Dypnopinacol. Part III.[1] The Photochemistry of 4-Methyl-2,4,6-triphenylcyclohexa-2,6-dienyl Phenyl Ketone (Isodypnopinacolone)

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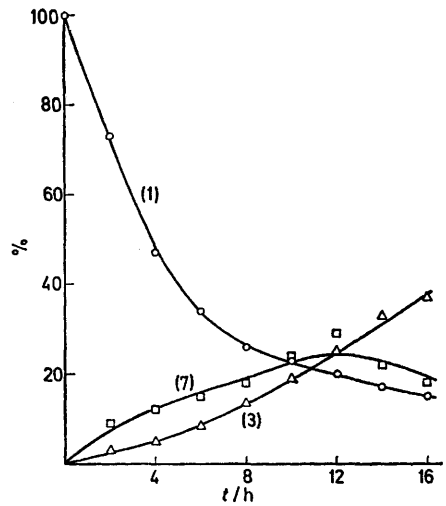
The two products of photorearrangement of 4-methyl-2,4,6-triphenylcyclohexa-2,6-dienyl phenyl ketone (isodypnopinacolone), first noted by Delacre in 1896, are now shown to be characteristic of cyclohexa-1,3-diene photo-transformations. Degradative reactions of the major product have shown it to be 6-*exo*-methyl-1,3,6-triphenylbicyclo[3,1,0]hex-2-en-2-yl phenyl ketone (α-photodypnopinacolone). The minor product is the 6-*endo*-methyl isomer (β-photodypnopinacolone).

We have previously[2] deduced the structures of a number of compounds [including isodypnopinacolone (1)] related to dypnone and obtained by Delacre as part of an extensive series of investigations. The action of sunlight on 5×10^{-3}M-solutions of isodypnopinacolone in ethanol denatured with butan-2-one, as examined by Delacre,[3] gave α- and β-photodypnopinacolone, both of which were converted by the action of base into δ-photodypnopinacolone. γ-Photodypnopinacolone was obtained from the α-isomer by the action of weak base and gave the δ-isomer on more vigorous treatment. All four compounds are isomeric and the conversion of the α- and β- into the γ- and δ-isomers does not require the action of light. Delacre[4] had previously reported the interconversion of these photodypnopinacolones under the names of β-, γ-, δ-, and ε-isodypnopinacolone; the α-isomer in this series is compound (1). We find the photoisomers to have a structure fundamentally different to that of isodypnopinacolone so that, if trivial names are to be retained for these products, the sequence based on photodypnopinacolone is more satisfactory. No previous structural studies on these compounds have been reported.

The photo-reaction of isodypnopinacolone in ethanol, or (better) ethanol containing butan-2-one, with Pyrex-screened medium-pressure mercury lamp proceeded readily to give the products isolated previously by Delacre. The reaction was followed by ^{1}H n.m.r. spectroscopy (see Figure). β-Photodypnopinacolone is formed initially at a greater rate than the α-isomer. However irradiation of either pure isomer in ethanol affords the same equilibrium mixture of the two containing 80% of the α-photodypnopinacolone as reported by Delacre. In consequence of this equilibration when most of the isodypnopinacolone has reacted the product is largely α-photodypnopinacolone.

Structures of α- and β-Photodypnopinacolone.—Elemental analysis[3] and mass spectral data confirm that α- and β-photodypnopinacolone are isomeric ($C_{32}H_{26}O$). Both show a low-frequency carbonyl i.r. absorption indicating the presence of extended conjugation (PhCO·C=C). The presence of this chromophore is confirmed by the u.v. spectra [$\lambda_{max.}$ 268 nm (ε 21,000)] and the fragment ion $PhCO^+$ is abundant in the mass spectra. The i.r. spectra also indicate the presence of a cyclopropane ring in each isomer [$\nu_{max.}$ 1028 cm^{-1} (ring deformation mode [5])].

