Topochemically Controlled Photodimerisation of Crystalline Methyl 6-Isobutenyl-2-methyl-4-oxocyclohex-2-enecarboxylate: A Chemical and *X*-Ray Crystallographic Study

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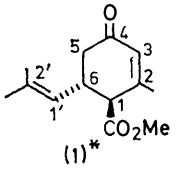
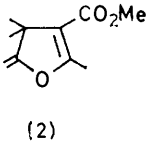
The chemistry of the cyclobutano-dimer (3), formed when methyl 6-isobutenyl-2-methyl-4-oxocyclohex-2-enecarboxylate (1) is irradiated with u.v. light in the crystalline state, is studied. Particular attention is given to the Baeyer–Villiger reactions of derivatives of (3) and the ensuing lactone isomerisations. This leads to a chemical proof of the antiparallel-*cis,anti,cis*-orientation of the dimer, the 1,2-substituents being *trans*-equatorial.

The topology of the system is examined in detail by *X*-ray crystallographic studies of the cyclohexenone (1) and its cyclobutano-dimer (3). Although the centre-to-centre distance of the nearest-neighbour double bonds falls within the usual range (3.86 Å), the geometry is apparently not ideal. Neighbouring monomer molecules move *ca.* 2.3 Å within the ring plane, as well as *ca.* 2.2 Å towards each other perpendicular to the ring plane, in order to take up the final dimer geometry.

PHOTOCHEMICAL [2 + 2]-cycloaddition dimerisations of α-unsaturated carbonyl compounds are numerous, but cases in which such dimerisation proceeds in the solid state are considerably fewer and there is a need for enlargement of current knowledge of the topochemistry of such systems.[1,2] During an earlier study it was established that the cyclohexenone ester (1) is formed,



(1)*



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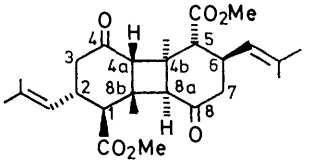

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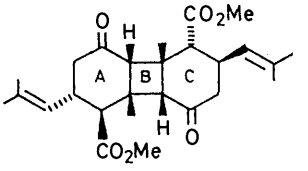

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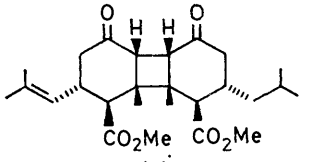

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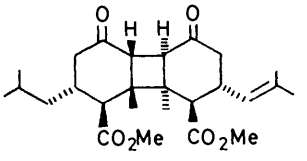
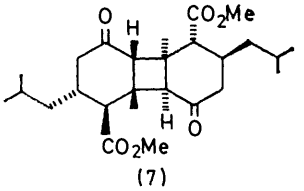


(6)

together with the methylenedihydrofuran (2), methyl 5-methylsorbate, and other products, when 3-chloro-3-methylbutyne is treated with methyl sodioacetoacetate: the mechanism of formation of these products has been considered.[3,4] On exposure to sunlight or ultraviolet light the massive lozenge-shaped crystals of the cyclohexenone become opaque and powdery and the product was shown to be a dicyclohexanocyclobutane photodimer.[3] It was not, however, known whether the monomeric ketone units dimerised antiparallel [(3),(4)] or parallel [(5),(6)] to each other, or whether the A- and C-rings were *syn* [(4),(5)] or *anti* [(3),(6)] to each other. Chemical proof of the antiparallel *cis,anti,cis*-structure (3) for the dimer is now presented along with a study of some aspects of its chemistry. The topology of the system is examined in detail by an *X*-ray single-crystal study of both the monomer (1) and the dimer (3).†

The *trans*-quasi-equatorial 1-ester, equatorial 6-isobutenyl, arrangement (1) is shown by n.m.r. data ($J_{1,6}$ 11 Hz) and persists in the dimer ($J_{1,2}$ 11.5 Hz). The latter readily forms a bis-2,4-dinitrophenylhydrazone, a bis-benzylidene derivative, and, on catalytic hydrogenation, a tetrahydro-compound; the ester group is very hindered and resistant to base hydrolysis.[3] Ozonolysis of (3) gives acetone and the expected diester-dicarboxylic acid.[3] Although resistant to perbenzoic and peracetic acids, the tetrahydro-dimer (7) gave a crystalline



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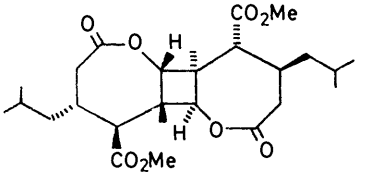

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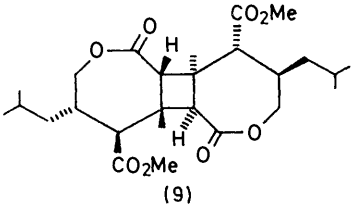


(9)

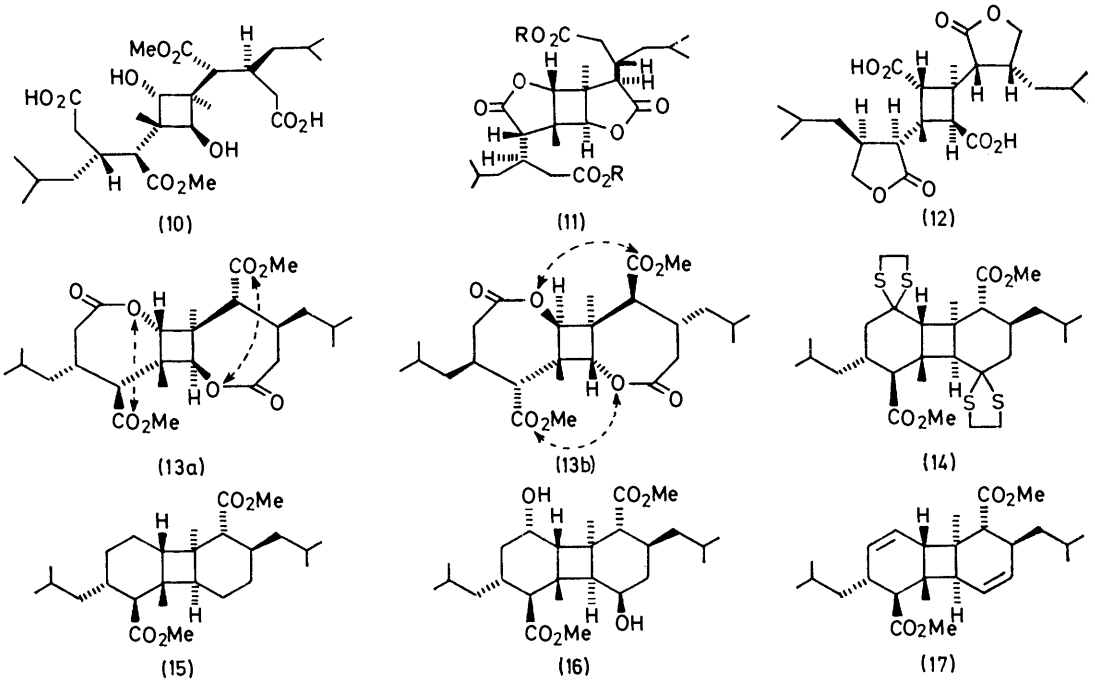
*All structures imply (±) compounds

† The non-crystallographic work described in this paper was carried out at Kings College, London, during 1958—1961; it was set aside until the *X*-ray crystallographic study could be undertaken.

dilactone when treated with trifluoroperoxyacetic acid and n.m.r. evidence showed that it was the expected product [5] (8) rather than the isomer (9). Thus the ratio of the integrals for the protons α to the ring oxygen (δ 4.50) and those α to lactonic carbonyl and ester (near δ 2.49) is 1 : 3, whilst in the isomeric structure (9) it would be 1 : 1.

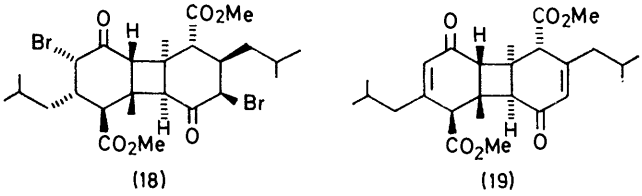
(8) as the antiparallel *trans,syn,trans*-geometry gives the same result, as implied in (13a) and (13b).

Formation of the bis-deoxy-dimer (15) was achieved by Raney nickel desulphurisation of the bis-thioacetal (14). It was also formed when the dimer (3) was hydrogenated over Adams platinum under acid conditions, but the extent to which this proceeds *via* direct



Hydrolysis of the dilactone (8) gave two products. One, (10), failed to react with periodate, and only slowly with lead tetra-acetate, showing that the two hydroxy-groups are not 1,2-*cis* to each other as would be required if the dilactone originated from a parallel dimer structure (5). The second hydrolysis product was the dilactone (11; R = H) containing two 5-membered lactone rings (ν 1 770 cm^{-1}) and two carboxylate residues (ν 1 709 cm^{-1}). The ester groups in (10) are much less hindered than in the original dimer (3) and on further hydrolysis and acidification lactonisation ensued giving (11; R = H). When treated with diazomethane (11; R = H) gave the same product (11; R = Me) as was produced when the dilactone (8) was treated with methanolic sulphuric acid. As required, the ratio of α-ester and α-lactone proton resonances (*ca.* δ 2.39—2.49) to α-ring oxygen proton resonances (*ca.* 4.5) in (11; R = Me) was 3 : 1: the alternative (12), derived from (9), requires 1 : 1. In addition, the nitro-compound formed from (11; R = H) by Hunsdiecker degradation of the disilver salt, and treatment of the resulting iodide with silver nitrite, is primary (nitrolic salt test), and not secondary. A point noted in passing is that the great ease with which the 5-membered lactone rings close to give the dilactone (11) is not unambiguous evidence for an antiparallel *cis,anti,cis*-arrangement

hydrogenolysis, or *via* dehydration of an intermediate diol followed by saturation, is uncertain. The diol (16), a product of borohydride reduction, required 14 days for dehydration to (17) under the acid conditions of the hydrogenation suggesting this is a less-favoured pathway. Measurement of the dipole moment of both the tetrahydro-dimer (7) and the tetrahydro bis-deoxy compound (15) gave values of zero within experimental error and this is clear evidence for an antiparallel arrangement: the parallel arrangements of (15) derived from (5) or (6) would have an appreciable dipole moment of *ca.* 2.0 D. It follows that the photo-dimer has either the antiparallel *cis,anti,cis*-structure (3) or the antiparallel *cis,syn,cis*-structure (4).



