molecules are likely to be parallel by analogy with the crystal structure of dimethyl trans-trans-muconate (8). Since the unit cell does not have a 4 Å axis [which should yield (VIII)] the only other symmetrical dimer to be expected from a topochemically controlled reaction is (II).

The formation of a cyclodimer from a crystalline hexatriene derivative shows that this solid-state reaction occurs with a minimum amount of molecular motion; first, the trans-configuration of the triene system is preserved, after reaction, both in the cyclobutane and its substituent groups; secondly, we have found no other dimers or rearranged monomeric compounds. In particular, the latter which are characteristic products of the solution-photochemistry of acyclic trienes and which are formed via trans-cis-isomerisation and ring-closure (15), are not observed in the solid-state reaction.

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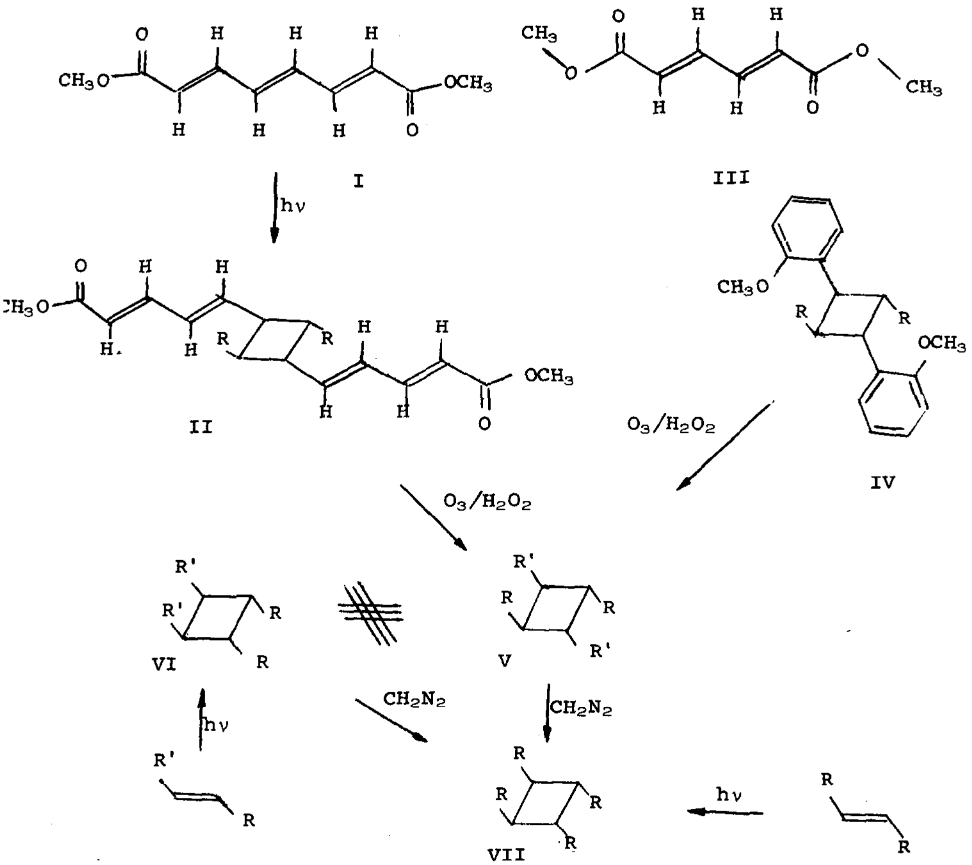
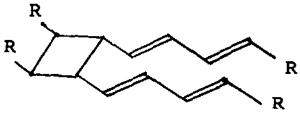


$R = CO_2CH_3$
$R' = CO_2H$



VIII

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