The n.m.r. spectra each show the presence of four phenyl groups and a tertiary methyl group (τ 8·32 for α- and 8·74 for β-isomer). The methyl signal for the α-isomer could be considered as being due to a methyl group attached to an olefinic carbon atom. However



Formation of α- (3) and β-photodypnopinacolone (7) by irradiation of isodypnopinacolone (1) ($5{\cdot}2 \times 10^{-3}$M) in ethanol

in view of the position of this signal in spectra of various derivatives of α-photodypnopinacolone this second postulate appears unlikely. Each isomer shows signals for three other aliphatic protons, with coupling constants J_{ab} 18, J_{ac} 8, J_{bc} 0 or 1 Hz, which suggest the arrangement $-CH_aH_b{\cdot}CH_c\langle$. This part of the spectrum of the α-isomer assumed more of a first-order character with [$^2H_6$]benzene as solvent than with [^{2}H]chloroform. In spite of its being attached to the tertiary carbon atom H_c gave the signal at highest field in the spectra of both isomers, which suggests that it is attached to the cyclopropane ring. We are assuming in this discussion that long-range coupling effects will be negligible, though this may not be so. In support of the vicinal arrangement

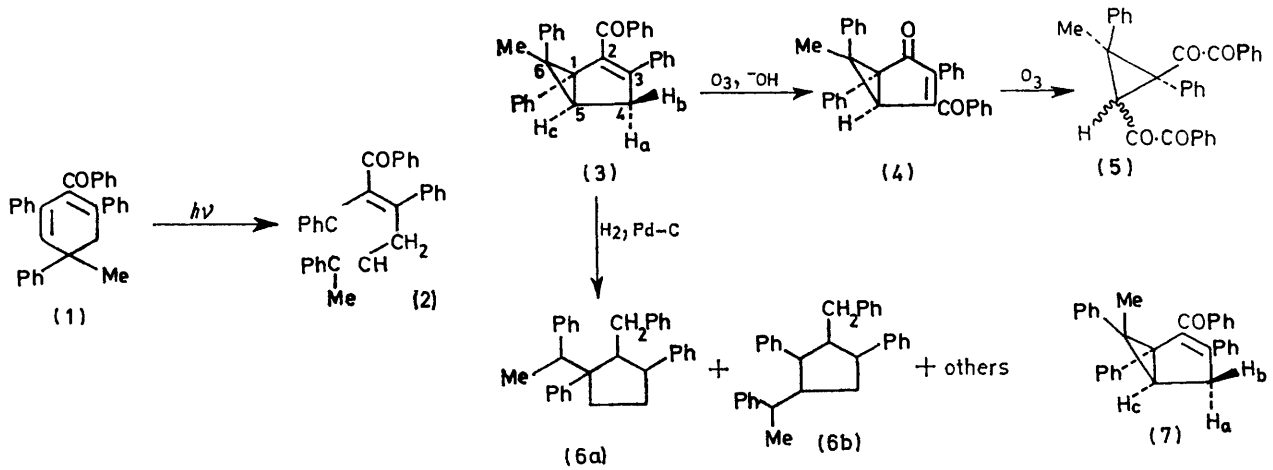
[1] Part II, C. W. Alexander and J. Grimshaw, preceding paper.
[2] Part I, J. Grimshaw and W. B. Jennings, *J. Chem. Soc.* (*C*), 1970, 817.
[3] M. Delacre, *Bull. Soc. chim. France*, 1925, [**4**] **87**, 440.
[4] M. Delacre, *Bull. Acad. roy. belg.*, 1896, [3] **32**, 95.
[5] J. M. Derfer, E. E. Pickett, and C. E. Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 2482.

of H_a and H_c, α-photodypnopinacolones is converted by base into a γ-isomer in which two vicinal protons must be present as a CH=CH group.[6]

Reduction of α-photodypnopinacolone with lithium aluminium hydride in ether gave an alcohol which could be oxidised to the starting ketone. This alcohol no longer contains the PhCO chromophore, yet it still apparently possesses an unsaturated group conjugated to the benzene ring. The u.v. absorption [$\lambda_{max.}$ 260 nm (ε 4900)] is stronger than expected for four isolated phenyl groups [tetraphenylmethane[7] has $\lambda_{max.}$ 262 nm (ε 1300)] and is probably due to a substituted styrene system [styrene has $\lambda_{max.}$ 244 nm (ε 13,000)] since the results of hydrogenation and ozonolysis experiments on α-photodypnopinacolone indicate the presence of an olefin. The alcohol also shows i.r. evidence ($\nu_{max.}$ 1020 cm^{-1}) for a cyclopropane ring and n.m.r. evidence for the CH_2·CH group.