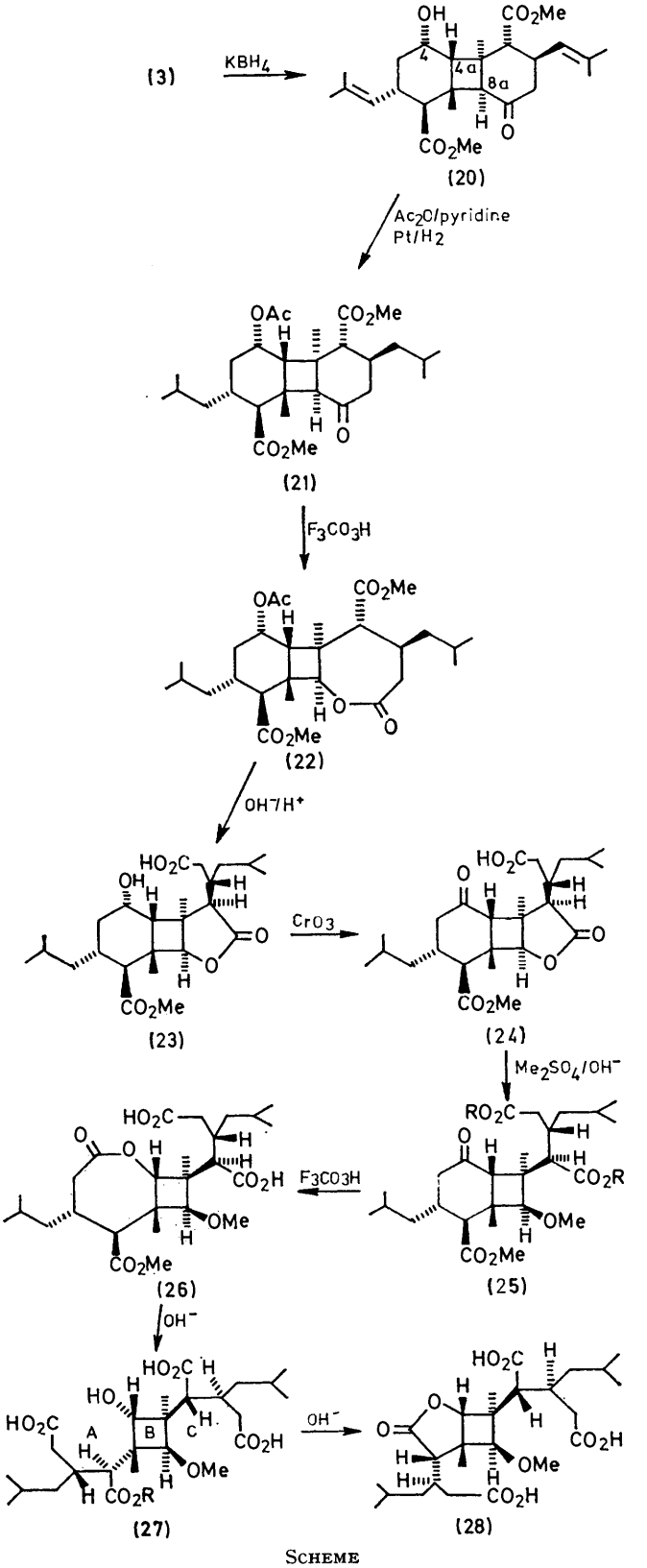
Some evidence that the former is the correct representation came from preparation of the dienone (19) by dehydrohalogenation of the axial bromination product (18) of the tetrahydro-dimer (7). Repeated attempts to

bring about photochemical ' box ' type dimerisation in the solid state, or in solution, failed, as it should for the *anti*-case (19). However, such evidence is negative, and a sequence giving positive proof was designed (see Scheme).

The scheme required selective opening of one six-membered ring of the tetrahydrophoto-dimer (7) but attempts to employ restricted amounts of pertrifluoroacetic acid gave mixtures of dilactone and unchanged diketone. Attempts to use catalytic hydrogenation selectively also failed, but selective reduction of one keto-function in the parent photodimer (3) was achieved by using the calculated quantity of potassium borohydride. Experiments using sodium borohydride were a failure, and the selectivity is probably due to the insolubility of the monopotassium complex in tetrahydrofuran. The crystalline ketol (20) * formed a mono-2,4-dinitrophenylhydrazone, and it was acetylated and hydrogenated to give (21). Baeyer–Villiger oxidation of the latter gave the ε-lactone (22) which on hydrolysis and then acidification gave the five-membered lactonic acid (23). Because of the *cis*-arrangement, the relactonisation is extremely rapid.

The alcohol (23) was oxidised by chromium trioxide to the ketone (24) which was methylated under basic conditions to give the methoxy-trimethyl ester (25; R = Me): base hydrolysis then produced the methoxy-monomethyl ester (25; R = H), the third ester function surviving because of its hindered situation. The intact ketonic ring was now expanded by Baeyer–Villiger reaction to give the seven-membered lactone (26). Mild hydrolysis of this gave two products. The first was the five-membered lactone (28) [$\nu_{max.}$ 1 770 (5-membered lactone), 1 712 cm^{-1} (acid)] whilst the second was the monocyclic tricarboxylic acid (27; R = Me) possessing hydroxylic absorption and i.r. bands due to ester (1 732 cm^{-1}) and acid (1 710 cm^{-1}). Under mild conditions which sufficed to lactonise the precursors of the dilactone (11) and monolactone (23), it failed to lactonise. This is clear, but negative, evidence that the free hydroxy-group and the side-chain residue C in (27; R = Me) are *trans*-disposed, *i.e.* that in the original dimer (3) rings A and C have an *anti*-relationship. The evidence became positive and rigorous when the monoester (27; R = Me) was hydrolysed with alkali and then acidified. Base hydrolysis formed the salt of the tetra-acid (27; R = H): except for stereochemical arrangement relative to the hydroxy-group, branches A and C are identical. On acidification the *cis*-branch A now lactonised immediately to give a five-membered lactonic acid identical with (28), mentioned above. This shows that the photodimer has the antiparallel *cis,anti,cis*- structure (3).

In order to pursue the topochemical aspects of the solid-state dimerisation, the crystal structures of the cyclohexenone (1) and its photodimer (3) were deter-



SCHEME

* This semi-reduction breaks the symmetry of the dimer and, when n.m.r. data became available, gave further evidence inconsistent with a parallel arrangement in either *syn*- or *anti*-form. The 4a-proton in (20) is now a doublet δ 2.41 (*J* 6 Hz) coupled to the quasi-axial 4-proton at 4.13 (eight line multiplet); it shows no coupling with the other cyclobutane proton, which is a singlet at 2.94, and hence has neither a *cis*, nor a *trans*, vicinal relationship to it.

mined by direct-phasing procedures from diffractometer data.[6] Refinement of the atomic parameters by least-squares and difference-Fourier methods converged to R 6.0% (cyclohexenone) and R 6.6% (photodimer) over 1 259 and 1 631 independent observed reflections

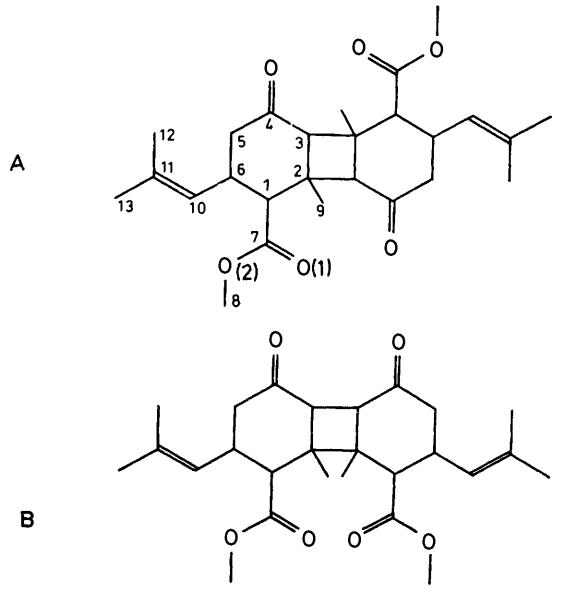


FIGURE 1 Two possible orientations for the photodimer with crystallographic numbering.

respectively. The photodimer was found to show the centrosymmetric antiparallel structure (Figure 1A) rather than the alternative mirror plane parallel structure (Figure 1B), in agreement with chemical conclusions. Indeed the asymmetric unit contained only one ' monomer ' unit and the two halves of the molecule are related by a crystallographic centre-of-symmetry in the triclinic space-group $P\bar{1}$. In the structure of the cyclohexenone, the molecules are arranged in the crystal lattice such that nearest-neighbour double bonds are related across a centre of symmetry, accounting for the geometry of the dimer structure.

For crystallographic purposes the cyclohexenone was numbered as in Figure 2, and a similar system was adopted for the dimer (Figure 1). Bond lengths and angles are displayed in Figures 3 and 4: none of these

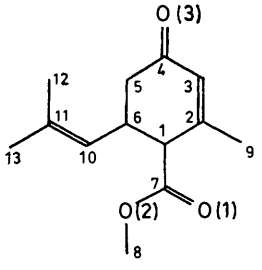


FIGURE 2 Crystallographic numbering scheme for the cyclohexenone (1)

differ significantly from expected values and they are remarkable only for the close agreement (where appropriate) between cyclohexenone and photodimer structures. The arrangement of the molecules within their respective unit cells is shown in Figures 5 and 6. In the cyclohexenone structure (monoclinic space-group $P2_1/c$, projected along the b-axis) the close approach of the double bonds [C(2)–C(3)] around the centre of symmetry at (0.5, 0.5, 0.5) is clearly visible giving rise directly to a centrosymmetric photodimer. In the photodimer structure (shown projected along the a-axis of the triclinic unit cell), the molecular centre of symmetry coincides with the crystallographic centre at the origin (0, 0, 0). The different cell dimensions and symmetries afford no other direct comparisons between these packing views. No intermolecular contacts less than the sum of the van der Waals radii were discovered in either structure, the shortest contact being 3.47 Å.

The packing of the molecules around the apparent locus of the solid-state photodimerisation reaction is shown more clearly in Figures 7 and 8. Figure 7(a) depicts the two cyclohexenone molecules related by the

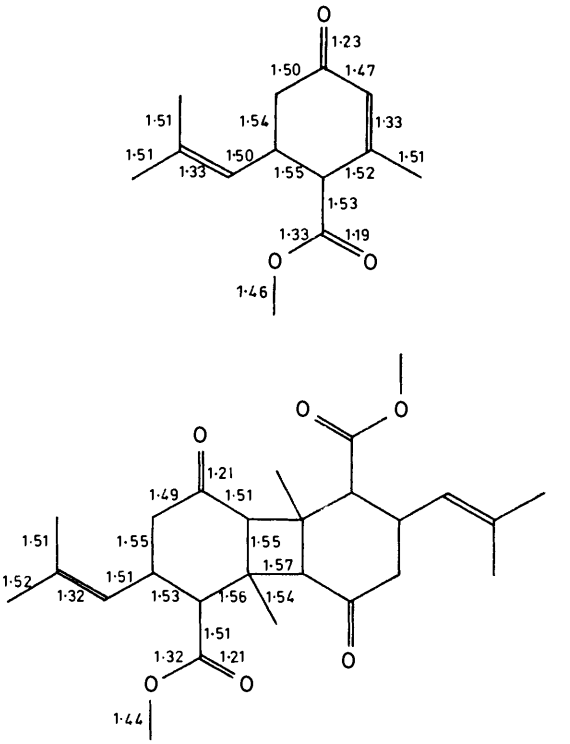


FIGURE 3 Bond lengths in Angstrom units. Largest standard deviations 0.006 A

centre of symmetry at (0.5, 0.5, 0.5) projected onto the plane of the enone [C(2), C(3), C(4)]. Figure 7(b) shows the same view of the photodimer molecule. Figure 8 illustrates the same pair of molecules and the resultant photodimer viewed parallel to this plane and perpendicular to the C(2)–C(3) bond. The centre-to-centre distance of the nearest neighbour double bonds that undergo photodimerisation [C(2)–C(3′)] is 3.86 Å. This lies within the range 3.5—4.2 Å previously observed for such reactions in the solid state.[7] However, inspection of Figures 7 and 8 reveals that although the molecules are

sufficiently close, the packing geometry is not ideal for such a reaction which formally requires the *p*-orbitals of

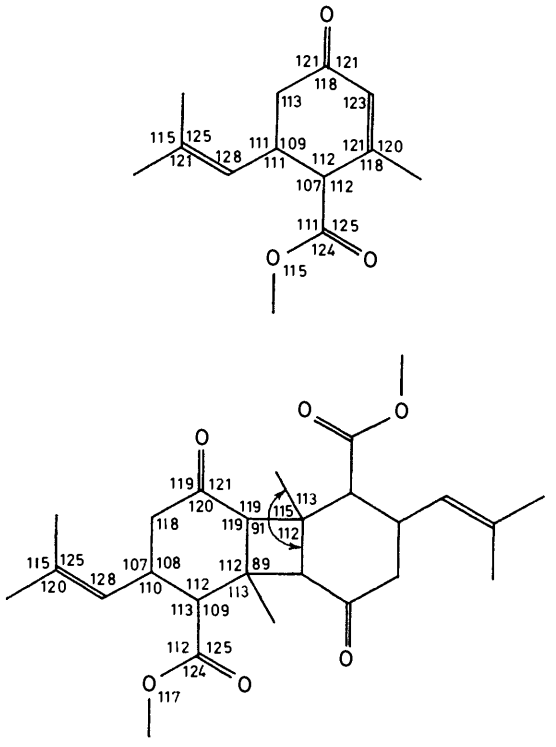


FIGURE 4 Bond angles in degrees. Largest standard deviations 0.5°

C(2′)–C(3′) and C(3)–C(2) to be directed towards one another. This deviation from ideality is bext expressed as the dihedral angle between the planes containing C(2), C(3), C(2′), C(3′) and C(2), C(3), C(4) which is 72.8° rather than an ideal value of 90°. Confirmation of the distortion comes from an observed C(2)–C(3)–C(2′) angle of 77.9°. fact Figure 7(*a*) shows that C(2) and C(4′) eclipse each other and comparison with Figure 7(*b*) reveals that neighbouring molecules are moved about 2.3 Å within the ring plane in the approximate direction of the C(4)–C(3) bond during the course of the photodimerisation reaction. Figure 8 shows that the perpendicular distance between the planar portions of the cyclohexenone rings in the related molecules is 3.5 Å, while in the photodimer this is reduced to 1.3 Å. Thus

