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TOPOCHEMICALLY-CONTROLLED SOLID-STATE PHOTODIMERIZATION TO A TRICYCLO[6.2.0.0.^{3,6}]-DECANE DERIVATIVE

Bernard S. Green and G.M.J. Schmidt
Department of Chemistry, Weizmann Institute of Science, Rehovot, Israel

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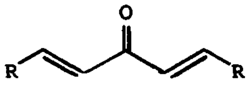
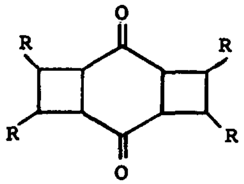
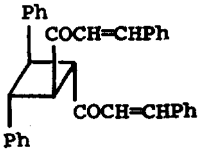
The tricyclo[6.2,0.0.^{3,6}]-decane ring system has been claimed for only one compound, the solid-state photodimer 2 of dimethyl 3-keto-penta-1,4-*trans*,*trans*-diene-1,5-dicarboxylate, 1;[1,2] however, the stereochemical assignment for 2 is ambiguous.[1] The photo-behaviour of 1 has long appealed to us[3] as a particularly interesting example of a topochemical reaction, reactivity and reaction products being determined by the crystal lattice of the starting material. Thus, the dimethyl ester 1 photodimerizes in the solid whilst the diethyl ester 3 is reported[2] to give only polymeric material and the diphenyl analogue 4 is light-stable[4] under these conditions. The solid diacid 5 has also been reported to photodimerize to a compound which after esterification is identical with the solid dimethyl ester photodimer 2.[5] In solution 4 undergoes photodimerization to the *all*-*trans*-substituted cyclobutane 6.[6]



1 R = CO_2Me
3 R = CO_2Et
4 R = C_6H_5
5 R = CO_2H
7 R = 3,4-$C_6H_3Cl_2$



2 R = CO_2Me
8 R = 3,4-$C_6H_3Cl_2$



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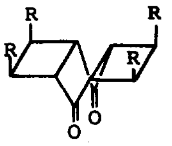
Recently it has been shown that halogen substitution in aromatic and related molecules favours crystal lattices with close-packed, translationally-related (head-to-head) molecular arrangements, having shortest unit-cell axes of *ca*. 4 Å.[7] Cyclobutanes produced under lattice control from such crystals will have mirror symmetry with respect to the two monomeric constituents. To test the general utility of this technique we have examined the photobehaviour of the tetrachloro-substituted diphenyldienone *7* which would be expected, if the above considerations hold, to produce a tricyclic ketone with the exactly defined stereochemistry *8a*.

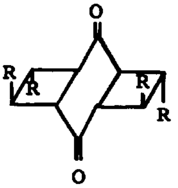
Irradiation through Pyrex of thin layers of 1,5-di(3,4-dichlorophenyl)-penta-1,4-*trans*,*trans*-dien-3-one, *7*, (yellow needles, m.p. 203-205°; ν_{max} (KBr) 1680, 1630, 1595 cm.$^{-1}$; λ_{max} (EtOH) 237 ($\epsilon \sim$ 20,000), 330 (36,000)nm; shortest unit-cell axis, 3.9 Å) with Westinghouse sunlamps or sunlight rapidly bleached the yellow color. Tlc (benzene eluent) analysis of the resulting creme-yellow solid (m.p. 105-115°; non-crystalline by powder photograph) revealed a strong spot more mobile than *7* in addition to "polymer" ($R_f \sim 0.0$). The photodimer was isolated by chromatography on a short silica gel column (chloroform) and then crystallized twice from carbon tetrachloride to give *8* as colorless prisms, m.p. 214-216° in *ca*. 20% yield. ν_{max} (KBr) 1730 cm.$^{-1}$; λ_{max} (EtOH) 296 nm sh ($\epsilon \sim$ 1920), 276 (2550), and 284 (2450). τ (CDCl$_3$) 2.6-3.4 (12H, m, aromatic hydrogens) and 5.5-5.9 (8H, m, cyclobutane hydrogens; A$_2$'B$_2$' pattern symmetric about 5.70). *m/e* 740 (M,Cl$_8$), 712 (M-CO), 370 (M/2,Cl$_4$), and 318 (C$_6$H$_3$Cl$_2$CH=CHC$_6$H$_3$Cl$_2$).

The formulated structure *8a* follows from the spectral data: the mass spectrum indicates that the photoproduct is indeed a dimer and the stilbene peak supports a 1,2-diarylcyclobutane structure; the i.r. and u.v. spectra show only simple ketone and non-conjugated phenyl absorption, respectively; the n.m.r. spectrum displays only aromatic and cyclobutane resonances, the latter having a highly symmetric pattern characteristic of mirror-type dimers.[8] Comparison with model compounds *9*[8] and *10*[9] corroborates the stereochemical assignment; in particular, the high field aromatic pattern, due to the mutually shielding 3,4-dichlorophenyl groups, is common to all three. The alternative structure *8b* is ruled out by the packing arrangement of the monomer crystal, the strain of *trans*-fusion of the cyclobutane rings, and the n.m.r. spectrum.



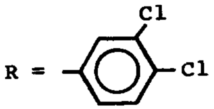
2a (R=CO_2Me)

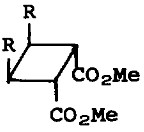
8a



2b (R=CO_2Me)

8b





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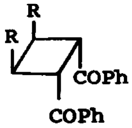

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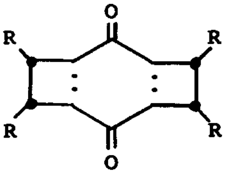

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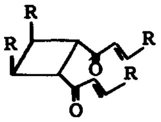

12

When the monomer was irradiated (sunlight) through Corning filters 0-53 (cut-off ~ 290 nm), 3-73 (~ 410 nm), or 3-72 (~ 445 nm) photodimer 8 and polymer were produced, as above; no new products could be detected. Irradiation through filter 3-71 (cut-off ~ 470 nm) led to no detectable change.

This experiment rules out the presence of an intermediate dicinnamoyl cyclobutane 12, which would have accumulated under such irradiation conditions, and implies simultaneous formation of both four-membered rings. A concerted, photochemical process, 6 + 6* → 8, is symmetry forbidden for an *n*-π* excited state which has an extra electron in the pi system; however, reaction may take place *via* interaction between one ground-state molecule and one excited-state molecule with simultaneous 1,1'-5,5' bonding to an intermediate "tetraradical", 11, which can then close to form the bridgehead bonds.[10] Alternatively, for a π-π* excited state the [4 + 4] double cycloaddition is a symmetry-allowed process leading directly to 8.

According to the cell constants of crystalline **1** (*a* = 15.45, *b* = 7.92, *c* = 3.96 Å, β = 102.3°, space group A2, Z = 2) photodimer **2** should, if produced in a lattice-controlled process, also have the mirror-plane configuration **2a** rather than the centro-symmetric configuration **2b** proposed earlier.[1]

Clarification of this point and additional work on the mechanism of these processes are presently being pursued.

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[10] We thank Dr. William C. Herndon for discussion of this point.