Partial structure (2) can be deduced for α-photodypnopinacolone. The proposed linkage of the groups follows from the evidence now presented. Ozonolysis of α-photodypnopinacolone in methanol followed by reduction with dimethyl sulphide[8] afforded a product (4) of molecular formula $C_{32}H_{24}O_2$, the formation of which can be explained as the result of ozonolysis to give a triketone followed by condensation with loss of water to give an olefinic diketone. This diketone has a simple n.m.r. spectrum, showing only singlet methyl and CH signals in the aliphatic region. It shows an abnormally high frequency i.r. carbonyl absorption and a complicated u.v. spectrum which will be discussed later. The i.r. spectrum also indicated the presence of a cyclopropane ring and the mass spectrum had a strong peak attributed to $PhCO^+$.

Ozonolysis of the diketone (4) afforded a tetraketone (5) ($C_{32}H_{24}O_4$), the n.m.r. spectrum of which also showed only two types of aliphatic proton (Me and CH singlets). The i.r. spectrum indicated the presence of a cyclopropane ring and both i.r. and u.v. spectra were characteristic of an α-diketone. In order to account for the formation of the diketone (4) is seemed necessary to link the PhCO·C=CPh unit in (2) with the CH_2·CH unit as shown. A three-carbon unit with one degree of unsaturation and bearing hydrogen and methyl substituents persists in both ketonic ozonolysis products. This must be the cyclopropane ring, whose presence in α-photodypnopinacolone has been deduced from i.r. and n.m.r. evidence. The structural units given in (2) account for all the atoms of the molecule, so the structure of α-photodypnopinacolone, thus far without stereochemistry, seems to be best accommodated in system (3). Structures (4) and (5) for the ozonolysis products follow.



Hydrogenation of α-photodypnopinacolone was attempted in order to determine the number of olefinic groups. With a palladium catalyst 4 mol. equiv. of hydrogen were taken up to give an oily hydrocarbon ($C_{32}H_{32}$) which on g.l.c. showed the presence of two components in approximately equal amounts. These could not be separated by preparative g.l.c. No evidence for carbonyl or hydroxy-functions was found in the i.r. spectrum and neither was there a peak attributable to a cyclopropane ring vibration. In the absence of oxygen functions, the mass spectral fragments at *m/e* 105 and 91 were assigned as $PhCH{\cdot}CH_3^+$ and $PhCH_2^+$, respectively. The n.m.r. spectrum showed the methyl resonance as a doublet (apparent *J* 7 Hz). Thus on hydrogenation of compound (3) the carbonyl function is reduced to CH_2 and four other hydrogen atoms are added with saturation of the olefinic link and rupture of the cyclopropane ring to give a mixture of hydrocarbons possibly containing compounds (6a) and (6b). Such reactions are known to be catalysed by palladium.[9]

Attempted selective hydrogenation with $[H(Me_2SO)_2]^+$

[6] Part IV, C. W. Alexander and J. Grimshaw, following paper.

[7] G. Kortum and G. Dreeson, *Chem. Ber.*, 1951, **84**, 182.

[8] J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Letters*, 1966, 4273.

[9] R. L. Augustine, 'Catalytic Hydrogenation,' Marcel Dekker, New York, 1965.

trans-$[Cl_4Ir^{III}(Me_2SO)_2]^-$ in propan-2-ol and water [10] resulted in no reaction. Use of poisoned palladium catalysts ($BaSO_4$–Pd–C) gave either the foregoing hydrocarbon mixture or resulted in no reaction.

The spectral data for α- and β-photodypnopinacolones are very similar. Both compounds have been converted by the action of base into δ-photodypnopinacolone,[3,4,6] so both probably have the same carbon skeleton. The α- and β-isomers are therefore considered to be 6-epimers.

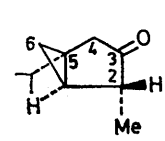
Stereochemistry of α- and β-Photodypnopinacolones.—The methyl chemical shifts (τ 8·32 in the α- and τ 8·74 in the β-isomer) allow stereochemical assignments to be made. The difference is attributed to shielding in one isomer, because of the anisotropy of the olefinic 2,3-bond. Such a shielding effect has been noted previously in a closely related bicyclo[3,1,0]hexene derivative (9),[11] where the *exo*-methyl group resonates at τ 9·0 and the *endo*-methyl at τ 9·3. Other related examples are known.[12] Thus α-photodypnopinacolone is assigned structure (3) (*exo*-Me) and β-photodypnopinacolone structure (7) (*endo*-Me).