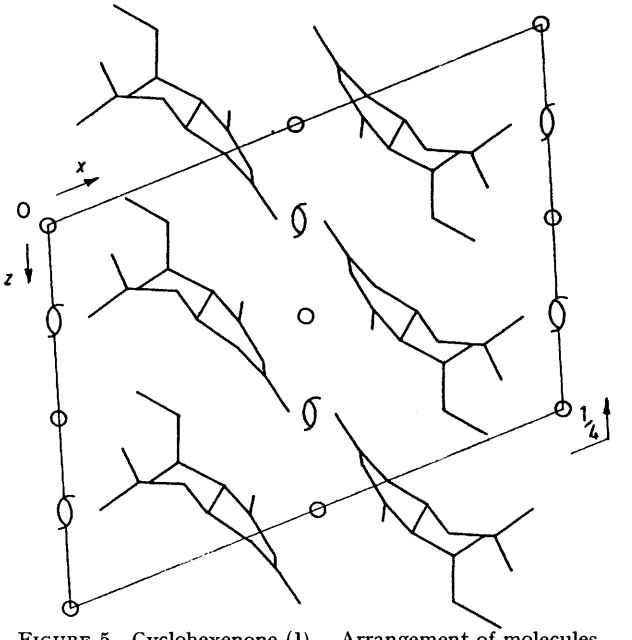


FIGURE 5 Cyclohexenone (1). Arrangement of molecules within unit cell projected perpendicular to *b* axis

neighbouring molecules are also moved 2.2 Å perpendicular to the ring plane during the course of photodimerisation. Comparison of the volumes of the

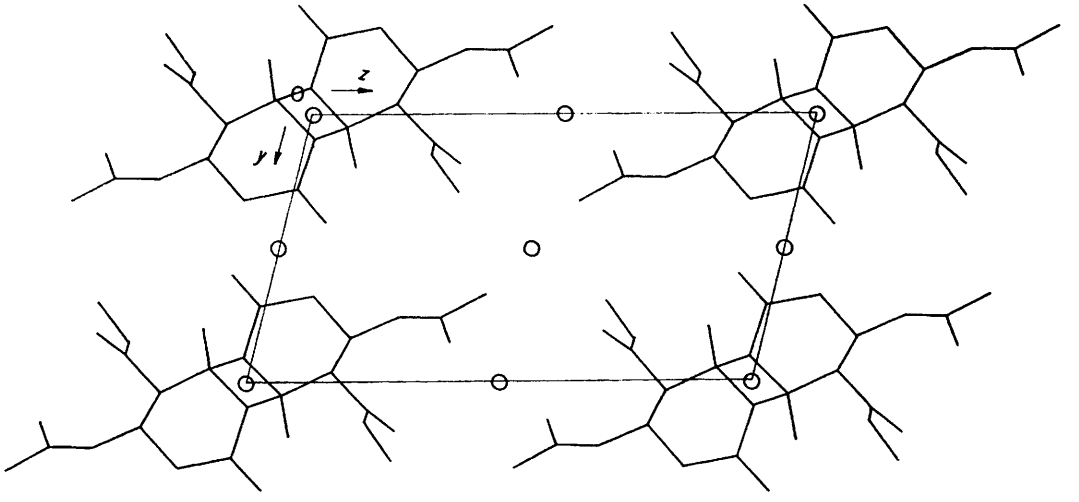


FIGURE 6 Photodimer. Arrangement of molecules within unit cell projected perpendicular to *a* axis

The deviation is also revealed in Figure 7(*a*) in which one would expect atoms C(2) and C(3′) in related molecules to eclipse each other for perfect reaction geometry. In respective unit cells reveals that there is a contraction of 3% in the photodimer lattice relative to the monomer lattice. The extent to which lattice defects may be

involved in the photodimerisation process [1] is at present uninvestigated.

Figures 7 and 8 also reveal fairly large conformational changes between the cyclohexenone and photodimer.

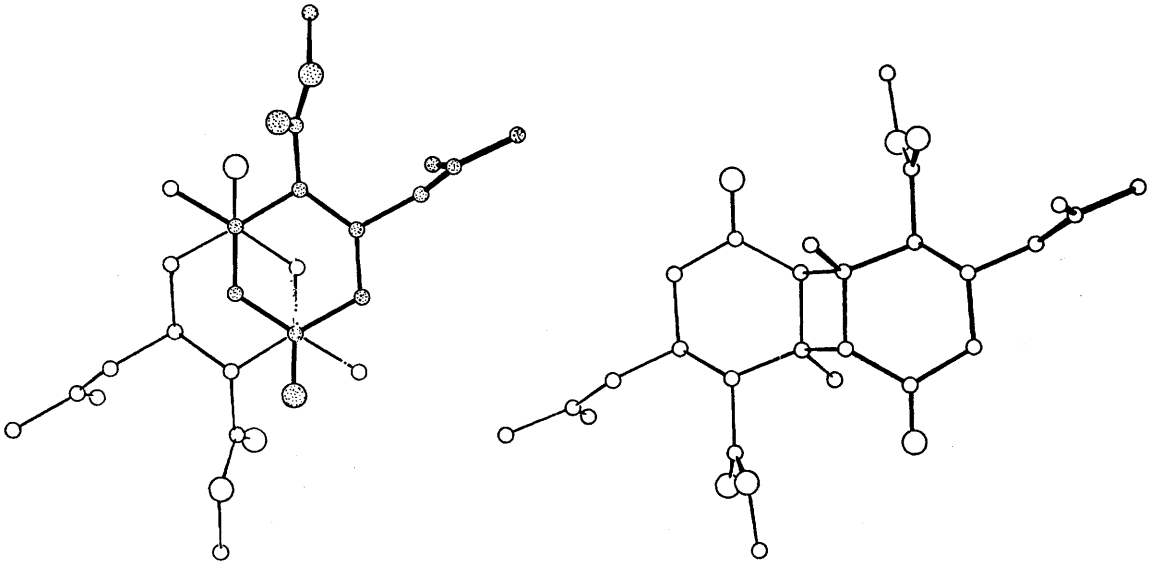


FIGURE 7 (*a*) Two centrosymmetrically-related cyclohexanone molecules, and (*b*) the photodimer viewed perpendicular to the ring plane

These changes are confirmed by a comparison of the torsion angles shown in Table 1: these display far less agreement between structures than bond lengths and angles. Such differences are partly due to the change in ring shape from cyclohexenone to cyclohexanone and are most noticeable in the neighbourhood of the carboxylate: they are presumably caused partly by closer van der Waals contacts in the photodimer molecule.

Attempts were made to dimerise photochemically a few compounds closely related in structure to ester (3). The acid (29; R = CO_2H, R′ = $Me_2C{:}CH{\cdot}$) [3] did not dimerise either in solution or the crystalline state, and neither did the ester (29; R = CO_2Me, R′ = $Me_2CH{\cdot}CH_2$). When irradiated as pure liquids, the ketones (29; R = H, R′ = $Me_2C{:}CH$) and (29; R = H, R′ = $Me_2CH{\cdot}CH_2$) also gave no dimer and the only other successful dimerisation was of the ethyl ester (29; R = CO_2Et, R′ = $Me_2C{:}CH$), made by diazomethane esterification from the acid. This, like the methyl ester, dimerised in the crystalline state but not in solution

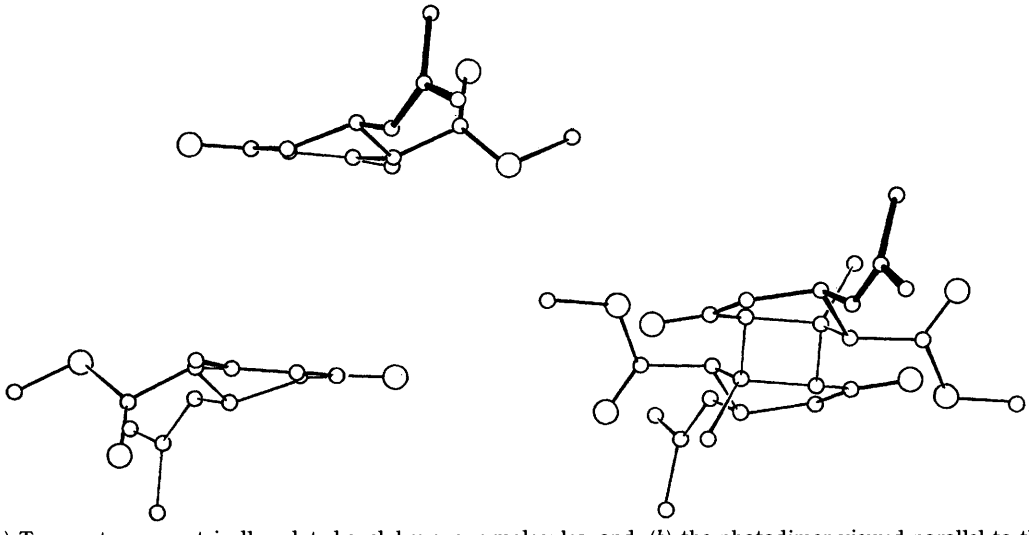
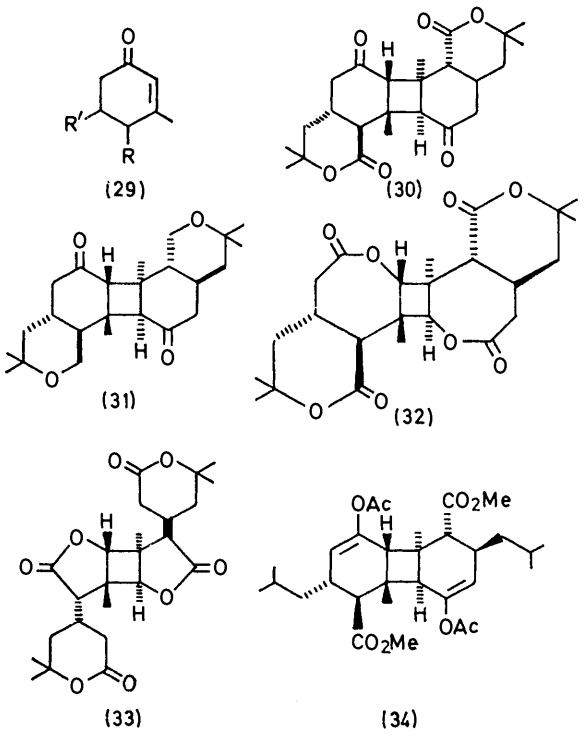


FIGURE 8 (*a*) Two centrosymmetrically-related cyclohexenone molecules, and, (*b*) the photodimer viewed parallel to the ring plane

experiments. As the dimer diethyl ester could not be hydrolysed in order to see if it was of the same orientation and stereochemistry as the dimer dimethyl ester, both were refluxed with boron trifluoride in aqueous acetic acid and gave one and the same pentacyclic dilactone (30).

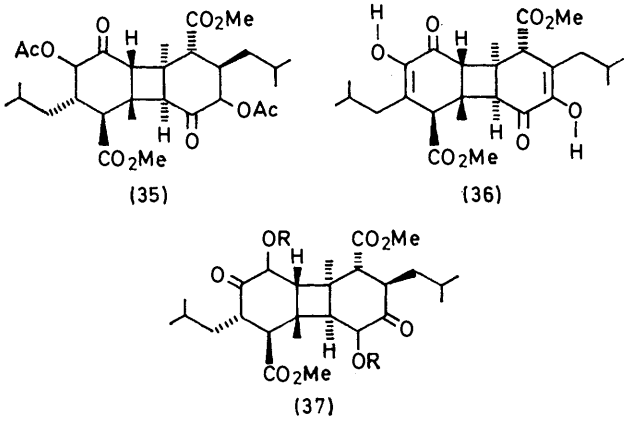
The pentacyclic dilactone (30) could also be made in stepwise fashion by adding hydrogen chloride to the

dimer (3): the dichloride was solvolysed to the diol and cyclised with acid. However, the dilactone (30) was originally encountered in another way. Reduction of



the photodimer (3) with lithium aluminium hydride, followed by oxidation with chromium trioxide, gave a ketone showing no hydroxlic absorption. It showed a single carbonyl absorption at 1 695 cm^{-1}, which disappeared when a bis-2,4-dinitrophenylhydrazone was made: the compound was formulated as (31). Further oxidation of (31) with chromium trioxide then gave the dilactone (30) identical with the specimens mentioned above.

Treatment of the pentacyclic dilactone (30) with



peroxytrifluoroacetic acid apparently formed the pentacyclic tetralactone (32) and on hydrolysis and acidification rearrangement to the pentacyclic quaterlactone (33) occurred. Rearrangement to (33) seems to occur partially during the Baeyer–Villiger step as it has not been possible to isolate (32) pure: from infrared evidence the product appears to be a mixture of (32) and (33) until treated with base.

TABLE 1

Torsion angles in degrees

	Monomer	Dimer
C(6)–C(1)–C(2)–C(3)	−21	−51
C(7)–C(1)–C(2)–C(3)	−146	−177
C(6)–C(1)–C(2)–C(9)	156	77
C(7)–C(1)–C(2)–C(9)	36	−49
C(1)–C(2)–C(3)–C(4)	−2	10
C(9)–C(2)–C(3)–C(4)	175	−118
C(2)–C(3)–C(4)–C(5)	2	16
C(2)–C(3)–C(4)–O(3)	−177	−165
C(3)–C(4)–C(5)–C(6)	27	−1
O(3)–C(4)–C(5)–C(6)	−154	179
C(4)–C(5)–C(6)–C(1)	−53	−37
C(4)–C(5)–C(6)–C(10)	−176	−157
C(5)–C(6)–C(1)–C(2)	52	64
C(10)–C(6)–C(1)–C(2)	175	−179
C(5)–C(6)–C(1)–C(7)	175	−172
C(10)–C(6)–C(1)–C(7)	−62	−55
C(2)–C(1)–C(7)–O(1)	58	87
C(2)–C(1)–C(7)–O(2)	−123	−90
C(6)–C(1)–C(7)–O(1)	−65	−38
C(6)–(1)–C(7)–O(2)	114	145
C(1)–C(7)–O(2)–C(8)	−175	173
O(1)–C(7)–O(2)–C(8)	4	−4
C(1)–C(6)–C(10)–C(11)	110	126
C(5)–C(6)–C(10)–C(11)	−129	−116
C(6)–C(10)–C(11)–C(12)	−1	−2
C(6)–C(10)–C(11)–C(13)	−180	179
C(1)–C(2)–C(3)–C(2′)		−114
C(9)–C(2)–C(3)–C(2′)		117
C(3′)–C(2)–C(3)–C(4)		124
C(3′)–C(2)–C(3)–C(2′)		0
C(1)–C(2)–C(3′)–C(2′)		113
C(3)–C(2)–C(3′)–C(2′)		0
C(9)–C(2)–C(3′)–C(2′)		−114
C(1)–C(2)–C(3′)–C(4′)		−122
C(3)–C(2)–C(3′)–C(4′)		124
C(9)–C(2)–C(3′)–C(4′)		10
C(6)–C(1)–C(2)–C(3′)		−150
C(7)–C(1)–C(2)–C(3′)		84
C(2′)–C(3)–C(4)–C(5)		125
C(2′)–C(3)–C(4)–O(3)		−56

The tetrahydro-photodimer (7) formed a bis-enol acetate (34) on treatment with isopropenyl acetate and acid and could be α-acetoxylated with lead tetra-acetate to give (35). This could be hydrolysed to a bis-ketone and the latter, on oxidation, gave the tetraketone (diosphenol) (36). However, the bis-ketol, on reacetylation gave a bis-acetate which was not identical with the lead tetra-acetate product. This new bis-acetate gave back the original ketol on hydrolysis and thus might be an epimer of the original bis-acetate. However, Huang-Minlon reduction yielded the same diol as is produced when the tetrahydro-photodimer is reduced with borohydride. The second ketol acetate, and the ketol thus appear to be derived from the isomeric form (37; R = OAc and R = H respectively).

EXPERIMENTAL

Except where stated otherwise, u.v. data refer to pure ethanol solutions. For i.r. measurements, liquid samples were normally examined as films, and solid samples as

mulls. N.m.r. data were usually determined at 60 MHz ($CDCl_3$).

Methyl 6-Isobutenyl-2-methyl-4-oxocyclohex-2-enecarboxylate (1).—Prepared as previously described, this compound had m.p. 73 °C (lit.,[3] m.p. 73 °C). N.m.r. data: δ 1.64 (3 H, d, *J* 1 Hz), 1.69 (3 H, d, *J* 1 Hz) (isobutenyl-methyls), 1.97 (3 H, d, *J* 1.7 Hz, 2-Me), 2.26 (1 H, dd, *J* 7, 16 Hz, 5-H_{ax}), 2.56 (1 H, dd, *J* 4, 16 Hz, 5-H_{eq}), 3.02—3.48 (1 H, m, 6-H), 3.25 (1 H, d, *J* 11 Hz, 1-H), 3.72 (3 H, s, ester Me), 5.09br (1 H, d, *J* 8.7 Hz, isobutenyl 1-H), and 6.02 (1 H, q, *J* 1.7 Hz, 3-H).

Photodimer, Dimethyl 2,6-Di-isobutenyl-4b,8b-dimethyl-4,8-dioxodicyclohexanocyclobutane-1,5-dicarboxylate (3).—Prepared as previously described, this compound had m.p. 252 °C (lit.,[3] m.p. 250 °C). N.m.r. data (220 MHz): 1.28 (6 H, s, 4b- and 8b-Me), 1.65br (12 H, s, isobutenyl methyls), 1.96 (2 H, dd, *J*, 11, 18.5 Hz, 3-H, 7-H), 2.54 (2 H, dd, *J*, 7, 18.5 Hz, 3-H, 7-H), 2.56 (2 H, d, *J* 11.5 Hz, 1-H, 5-H), 2.85 (2 H, s, 4a-H, 8a-H), 3.06 (2 H, dddd, *J*, 11.5, 8.5, 11, 7 Hz, 2-H, 6 H), 3.67 (6 H, s, ester-Me), and 4.78br (2 H, d, *J* 8.5 Hz, isobutenyl 1-Hs).

Catalytic Hydrogenation of Dimethyl 2,6-Di-isobutenyl-4b,8b-dimethyl-4,8-dioxodicyclohexanocyclobutane-1,5-dicarboxylate (3).—The photodimer (3) (2.5 g) suspended in ethyl acetate (750 ml) containing Adams platinum (300 mg) and concentrated sulphuric acid (5 ml), was shaken with hydrogen until 2 mol equiv. had been absorbed. Work-up gave the tetrahydro-compound (7) (2.3 g), needles, m.p. 216 °C from ethyl acetate. Crystallised from chloroform–methanol it separated as plates which changed to needles at 195—200 °C and finally melted at 216 °C. Solutions of the plate and needle forms had i.r. spectra identical with that of an authentic specimen,[3] m.p. 212 °C, $\nu_{max.}$ 1 733 (ester) and 1 691 cm^{-1} with no band at 850 cm^{-1}. The compound had $\lambda_{max.}$ 298 nm (ε 61). N.m.r. data δ 0.87 (12 H, d, *J* 6 Hz, isobutyl methyls), 1.26 (6 H, s, 4b- and 8b-methyls), 2.77 (2 H, s, 4a- and 8a-H), 3.72 (6 H, esters): the remaining signals formed a complex series of bands between 1.15 and 2.55.

If hydrogenation was continued until 4 mol. equiv. of hydrogen were absorbed, dimethyl 2,6-di-isobutyl-4b,8b-dimethyl-4,8-dihydroxydicyclohexanocyclobutane-1,5-dicarboxylate (16) (1.9 g) was obtained, needles, m.p. 189 °C from ethyl acetate. It was identical with a specimen obtained by reducing the tetrahydro-derivative of the photodimer with borohydride (below).

Continued hydrogenation resulted in absorption of 6 mol equiv. of hydrogen, and gave dimethyl 2,6-di-isobutyl-4b,8b-dimethyldicyclohexanocyclobutane-1,5-dicarboxylate (15) (1.5 g) as silky needles from ethyl acetate, m.p. 227 °C, $\nu_{max.}$ 1 736 cm^{-1} with no hydroxylic absorption and no other ketonic bands. It was identical with a specimen obtained by desulphurisation of (14).

Using a commercial Adams catalyst (Baker Platinum Co.) the tetrahydro-photodimer could be prepared without addition of acid. The photodimer (2.5 g) suspended in ethyl acetate (500 ml) containing catalyst (200 mg) was shaken in hydrogen: reaction ceased when 2 mol. equiv. had been absorbed. Work-up gave the tetrahydro-photodimer (7) (2.5 g) as needles, m.p. 216 °C from ethyl acetate.

Baeyer–Villiger Oxidations.—A suspension of 90% hydrogen peroxide (1 ml) in dry methylene chloride (8 ml) was cooled in ice, moisture being rigorously excluded. Trifluoroacetic anhydride (10 g) was added dropwise with stirring, and stirring was continued for 30 min to give a 2.6M-solution of trifluoroperoxyacetic acid in trifluoroacetic acid–methylene chloride which could be kept at 0 °C for seven days without significant loss of activity. The peracid solution (2.2 mol equiv.) at 0° was added slowly and with stirring to a solution of the cyclic ketone (1 mol equiv.) in dry methylene chloride. Stirring was continued for 1 h and the solution was diluted with twice its volume of chloroform and washed with water, sodium hydrogen carbonate solution, and brine. The organic layer was dried, evaporated, and the residue purified by crystallisation.

Baeyer–Villiger Oxidation of the Tetrahydro-photodimer (7).—The dimer (7) (3.6 g), oxidised as above, gave needles (2 g) (chloroform–methanol) of the *di-ε-lactone* (8), m.p. 286—287 °C (Found: C, 64.8; H, 8.4. $C_{26}H_{40}O_8$ requires C, 65.0; H, 8.4%), $\nu_{max.}$ 1 738 cm^{-1}, broad (7-membered lactone and saturated ester). N.m.r. data: δ 0.88 (6 H, d, *J* 6 Hz), 0.92 (6 H, d, *J* 6 Hz) (isobutyl methyls), 1.25—2.03 (8 H, complex, 4- and 9- and isobutyl 1- and 2-H), 1.33 (6 H, s, 5a-, 10a-methyls), 2.49 (6 H, m, 3-, 5-, 8-, 10-H),[1] 3.75 (6 H, s, ester methyls), and 4.50 (2 H, s, 5b-, 10b-H).

Partial Hydrolysis of the Di-ε-lactone (8).—The dilactone (1 g) in tetrahydrofuran (60 ml) was warmed with N-sodium hydroxide (4 ml) for 30 min. The product was poured into water, acidified to Congo Red, and extracted with chloroform. Repeated crystallisation of the solid (600 mg) from methanol gave the *hydroxy-acid* (10) as needles, m.p. 222—223 °C (Found: C, 60.7; H, 8.5. $C_{26}H_{44}O_{10}$ requires C, 60.4; H, 8.6%), $\nu_{max.}$ 3 488 (intramolecularly bonded OH), 1 736 (ester), and 1 709 cm^{-1} (acid).