Stereochemistry (*exo*- or *endo*-) can be assigned to H_a and H_b of the CH_2 groups in α- and β-photodypnopinacolone from the values of their coupling constants to H_c. There is a large geminal coupling constant J_{ac} (18 Hz). The very small coupling constant J_{bc} (1 Hz for α-, *ca.* 0 for β-isomer) implies a dihedral angle between the protons of *ca.* 90° on the basis of the Karplus equation, and H_b is therefore *endo* in both α- and β-isomers. The *exo*-proton is H_a in both isomers, with J_{ac} 8 Hz. In support of these conclusions is the observation [13] that the coupling constant between H-1 and H-2 (*endo*-stereochemistry) of (—)-thujone (8) is zero.

Nuclear Overhauser effect experiments were attempted with each photodypnopinacolone, by irradiation at the methyl frequency. The solutions were degassed by repeated freezing and thawing and finally sealed under nitrogen. However no effect was observed.

Spectral Properties of the Diketone (4).—This diketone shows a complex u.v. spectrum ($\lambda_{max.}$ 225, 262, and 309 nm) which strongly resembles the spectrum of umbellulone (10) ($\lambda_{max.}$ 220, 265, and 300 nm).[14] The phenyl and carbonyl substituents extra to the umbellulone chromophore appear to make no contribution to the conjugation and are probably twisted out of plane owing to steric crowding. The abnormal i.r. carbonyl absorption (1730 cm^{-1}) shown by compound (4) agrees with that observed for umbellulone; in addition a band at 1640 cm^{-1} appears for the exocyclic carbonyl function.

Ketone–Alcohol Interconversion of α-Photodypnopinacolone.—Reduction of α-photodypnopinacolone with lithium aluminium hydride gave one stereoisomer of the corresponding secondary alcohol. The mass spectrum of this product indicated the addition of only two hydrogen atoms. There was no further reduction of the olefinic bond, such as can occur with less hindered αβ-unsaturated ketones and allylic alcohols.[15]



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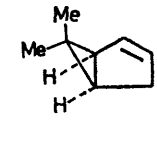

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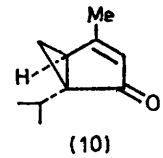

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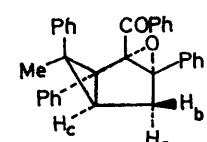


(11)

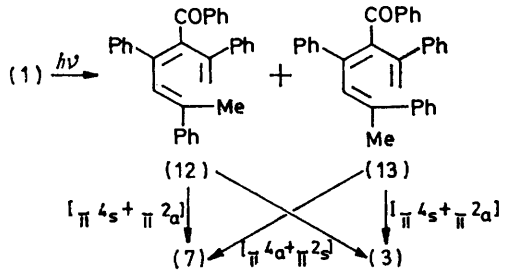
Oxidation of the alcohol with chromic acid–sulphuric acid afforded α-photodypnopinacolone as the major product, along with a second compound ($C_{32}H_{26}O_2$), m.p. 160—164°, showing a carbonyl absorption (1675 cm^{-1}) and a cyclopropane ring vibration (1025 cm^{-1}). The n.m.r. spectrum indicates structure (11) for this compound with the arrangement of aliphatic protons in a CH_2·CH group.

Hickinbottom's studies [16] show that epoxides can be formed from the oxidation of highly substituted ethylenes with chromic acid. The stereochemistry of the epoxide is probably as shown since steric effects will favour attack of the oxidising agent from the less hindered *exo*-face of the olefin. Oxidation of the secondary alcohol with chromic acid–pyridine gave only α-photodypnopinacolone.

Dehydrogenation of α-Photodypnopinacolone with Sulphur.—In this reaction two products were formed. The main product was 2,4,6-triphenylbenzophenone, which has also been obtained by dehydrogenation of α-, β-, and iso-dypnopinacolones.[2,17] It must result from a phenyl migration; migration of substituents has been observed previously during dehydrogenations with sulphur.[18] The minor product was a crystalline ketone which we have not identified.