Full Hydrolysis of the Di-ε-lactone (8).—The dilactone (1 g) in tetrahydrofuran (60 ml) was warmed with N-sodium hydroxide (15 ml) for 5 min. Work-up (chloroform) by acidification and crystallisation from ether–light petroleum gave the *di-γ-lactonic diacid* (11; R = H) (800 mg), m.p. 240—241 °C, (Found: C, 63.7; H, 8.0. $C_{24}H_{36}O_8$ requires C, 63.7; H, 8.0%), $\nu_{max.}$ 1 770 (γ-lactone) and 1 709 (acid) cm^{-1}. The *dimethyl ester* was formed by treatment of the dilactone with acid methanol or of the diacid with diazomethane, m.p. 171—172 °C (Found: C, 64.8; H, 8.5. $C_{24}H_{40}O_8$ requires C, 65.0; H, 8.4%), $\nu_{max.}$ 1 770 (γ-lactone) and 1 734 (ester) cm^{-1}.

Hunsdiecker Degradation of the Di-γ-lactonic Diacid (11; R = H).—The diacid (400 mg) was converted into the silver salt (510 mg) by treating its ammonium salt with silver nitrate. Vacuum-dried silver salt (500 mg), $\nu_{max.}$ 1 770 cm^{-1} (γ-lactone), suspended in dry benzene (50 ml) was treated slowly with freshly sublimed iodine (250 mg) in dry benzene (100 ml), moisture being rigorously excluded. After being refluxed (3 h) the mixture was filtered and the filtrate was washed with sodium thiosulphate solution, dried, and evaporated to give a gum (200 mg) which crystallised from ether–light petroleum to give the di-iodide as plates, m.p. 104 °C (Found: C, 43.5; H. 5.9. $C_{22}H_{34}I_2O_4$ requires C, 42.9; H, 5.5%), $\nu_{max.}$ 1 770 (γ-lactone).

The di-iodide (100 mg) in dry chloroform (5 ml) was shaken for 3 days at 20 °C with silver nitrite (90 mg) suspended in dry ether–chloroform (10 ml), the initial addition being carried out at 0 °C. After filtration and work-up a yellow gum was obtained which when triturated with ether–light petroleum gave a white powder (50 mg). A portion (5 mg) in 0·1M-sodium hydroxide (1 ml) was

treated with 10% sodium nitrite solution (1 ml). Water (2 ml) was added and then dilute sulphuric acid, dropwise. The solution became deep red but the colour disappeared on full acidification: the colour returned when the solution was made alkaline again.

Reaction of the Tetrahydro-photodimer (7) *with Ethanedithiol*.—The tetrahydro-dimer (500 mg) in ethanedithiol (15 ml) was treated with boron trifluoride–diethyl ether (10 ml). After 24 h the product was filtered off and crystallised from ethyl acetate to give the bis-thioacetal (14) as needles, m.p. 235—236 °C (Found: C, 59.8; H, 7.8. $C_{30}H_{48}O_4S_4$ requires C, 60.0; H, 8.0%), $\nu_{max.}$ 1 730 (ester) cm^{-1}, with no max near 1 700 cm^{-1}. By treating the original filtrate with ethyl acetate more bis-thioacetal was isolated (150 mg total).

Desulphurisation of the Bis-thioacetal (14).—The bis-thioacetal (100 mg) in dry dioxan (10 ml) was refluxed with Raney nickel (300 mg, W4) for seven days. Crystallisation from ethyl acetate gave *dimethyl* 2,6-*di-isobutyl*-4b,8b-*dimethyldicyclohexanocyclobutane*-1,5-*dicarboxylate* (15) (90 mg), as needles, m.p. 226 °C (Found: C, 74.2; H, 10.6. $C_{26}H_{44}O_4$ requires C, 74.2; H, 10.5%), $\nu_{max.}$ 1 736 cm^{-1} (ester).

α-Bromination of the Tetrahydro-photodimer (7).—The tetrahydro-dimer (1 g) in acetic acid (70 ml) and chloroform (30 ml) was stirred and treated dropwise with bromine (400 mg) in acetic acid (20 ml) containing hydrobromic acid (1 drop). The mixture was stirred for 24 h after which an equal volume of chloroform was added and the solution was worked up. Crystallisation from chloroform–methanol gave *dimethyl* 3,7-*dibromo*-2,6-*di-isobutyl*-4b,8b-*dimethyldicyclohexanocyclobutane*-1,5-*dicarboxylate* (18) (600 mg) as needles, m.p. 228—229 °C (Found: C, 51.7; H, 6.2. $C_{26}H_{38}Br_2O_6$ requires C, 51.5; H, 6.3%), $\nu_{max.}$ 1 735 (ester) and 1 701 cm^{-1} (α-halogeno-ketone); $\lambda_{max.}$ (dioxan) 320 nm (ε 250).

Dehydrobromination of the Dibromo-diketone (18).—The dibromo-diketone (150 mg) in dry pyridine (5 ml) was refluxed for 2 h. Crystallisation from methanol–chloroform gave the 2,3 : 6,7-*bisdehydroketone* (19) (40 mg) as needles, m.p. 285 °C (decomp.) (Found: C, 69.8; H, 8.0. $C_{26}H_{36}O_6$ requires C, 70.2; H, 8.2%), $\nu_{max.}$ 1 740 (ester), 1 700 (α-unsaturated 6-membered ketone), and 1 623 cm^{-1} (conj. C=C); $\lambda_{max.}$ 233 nm (ε 25 300).

Reduction of the Tetrahydro-photodimer (7) *with Potassium Borohydride*.—The tetrahydro-photodimer (1 g) in tetrahydrofuran (80 ml) was kept with potassium borohydride (300 mg) in water (15 ml) at 50 °C for 1 h and then at 20 °C overnight. Ammonium chloride solution was added and the product was extracted with chloroform. Drying and evaporation gave *dimethyl* 4,8-*dihydroxy*-2,6-*di-isobutyl*-4b,8b-*dimethyldicyclohexanocyclobutane*-1,5-*dicarboxylate* (16) (900 mg), m.p. 189—191 °C (Found: C, 69.3; H, 9.8. $C_{26}H_{44}O_6$ requires C, 69.0; H, 9.8%), $\nu_{max.}$ ($CHCl_3$) 3 625 (free secondary OH), 3 570 and 3 541 (intramolecularly bonded OH), 1 742 (free ester), and 1 712 cm^{-1} (bonded ester). In paraffin mulls the peak at 1 712 cm^{-1} was absent. A *diacetate*, m.p. 127 °C from chloroform–methanol, was prepared by the acetic anhydride–pyridine method (Found: C, 66.9; H, 9.3. $C_{30}H_{48}O_8$ requires C, 67.1; H, 9.0%), $\nu_{max.}$ 1 741 cm^{-1} (ester). N.m.r. data: δ 0.86 (12 H, isobutyl methyls), 1.15 (4 H, 2 × isobutyl 1-Hs, *J* 6.6 Hz), 1.24 (6 H, 4b- and 8b-methyls), 2.06 (6 H, acetyl methyls), 2.49 (2 H, 4a-, 8a-H, *J* 7 Hz), 2.69 (2 H, 1-, 5-H, *J* 10.3 Hz), 3.66 (6 H, 1-,5-ester methyls), 5.18 (2 H, 4-, 8-H, *J* 7 and 10.7 Hz). When treated with toluene-*p*-sulphonyl chloride and pyridine the diol formed a *bistoluene*-p-*sulphonate*, needles, m.p. 219 °C from chloroform–methanol (Found: C, 63.0; H, 7.4. $C_{40}H_{56}O_{10}S_2$ requires C, 63.1; H, 7.4%), $\nu_{max.}$ 1 736 (ester) and 1 600 cm^{-1} (aryl).

Reduction of the Photodimer (3) *with Potassium Borohydride*.—In a similar way *dimethyl* 2,6-*di-isobutenyl*-4b,8b-*dimethyl*-4,8-*dihydroxydicyclohexanocyclobutane*-1,5-*dicarboxylate*, m.p. 220—221 °C from chloroform–methanol or ethyl acetate, was formed (Found: C, 69.7; H, 9.1. $C_{26}H_{40}O_6$ requires C, 69.6; H, 9.0%). It had $\nu_{max.}$ ($CHCl_3$) 3 623 (free OH), 3 535 and 3 569 (intramolecularly bonded OH), 1 745 (free ester), and 1 712 cm^{-1} (bonded ester). In paraffin mulls the band at 1 712 cm^{-1} was absent. The diol formed a *diacetate*, m.p. 145 °C (Found: C, 67.7; H, 8.7. $C_{30}H_{44}O_8$ requires C, 67.6; H, 8.3%), $\nu_{max.}$ 1 741 cm^{-1} (ester). N.m.r. data: δ 1.28 (6 H, 4b- and 8b-methyls), 1.63 (12 H, isobutenyl methyls), 2.05 (6 H, acetyl methyls), 2.47 (2 H, 4a-, 8a-H, *J* 6 Hz), 3.58 (6 H, 1-, 5-ester methyls), 4.81 (2 H, 2 × isobutenyl 1-H, *J* 8 Hz), 5.18 (2 H, 4-, 8-H, *J* 6, 11.7, and 1.3 Hz).

Oxidation with chromium trioxide in acetone reconverted this diol into the parent photodimer (3). The tetrahydrodiol (16) was similarly reconverted into the parent tetrahydro-photodimer (7).

Reaction of the Tetrahydro-photodimer (7) *with Isopropenyl Acetate*.—The tetrahydro-photodimer (1g) was refluxed for 90 min with isopropenyl acetate containing a few drops of concentrated sulphuric acid. The mixture was poured into water and the product was extracted with chloroform; the extract was washed with sodium hydrogencarbonate solution, dried, and evaporated to give a brown gum which crystallised (650 mg) when triturated with methanol. Recrystallisation from ethyl acetate or a large volume of methanol gave the *bis-enol acetate* (34) as needles, m.p. 164 °C (Found: C, 67.4; H, 8.3. $C_{30}H_{44}O_8$ requires C, 67.6; H, 8.3%), $\nu_{max.}$ 1 761 (vinyl ester), 1 732 (ester), and 1 675 cm^{-1} (C=C).

Reaction of the Photodimer (3) *with Isopropenyl Acetate*.—Under conditions similar to those above the *bis-enol acetate* was formed as white plates from chloroform–methanol, m.p. 173—174 °C (Found: C, 68.2; H, 7.5. $C_{30}H_{40}O_8$ requires C, 68.2; H, 7.6%), $\nu_{max.}$ 1 760 (vinyl ester), 1 736 (ester), and 1 673 cm^{-1} (C=C).

Catalytic Hydrogenation of the Enol-acetate (34).—The enol-acetate (200 mg) and Adams platinum catalyst (40 mg) were suspended in ethyl acetate (50 ml) containing concentrated sulphuric acid (0.5 ml) and shaken with hydrogen: 2 mol equiv. were absorbed. Crystallisation from ethyl acetate gave the diol (16) as needles, m.p. 190 °C (and mixed m.p. with the specimen prepared by reducing the tetrahydro-photodimer with potassium borohydride).

Bromination of the Enol-acetate (34).—Bromine (500 mg) in chloroform was added to the enol-acetate (600 mg) in chloroform (40 ml). The mixture was agitated for two days at 20 °C and worked up. The product (500 mg) was crystallised from chloroform–methanol to give needles, m.p. 227—230 °C, identical with the α-bromo-ketone (18) above (mixed m.p. and i.r. spectrum).

Reaction of the Tetrahydro-photodimer (7) *with Lead Tetra-acetate*.—The tetrahydro-dimer (2 g) and lead tetra-acetate (5 g) in dry benzene (100 ml) were refluxed with exclusion of moisture for 8 h. The product (1.6 g) on crystallisation from methanol–chloroform gave *dimethyl* 2,6-*di-isobutyl*-4b,8b-*dimethyl*-3,7-*diacetoxy*-4,8-*dioxodi-*

cyclohexanocyclobutane-1,5-*dicarboxylate* (35), m.p. 242—243 °C, needles (or plates, m.p. 238—239 °C from ethyl acetate) (Found: C, 63.7; H, 7.7. $C_{30}H_{44}O_{10}$ requires C, 63.8; H, 7.8%), $\nu_{max.}$ 1 736 (satd. ester) and 1 720 (α-acetoxy ketone) cm^{-1}, $\lambda_{max.}$ 304 nm. The compound gave no ferric chloride colour and did not give a quinoxaline derivative.

Reaction of the Photodimer (3) *with Lead Tetra-acetate.*—Using a procedure similar to that above, *dimethyl* 3,7-*diacetoxy*-2,6-*di-isobutenyl*-4b,8b-*dimethyl*-4,8-*dioxodicyclohexanocyclobutane*-1,5-*dicarboxylate* was obtained as needles from methanol–chloroform, m.p. 273—274 °C (Found: C, 64.0; H, 7.0. $C_{30}H_{40}O_{10}$ requires C, 64.3; H, 7.2%), $\nu_{max.}$ 1 737 (ester) and 1 723 cm^{-1} (α-acetoxy-ketone).

Hydrolysis of the α-Acetoxyketone (35).—The α-acetoxy-ketone, m.p. 242—243 °C (35) (500 mg) was refluxed for 1 h with 5% aqueous methanol containing sodium hydroxide (2.2 equiv.) and poured into water. Work-up gave the α-ketol thought to be (37; R = H) (400 mg) as needles, m.p. 263—265 °C from chloroform–methanol (Found: C, 64.6; H, 8.0. $C_{26}H_{40}O_8$ requires C, 65.0; H, 8.4%), $\nu_{max.}$ 3 470 (intramolecularly bonded OH), 1 733 (ester), and 1 701 cm^{-1} (α-hydroxy-ketone); $\lambda_{max.}$ 288 nm.

The *α-ketol* (37; R = H but with isobutenyl unsaturation) obtained similarly, formed needles, m.p. 302—303 °C from chloroform (Found: C, 56.3; H, 7.7. $C_{26}H_{36}O_8$ requires C, 65.6; H, 7.6%), $\nu_{max.}$ 3 497 (intramolecularly bonded OH), 1 738 (ester) and 1 708 (α-hydroxy-ketone) cm^{-1}.

Acetylation of the α-Ketol (37; R = H).—The α-ketol (100 mg) was shaken for 24 h with pyridine (10 ml) and acetic anhydride (10 ml). Water was added and the product was worked up to give the *ketol acetate* (37; R = Ac) (85 mg) as needles from chloroform, m.p. 320—321 °C (Found: C, 63.6; H, 7.8. $C_{30}H_{44}O_{10}$ requires C, 63.8; H, 7.8%), $\nu_{max.}$ 1 740 (ester) and 1 718 cm^{-1} (α-acetoxy ketone). On hydrolysis with base the ketol acetate gave the original ketol in good yield.

Huang–Minlon Reduction of the Ketol Acetate (37; R = Ac).—The ketol acetate (65 mg) was refluxed in ethylene glycol (2 ml) containing hydrazine hydrate (0.1 ml) for 30 min. Potassium hydroxide (250 mg) in water (0.5 ml) was added and the mixture was boiled to remove the water and then refluxed for 90 min and poured into water. The precipitate (15 mg) crystallised from methanol as needles, m.p. 189 °C, identical (mixed m.p. and i.r. comparison) with authentic tetrahydro-diol (16).

Reduction of the α-Ketol (37; R = H) *with Potassium Borohydride.*—The ketol (200 mg) in tetrahydrofuran (15 ml) was warmed at 40 °C for 30 min with potassium borohydride (50 mg) in water (4 ml). The mixture was kept at 20 °C overnight and then ammonium chloride solution was added to it; the solution was then extracted with chloroform to give *dimethyl* 3,4,7,8-*tetrahydroxy*-2,6-*di-isobutyl*-4b,8b-*dimethyldicyclohexanocyclobutane*-1,5-*dicarboxylate* as needles, m.p. 249 °C (Found: C, 64.2; H, 8.8. $C_{26}H_{44}O_8$ requires C, 64.4; H, 9.1%), $\nu_{max.}$ 3 450 (OH) and 1 733 cm^{-1} (ester).

Oxidation of the α-Ketol (37; R = H).—The α-ketol (100 mg) and cupric acetate (200 mg) in glacial acetic acid (10 ml) were refluxed for 15 min and the product was poured into water and extracted with chloroform. The product (80 mg) was crystallised from glacial acetic acid to give *dimethyl* 2,6-*di-isobutyl*-4b,8b-*dimethyl*-3,4,7,8-*tetraoxodicyclohexanocyclobutane*-1,5-*dicarboxylate* (36) as cubes, m.p. 179—181 °C (Found: C, 65.2; H, 7.5. $C_{26}H_{36}O_8$ requires C, 65.5; H, 7.6%), $\nu_{max.}$ 3 410 (intramolecularly bonded enol), 1 733 (ester), and 1 695, 1 667, and 1 645 (ketone or olefin); $\lambda_{max.}$ (dioxan) 286 nm; $\lambda_{max.}$ (alkaline dioxan) 344 nm. The dione, behaving as a diosphenol, gave an olive-green colour with ferric chloride.

In a similar way the *dimethyl* 2,7-*di-isobutenyl-tetraketone* [*cf.* (36)] was obtained as needles, m.p. 206—208 °C from chloroform (Found: C, 66.0; H, 6.4. $C_{26}H_{32}O_8$ requires C, 66.1; H, 6.8%), $\nu_{max.}$ 3 195, 1 742, 1 695, 1 661, and 1 626 cm^{-1}; $\lambda_{max.}$ (dioxan) 317 nm; $\lambda_{max.}$ (alkaline dioxan) 380 nm.

Reduction of the Photodimer (3) *with Lithium Aluminium Hydride.*—The photodimer (500 mg) in dry dioxan (70 ml) was refluxed under nitrogen with lithium aluminium hydride (500 mg) in dioxan for 90 min. The mixture was cooled, ethyl acetate and dilute acid were added to it, and the whole was extracted with chloroform. Work-up and crystallisation from ether gave the *pentacyclic diol* (31; carbonyls reduced) as needles, m.p. 287—288 °C (Found: C, 73.3; H, 10.1. $C_{24}H_{40}O_4$ requires C, 73.4; H, 10.3%), $\nu_{max.}$ 3 410 cm^{-1} (hydroxy).

Oxidation of the Pentacyclic Diol.—The diol (100 mg) was warmed in acetone (10 ml) with the calculated quantity of chromium trioxide for 30 min at 40 °C and then kept at 20 °C overnight and filtered. The filtrate on evaporation and crystallisation from methanol–chloroform gave the *pentacyclic diketone* (31) as needles, m.p. 162 °C (Found: C, 74.5; H, 9.4. $C_{24}H_{36}O_4$ requires C, 74.2; H, 9.3%), $\nu_{max.}$ 1 695 cm^{-1} (6-membered ketone). The *bis*-2,4-*dinitrophenylhydrazone* crystallised from tetrahydrofuran as yellow needles, m.p. 197—199 °C (decomp.) (Found: N, 15.4. $C_{36}H_{44}N_8O_{10}$ requires N, 15.0%).

Oxidation of the Pentacyclic Diol to the Pentacyclic Dilactone (30).—The pentacyclic diol (400 mg) in acetone (8 ml) was treated with 8N-chromic acid (5 ml) at 0—5 °C. After being kept overnight at 20 °C the solution was diluted with acetone, treated with sulphur dioxide, and poured onto ice. The product was extracted with chloroform to yield solid (250 mg), m.p. 250—315 °C after crystallisation from ethyl acetate. Extraction of these crystals with cold chloroform left a residue (110 mg) which crystallised from a large volume of chloroform as needles, m.p. 319—325 °C. This compound was identical (mixed m.p. and i.r. comparison) with the pentacyclic dilactone (30) prepared below.

Pentacyclic Dilactone (30).—(a) The photodimer (400 mg) was suspended in glacial acetic acid (10 ml) and water (5 ml) and boron trifluoride–acetic acid complex (3 ml) was added. After being refluxed for 2 h the pentacyclic dilactone (30) (340 mg) separated as needles on cooling, m.p. 320—326 °C (decomp.), unchanged by crystallisation from glacial acetic acid or chloroform–methanol (Found: C, 69.1; H, 7.7. $C_{24}H_{32}O_6$ requires C, 69.2; H, 7.7%), $\nu_{max.}$ 1 726 (δ-lactone) and 1 695 cm^{-1} (6-membered ketone).

(b) The photodimer (500 mg) dissolved in concentrated sulphuric acid (15 ml) was kept overnight and then poured onto ice. Extraction with chloroform and work-up gave the pentacyclic dilactone (30) (400 mg), m.p. 320—325 °C.

Side-chain Hydration of the Photodimer (3).—The photodimer (1 g) suspended in water (10 ml) containing sodium acetate (4 g) and acetic acid (3 g) was refluxed for 2 h with boron trifluoride–acetic acid complex (1 ml). The mixture was cooled and the product extracted with chloroform to give the *diol* (800 mg) as needles, m.p. 229—230 °C from ethyl acetate (Found: C, 65.0; H, 8.5. $C_{26}H_{40}O_8$ requires

C, 65.0; H, 8.4%), $\nu_{max.}$ 3 415 (bonded OH), 1 736 (satd. ester), and 1 701 and 1 695 cm^{-1} (bonded ester and 6-membered ketone).

When refluxed with acetic acid–hydrochloric acid for 1 h and crystallised from chloroform, the diol yielded the pentacyclic dilactone (30) as needles, m.p. 320—324 °C (decomp.).

Addition of Hydrogen Chloride to the Photodimer (3).—Dry hydrogen chloride was passed through an ice-cold solution of the photodimer (500 mg) in chloroform (15 ml) containing glacial acetic acid (60 ml). The needles were filtered off (480 mg) and crystallised from chloroform–methanol to give the *dichloride* as rods, m.p. 202—203 °C with evolution of gas (Found: C, 60.0; H, 7.1. $C_{26}H_{38}Cl_2O_6$ requires C, 60.4; H, 7.3%), $\nu_{max.}$ 1 733 (ester) and 1 698 cm^{-1} (ketone). The residue after determination of the m.p. re-melted at 243—246 °C. Pyrolysis of the dichloride *in vacuo* gave the photodimer (3) (95%) as a glistening sublimate.

The dichloride (300 mg) was stirred with finely divided calcium carbonate suspended in water at 60 °C for 2 h. Cooling and extraction with chloroform gave the diol (210 mg), m.p. and mixed m.p. 228—229 °C with the specimen above. The identity was confirmed by i.r. methods.

Preparation of the Pentacyclic Quaterlactone (33).—The pentacyclic dilactone (30) (1 g) was subjected to the Baeyer–Villiger oxidation as above to give a mixture of lactones (800 mg), m.p. 280—315 °C after crystallisation from methanol. The mixture (700 mg) was warmed with aqueous sodium hydroxide, kept for 5 min, and then acidified to Congo Red. Filtration and crystallisation from a large volume of chloroform gave the pentacyclic quaterlactone (33) as plates, m.p. 342—344 °C after charring near 335 °C (Found: C, 64.2; H, 6.9. $C_{24}H_{32}O_8$ requires C, 64.3; H, 7.2%), $\nu_{max.}$ 1 764 (γ-lactone) and 1 712 cm^{-1} (δ-lactone).

Dehydration of the Tetrahydrodiol (16).—The diol (700 mg) was kept for three weeks with ethyl acetate (200 ml) containing concentrated sulphuric acid (5 ml). Washing with hydrogencarbonate solution, and isolation gave the *diene* (17) (600 mg) as needles (from chloroform–methanol), m.p. 235 °C (Found: C, 74.9; H, 9.3. $C_{26}H_{40}O_4$ requires C, 75.0; N, 9.7%), $\nu_{max.}$ 1 725 (satd. ester) and 1 650 cm^{-1} (C=C).

On hydrogenation of the diene (100 mg) in ethyl acetate (30 ml) over an Adams catalyst (30 mg) in the presence of concentrated sulphuric acid (0.5 ml), 2 mol equiv. of hydrogen were absorbed. Work-up gave the 4,8-bis-dioxy-derivative (15) of the tetrahydro-photodimer (80 mg), m.p. 226 °C from ethyl acetate. It was identical (mixed m.p. and i.r. spectrum) with the specimen above.

Preparation and Dehydrohalogenation of the 4,8-*Dichloro-compound.*—The tetrahydro-diol (16) (500 mg) in pyridine (20 ml) was treated slowly with phosphorus oxychloride (5 ml). After being kept for three days the mixture was poured onto ice and the 4,8-dichloro-compound was filtered off and crystallised from ethyl acetate as needles, m.p. 164 °C (Found: C, 63.7; H, 8.4. $C_{26}H_{42}Cl_2O_4$ requires C, 63.8; H, 8.6%), $\nu_{max.}$ 1 730 cm^{-1} (ester).

The chloro-compound (250 mg) was refluxed for 5 h in pyridine. Work-up and crystallisation of the gummy product (70 mg) from chloroform–methanol gave needles, m.p. 234—235 °C, identical (mixed m.p. and i.r. comparison) with the diene (17) above.

Preparation of Diethyl 2,6-*Di-isobutenyl*-4b,8b-*dimethyl*-4,8-*dioxocyclohexanocyclobutane*-1,5-*dicarboxylate.*— Methyl 6-isobutenyl-2-methyl-4-oxocyclohex-2-enecarboxylate (1) (1 g) was heated with 2N-sodium hydroxide (15 ml) until a clear solution was obtained. The product was rapidly cooled and extracted with ether. Evaporation and crystallisation from benzene–light petroleum (b.p. 60—80 °C), gave the acid corresponding to the above ester (560 mg), m.p. 111—112 °C with effervescence (lit.,[3] m.p. 109—110 °C). The i.r. spectrum was identical with that of an authentic sample. Esterification with diazoethane gave ethyl 6-isobutenyl-2-methyl-4-oxocyclohex-2-enecarboxylate (29; R = CO_2Et, R′ = MeC:CH), as needles from benzene, m.p. 38—39.5 °C.

The ethyl ester, when photodimerised as described for the methyl ester,[3] gave the *dicyclohexanocyclobutane* named in the title, m.p. 173—174 °C, as needles from ethanol. The conversion (on irradiation) was 60% (Found: C, 71.3; H, 8.5. *M* (Rast), 540. $C_{28}H_{40}O_6$ requires C, 71.2; H, 8.5%; *M*, 472). A second form, cubes, which changes into the needle form in the range 155—165 °C has been encountered.

Methyl 6-*Isobutyl*-2-*methyl*-4-*oxocyclohexanecarboxylate.*—Methyl 6-isobutenyl-2-methyl-4-oxocyclohex-2-enecarboxylate (1) (200 mg) in ethyl acetate was hydrogenated over palladium–charcoal; 2 mol equiv. of hydrogen were absorbed to give the *cyclohexane derivative* (170 mg) as needles from methanol, m.p. 99 °C (Found: C, 69.0; H, 10.0. $C_{13}H_{22}O_3$ requires C, 69.0; H, 9.8%). Methyl 6-isobutyl-2-methyl-4-oxocyclohex-2-enecarboxylate (200 mg) absorbed 1 mol equiv. of hydrogen on similar hydrogenation and gave the same product, m.p. and mixed m.p. 98—99 °C.

Methyl 6-*Isobutyl*-2-*methyl*-4-*oxocyclohex*-2-*enecarboxylate.*—Isovaleraldehyde (4 g), methyl acetoacetate (12 g), and piperidine (0.5 g) were mixed with external cooling. The mixture was then heated at 100 °C for 2 h. Anhydrous sodium sulphate was added and the liquid layer was poured into methanol (500 ml) containing dissolved sodium (1.2 g). After refluxing for 2 h most of the methanol was removed by distillation and water (20 ml) and acetic acid (5 ml) were added. Extraction with ether, and work-up, gave *methyl* 6-*isobutyl*-2-*methyl*-4-*oxocyclohex*-2-*enecarboxylate* (29; R = CO_2Me, R′ = Me_2CHCH_2) (6 g), b.p. 120 °C/0.1 mmHg, as rods, m.p. 59—60 °C (Found: C, 69.5; H, 9.0. $C_{13}H_{20}O_3$ requires C, 69.6; H, 9.0%), $\nu_{max.}$ 1 730 (ester), 1 661 (α-unsaturated ketone), and 1 629 cm^{-1} (conj. C=C).

The ester (2 g) was suspended in aqueous sodium hydroxide (25 ml) and heated under reflux (10 min). The yellow solution was cooled, extracted with ether, and the extracts rejected, and then acidified. Extraction with ether, evaporation, and crystallisation from benzene–light petroleum gave 6-*isobutyl*-2-*methyl*-4-*oxocyclohex*-2-*enecarboxylic acid* (29; R = CO_2H, R′ = Me_2CHCH_2) as rods, m.p. 79—80 °C (Found: C, 68.3; H, 8.5. $C_{12}H_{18}O_3$ requires C, 68.5; H, 8.6%).

Partial Reduction of the Photodimer (3) *with Borohydride.*—The photodimer (2 g) in purified tetrahydrofuran (300 ml) was treated slowly and dropwise with potassium borohydride (65 mg) in distilled water (30 ml). The solution, which was stirred vigorously during the addition, became slightly cloudy, and when all the reagent had been added stirring was maintained for 2 h. The product was set aside overnight, when a white coating covered the sides of the flask. Saturated ammonium chloride solution was added and the product (1.7 g) was isolated by extraction with chloroform. Crystallisation from ethyl acetate gave the *ketol* (20) (950 mg) as needles, m.p. 194—195 °C (Found: C,

70.1; H, 8.3. $C_{26}H_{38}O_6$ requires C, 69.9; H, 8.6%), $\nu_{max.}$ 3 520 (OH), 1 732 (ester), and 1 695 cm^{-1} (ketone). N.m.r. data (using CAT): δ 1.32 (6 H, s, 4b- and 8b-methyls), 1.65br (12 H, s, isobutenyl methyls), 2.41 (1 H, d, *J* 6 Hz, 4a-H), 2.94 (1 H, s, 8a-H), 3.61 (6 H-ester methyls), 4.13 (1 H, m, *J* 6, 11.7 and 2 Hz, 4-H), 4.95br (2 H, d., *J* 7.7, 1,1'-H). The 2,4-*dinitrophenylhydrazone* crystallised from tetrahydrofuran as yellow needles, m.p. 247—252 °C (decomp.) (Found: C, 61.5; H, 6.9. $C_{32}H_{42}N_4O_9$ requires C, 61.6; H, 6.8%).

Ketol-acetate (21).—The above ketol (800 mg) was kept with pyridine (5 ml) and acetic anhydride (10 ml) for 2 days. Work-up gave the *ketol-acetate* (750 mg) as needles from ethyl acetate, m.p. 179—181 °C (Found: C, 68.4; H, 7.9. $C_{28}H_{40}O_7$ requires C, 68.8; H, 8.2%), $\nu_{max.}$ 1 736 (ester) and 1 695 cm^{-1} (ketone). The acetate (500 mg) in ethyl acetate (300 ml) containing sulphuric acid (0.5 ml) was hydrogenated over Adams catalyst (100 mg). Work-up gave the *saturated ketol acetate* (21) (450 mg) as thick needles from ethyl acetate, m.p. 146—147 °C (Found: C, 68.3; H, 8.9. $C_{28}H_{44}O_7$ requires C, 68.3; H, 9.0%), $\nu_{max.}$ 1 734 (ester) and 1 710 cm^{-1} (ketone).

The Hydroxy-γ-lactone (23).—The ketol acetate (21) (300 mg) was oxidised by the general procedure for Baeyer–Villiger oxidations to give the ε-lactonic acetate (22) (170 mg) as needles from chloroform–methanol, m.p. 185 °C (Found: C, 66.0; H, 8.5. $C_{28}H_{44}O_8$ requires C, 66.1; H, 8.7%), $\nu_{max.}$ 1 733 (saturated ester and 7-membered ring lactone).

The lactonic acetate (250 mg) was dissolved in tetrahydrofuran (15 ml) and N-sodium hydroxide (3 ml) was added. After being warmed for 5 min the solution was diluted with water, acidified, and extracted with chloroform. The chloroform extract gave the hydroxy-γ-lactone (23) as needles from methanol–chloroform, m.p. 174—176 °C (Found: C, 66.0; H, 8.8. $C_{25}H_{40}O_7$ requires C, 66.3; H, 8.9%), $\nu_{max.}$ 3 610 (OH), 1 770 (γ-lactone), 1 730 (ester), and 1 706 cm^{-1} (acid).

Oxidation of the Hydroxy-γ-lactone (23).—The hydroxy-γ-lactone (200 mg) in acetone (10 ml) was kept at 40 °C for 30 min and then overnight at 20 °C with chromium trioxide in acetone. After being filtered, the solution was poured into water and extracted with chloroform to give the *keto-γ-lactone* (24) (180 mg) as needles from ethyl acetate, m.p. 198 °C (Found: C, 66.2; H, 8.2. $C_{25}H_{38}O_7$ requires C, 66.6; H, 8.5%), $\nu_{max.}$ 1 770 (γ-lactone), 1 730 (ester), 1 706, and 1 701 cm^{-1} (acid and cyclic ketone).

Preparation of the Ketonic Ether (25).—The keto-γ-lactone (24) (250 mg) was dissolved in tetrahydrofuran (30 ml) containing dimethyl sulphate (2 ml) and the solution was added to a vigorously stirred solution of sodium hydroxide (60 mg) in wet tetrahydrofuran. The solution was stirred for 45 min. Excess base was added and the solution was refluxed for 30 min, poured into water, and extracted with chloroform. The aqueous layer was acidified and again extracted with chloroform; this extract was dried and evaporated to give a gum (180 mg) which crystallised when triturated with ether–light petroleum. The *methyl ether of the ketone-acid* (25; R = H) recrystallised from ethyl acetate as plates, m.p. 190—191 °C (Found: C, 64.8; H, 8.9. $C_{26}H_{42}O_8$ requires C, 64.7; H, 8.8%), $\nu_{max.}$ 1 732 (ester) and 1 703 cm^{-1} (saturated acid and cyclic ketone) [Found: Equiv. (titration) 2.0 CO_2H. Requires 2.0 CO_2H].

Baeyer–Villiger Oxidation of the Ketonic Ether (25).—The methyl ether (25) (150 mg), when oxidised according to the general procedure gave the lactonic ether (26) as needles, m.p. 225 °C (Found: C, 62.4; H, 8.4. $C_{26}H_{42}O_9$ requires C, 62.6; H, 8.5%), $\nu_{max.}$ 1 735 (ester and ε-lactone) and 1 710 cm^{-1} (saturated acid).

Hydrolysis of the Lactonic Ether (26).—The lactonic ether (70 mg) in wet tetrahydrofuran (5 ml) containing sodium hydroxide (25 mg) was shaken for 10 min at 20 °C and then poured into water (20 ml). The solution was extracted with chloroform and the extract (a tetrahydrofuran–water–chloroform system containing sodium salt) was washed with dilute hydrochloric acid and then water. Drying and evaporation gave a solid (15 mg) which crystallised as small hexagons from ether–light petroleum to give the *monohydroxytricarboxylic acid* (27; R = Me), m.p. 135—136 °C (Found: C, 60.0; H, 8.3. $C_{26}H_{44}O_{10}$ requires C, 60.4; H, 8.6%), $\nu_{max.}$ 3 470 (OH), 1 732 (ester), and 1 710 cm^{-1} (acid) [Found: (Equiv.) 2.9 CO_2H. Requires 3.0 CO_2H].

The aqueous solution (above), after extraction with chloroform, was acidified and extracted with chloroform. Drying and evaporation gave a solid (50 mg) which was crystallised from light petroleum (b.p. 60—80 °C) to give a little more of the monohydroxytricarboxylic acid and the *γ-lactonic tricarboxylic acid* (28) as plates, m.p. 143—145 °C (Found: C, 61.9; H, 8.1. $C_{25}H_{40}O_9$ requires C, 62.0; H, 8.3%), $\nu_{max.}$ 1 770 (γ-lactone) and 1 712 cm^{-1} (acid) [Found: (Equiv.) 3.2 CO_2H. Requires 3 CO_2H].

Reduction of the Tetrahydro-photodimer with Lithium Aluminium Hydride.—The ketone (1 g) in dry dioxan (50 ml) was treated slowly under nitrogen with a slurry of lithium aluminium hydride (800 mg) in dry dioxan. After the mixture had been refluxed for 3 h ethyl acetate and water were added to it and the *tetraol* (550 mg) was isolated with chloroform, it formed needles from ethyl acetate, m.p. 176—177 °C (Found: C, 72.5; H, 11.0. $C_{24}H_{44}O_4$ requires C, 72.7; H, 11.2), $\nu_{max.}$ 3 300br cm^{-1} (hydroxy).

Dipole Moments.—The dipole moments were measured in anhydrous benzene in an apparatus of the Sutton and Hill type, using a Sayce–Briscoe cell and Guggenheim's method of calculation. Experimental values of 0.07 and 0.13 D were obtained for the dipole moments of the tetrahydro-photodimer (7) and the 4,8-deoxy-compound (15). These are probably zero within experimental error.

Crystallographic Analyses of Methyl 6-Isobutenyl-2-methyl-4-oxocyclohex-2-enecarboxylate (1) *and its Photodimer* (3).—Suitable specimens of both compounds were recrystallised from methanol. Oscillation and Weissenberg photographs were taken to establish unit-cell dimensions and space group. For intensity measurements of the monomer a crystal of dimensions *ca.* 1.2 × 0.6 × 0.2 mm^3 was mounted about the *a* axis on a Hilger and Watts linear diffractometer. An incident collimator of diameter 1.0 mm was used to accommodate the large crystal size. Unit-cell dimensions were refined on the positions of axial reflections found on the diffractometer. With Mo-K_α radiation, intensity data were collected on the levels 0—14*kl*, by the moving-crystal stationary-counter method. Each reflection was measured twice, and the mean taken in data reduction. For intensity measurement of the dimer (3) a crystal of dimensions *ca.* 0.6 × 0.5 × 0.1 mm^3 was mounted on a Hilger and Watts, computer-controlled four-circle diffractometer. Unit-cell dimensions were refined by a least-squares fit on the positions of 12 reflections found on the diffractometer. Intensity data were collected with

Mo-K_α radiation using an ω–2θ scan for $2\theta \leqslant 50°$. For both structures reflections with a net count greater than 3.0 standard deviations were considered observed and used in the subsequent structure refinement. Totals of 2 225 [for (1)] and 2 167 [for (3)] independent reflections were measured of which 1 259 [for (1)] and 1 631 [for (3)] were considered observed. No absorption corrections were made. Data reduction and subsequent crystallographic calculations were performed using the National Research Council (Ottawa) programs of Ahmed *et al.* for the monomer (1), and the ' X-Ray '70 ' system of programs[8] for the dimer (3). Atomic scattering factors were taken from ref. 9.

Crystal Data.—Monomer (1): $C_{13}H_{18}O_3$, $M = 222.3$, m.p. 73 °C, monoclinic, $a = 14.96 \pm 0.04$, $b = 8.20 \pm 0.02$, $c = 11.00 \pm 0.03$ Å, $\beta = 109.37 \pm 0.10°$, $U = 1\,273.0$ Å^3, $Z = 4$, $D_c = 1.16$ g cm^{-3}, $F(000) = 480$. Space group $P2_1/c$ uniquely from systematic absences. Mo-K_α radiation $\lambda = 0.710\,69$ Å, μ(Mo-K_α) 0.88 cm^{-1}.

Dimer (3): $C_{26}H_{36}O_6$, $M = 444.6$, m.p. 248 °C, triclinic, $a = 5.963 \pm 0.005$, $b = 7.721 \pm 0.007$, $c = 13.969 \pm 0.010$ Å, $\alpha = 103.49 \pm 0.05$, $\beta = 96.31 \pm 0.05$, $\gamma = 95.22 \pm 0.05°$ $U = 617.1$ Å^3, $Z = 1$, $D_c = 1.19$ g cm^{-3}, $F(000) = 240$. Space group $P\bar{1}$ from intensity statistics and subsequent refinement. Mo-K_α radiation $\lambda = 0.710\,69$ Å, μ(Mo-K_α) 0.90 cm^{-1}.

TABLE 2

Monomer (1). Atomic co-ordinates with their standard deviations in parentheses. Hydrogen atoms are numbered according to the atom to which they are bonded

Atom	*x/a*	*y/c*	*z/c*
O(1)	0.166 2(2)	0.357 6(4)	0.259 3(3)
O(2)	0.239 8(2)	0.433 7(4)	0.122 3(2)
O(3)	0.454 7(2)	0.616 8(4)	0.723 6(2)
C(1)	0.318 4(2)	0.490 1(4)	0.342 5(3)
C(2)	0.367 4(2)	0.365 4(4)	0.445 2(3)
C(3)	0.408 9(3)	0.409 8(5)	0.567 7(4)
C(4)	0.412 6(2)	0.580 0(5)	0.610 7(3)
C(5)	0.365 2(3)	0.707 4(5)	0.512 7(4)
C(6)	0.282 4(2)	0.639 1(5)	0.399 4(3)
C(7)	0.232 4(3)	0.417 9(5)	0.238 9(3)
C(8)	0.156 6(4)	0.379 9(7)	0.158(4)
C(9)	0.372 4(3)	0.190 6(5)	0.404 4(4)
C(10)	0.241 5(3)	0.767 4(5)	0.299 4(4)
C(11)	0.151(3)	0.811 8(5)	0.246 8(3)
C(12)	0.069 7(3)	0.736 5(7)	0.278 9(5)
C(13)	0.123 5(4)	0.944 0(6)	0.145 8(4)
H(1)	0.371	0.526	0.298
H(3)	0.441	0.316	0.638
H(5A)	0.418	0.759	0.474
H(5B)	0.340	0.805	0.560
H(6)	0.226	0.599	0.436
H(8A)	0.165	0.254	−0.007
H(8B)	0.096	0.391	0.048
H(8C)	0.147	0.455	−0.067
H(9A)	0.300	0.141	0.364
H(9B)	0.405	0.187	0.329
H(9C)	0.413	0.118	0.486
H(10)	0.293	0.832	0.266
H(12A)	0.095	0.644	0.352
H(12B)	0.033	0.830	0.314
H(12C)	0.020	0.681	0.194
H(13A)	0.069	0.902	0.060
H(13B)	0.185	0.982	0.120
H(13C)	0.097	1.050	0.183

Both structures were solved by direct methods using intensity data normalised from the SAP programs of Ahmed *et al.* (National Research Council, Ottawa) with k(s) values taken from a smooth curve drawn through the experimental points. The symbolic addition procedure of the same programs was used for the sign determination of the monomer (1). 149 Reflections with $E > 1.8$ were used of which 3 were allocated the signs to define the origin and a further 4 were allotted symbols. Inspection of the accumulated signs and symbols of these reflections readily suggested signs for all 4 unknown symbols. A subsequent E map based on the resulting signs showed 14 large peaks interpretable as the expected molecule with both terminal methyl groups of the isobutenyl side-chain missing. The intensity statistics for the dimer (3) clearly indicated the

TABLE 3

Dimer (3). Atomic co-ordinates with their standard deviations in parentheses. Hydrogen atoms are numbered according to the atom to which they are bonded.

Atom	*x/a*	*y/b*	*z/c*
O(1)	0.048 2(5)	0.186 6(4)	0.315 9(2)
O(2)	0.372 5(4)	0.150 1(4)	0.252 3(2)
O(3)	−0.268 3(6)	−0.403 8(4)	−0.081 1(2)
C(1)	0.048 7(6)	−0.036 0(5)	0.163 0(2)
C(2)	−0.035 7(6)	−0.050 4(4)	0.077 4(2)
C(3)	−0.158 4(5)	−0.092 5(4)	0.015 4(2)
C(4)	−0.216 1(6)	−0.282 0(5)	−0.007 1(3)
C(5)	−0.211 5(9)	−0.3208 (6)	0.092 7(3)
C(6)	−0.140 7(7)	−0.162 1(5)	0.185 4(3)
C(7)	0.153 3(6)	0 109 6(5)	0.252 7(3)
C(8)	0.487 2(8)	0.301 2(7)	0.328 6(4)
C(9)	−0.178 5(6)	0.204 4(5)	0.110 7(3)
C(10)	−0.054 2(7)	−0.240 3(5)	0.270 3(3)
C(11)	−0.140 7(8)	−0.237 1(5)	0.353 8(3)
C(12)	−0.346 4(11)	−0.147 1(8)	0.382 9(4)
C(13)	−0.031 6(10)	−0.326 3(7)	0.430 1(3)
H(1)	0.176(7)	−0.100(5)	0.140(3)
H(3)	−0.306(6)	−0.066(5)	−0.048(3)
H(5A)	−0.378(9)	−0.389(7)	0.093(4)
H(5B)	−0.130(13)	−0.427(10)	0.096(5)
H(6)	−0.276(8)	−0.100(6)	0.198(3)
H(8A)	0.653(9)	0.310(7)	0.325(4)
H(8B)	0.492(10)	0.263(8)	0.389(4)
H(8C)	0.478(9)	0.389(7)	0.304(4)
H(9A)	−0.227(6)	0.253(5)	0.054(3)
H(9B)	−0.079(5)	0.310(1)	0.160(2)
H(9C)	−0.314(5)	0.153(4)	0.134(2)
H(10)	0.102(9)	−0.274(7)	0.262(4)
H(12A)	−0.497(8)	−0.237(6)	0.390(3)
H(12B)	−0.423(11)	−0.079(8)	0.337(5)
H(12C)	−0.305(13)	−0.043(10)	0.436(5)
H(13A)	0.076(9)	−0.248(7)	0.492(4)
H(13B)	−0.137(9)	−0.431(7)	0.441(4)
H(13C)	0.104(10)	−0.362(8)	0.413(4)

presence of a centre of symmetry with $|E|$0.795 and $|E^2-1|$0.978, compared with the theoretical values [10] $|E|$0.798, $|E^2-1|$0.968 for centrosymmetric and $|E|$0.886, $|E^2-1|$0.736 for non-centrosymmetric structures. Sign determination then proceeded using the Multan program.[11] 189 Reflections with $E > 1.7$ were used and the best set of signs, excluding the all-positive set, had a figure of merit 1.198. A subsequent E map based on these signs revealed the structure as the 16 largest peaks in the map. Block-diagonal least-squares refinements of atomic positions and isotropic temperature factors were then commenced. An immediate Fourier synthesis for the monomer (1) revealed the positions of the 2 missing carbon atoms. Four cycles of refinement lowered the value of the agreement factor R to 14.8% for (1) and 15.5% for (3) following which the temperature factors of all atoms were allowed to vary anisotropically. Four further cycles of refinement reduced R to 9.4% for the monomer (1) and 10.6% for the dimer (3).

Difference Fourier syntheses were next calculated which revealed the approximate positions of all 18 hydrogen atoms amongst the highest peaks in the maps. For (1) the precise positions of the hydrogen atoms were calculated from bond length and angle considerations, compared with the peak positions, and included in the structure factor calculations, with the isotropic temperature factor of the carbon atom to which they were attached, but without refinement. For (3) the hydrogen atoms were included in the refinement with isotropic temperature factors. Further final cycles of refinement [three for (1) and four for (3)] lowered R to 6.0% for the momomer (1) and 6.6% for the dimer (3). At this stage the largest parameter shifts were of the order 0.5σ (1) and 1.0σ (3) indicating that refinement had converged after totals of 11 cycles (1) and 12 cycles (3). Final difference maps were calculated which both showed no peaks or depressions >0.2 e Å^{-3} confirming the correctness of the refined structures. Final atomic co-ordinates are listed in Tables 2 and 3; temperature factors and observed and calculated structure factors are listed in Supplementary Publication No. 22403 (23 pp).*

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* For details of the Supplementary Publication Scheme see Notice to Authors No. 7, *J.C.S. Perkin I*, 1978, Index issue.