[10] J. Trocha-Grimshaw and H. B. Henbest, *Chem. Comm.*, 1967, 546.
[11] J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, 1967, **89**, 1755.
[12] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, p. 84.
[13] M. S. Bergqvist and T. Norin, *Arkiv. Kemi*, 1964, **22**, 137 (*Chem. Abs.*, 1964, **60**, 12,058).
[14] R. H. Eastman and J. C. Selever, *J. Amer. Chem. Soc.*, 1954, **76**, 4118.
[15] F. A. Hochstein and W. C. Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3484; E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *ibid.*, 1967, **89**, 4245.
[16] W. J. Hickinbottom, D. Peters, and D. G. M. Wood, *J. Chem. Soc.*, 1955, 1360; W. A. Waters, *Quart. Rev.*, 1958, **12**, 288.
[17] D. Ivanov and C. Ivanov, *Ber.*, 1944, **77**, 173.
[18] D. J. Collins, *J. Chem. Soc.*, 1959, 531; D. H. R. Barton and G. S. Gupta, *ibid.*, 1962, 1961.

Mechanism of the Photochemical Reactions.—α- and β-Photodypnopinacolones are the normal photochemical reaction products expected from a cyclohexa-1,3-diene.[11,19-21] The first stage of reaction is a ring opening to a hexatriene which next undergoes a photochemical cyclisation to the bicyclo[3,1,0]hex-2-ene; application of this pathway to isodypnopinacolone (1) indicates the trienes (12) and (13) as intermediates. Such trienes have been detected as intermediates in the irradiation of a cyclohexa-1,3-diene [21] and have been cyclised photochemically.[22]

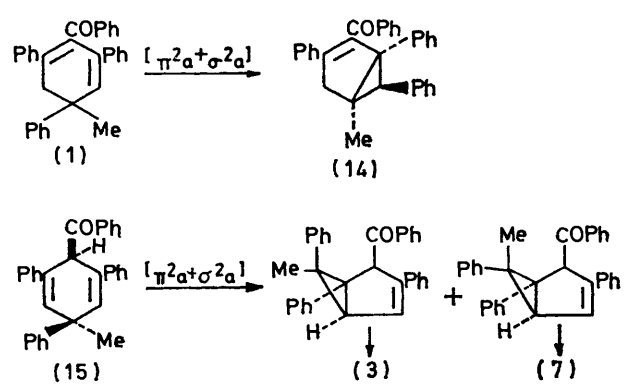


The orbital symmetry requirements for this concerted cyclisation of a triene have been examined.[23] Two symmetry-controlled reactions are theoretically possible, either $[_\pi 4_s + _\pi 2_a]$ or $[_\pi 4_a + _\pi 2_s]$. In one system, Padwa [22] has shown the $[_\pi 4_s + _\pi 2_a]$ route to be preferred. Ring opening of the cyclohexadiene (1) could lead to either triene (12) or (13) and the results of applying the two symmetry-controlled reactions to these trienes are illustrated. In Part II [1] we discussed the conformation of compound (1) and showed that, most probably, the methyl group has the pseudoaxial conformation. The photochemical reaction would therefore be expected to show a preference for formation of the triene (12), where the methyl group has rotated inwards thus minimising steric crowding in the transition state. Application of the $[_\pi 4_s + _\pi 2_a]$ route to (12) then leads to (7) as the kinetically preferred photoisomer. Our experimental observation for ethanolic solutions is that compound (7) is initially formed more rapidly than (3), but that the latter isomer predominates at equilibrium.

α- and β-Photodypnopinacolones are in photoequilibrium; this indicates that with this particular example the photochemical steps are all reversible. The cyclohexadiene-to-hexatriene step has been shown previously to be reversible,[19,22] but there is definite evidence in a case where two stereoisomeric bicyclo[3,1,0]hex-2-ene have been obtained that these are not interconvertible by the action of light.[22] The photodypnopinacolone system differs from the others examined in that a ketone function is also present and this function may sensitise the reverse photochemical reactions.

Attempts were made to demonstrate the presence of trienes (12) and (13) in reaction mixtures by u.v. and n.m.r. spectroscopy, all without success. It emerged however that photolysis of isodypnopinacolone (1) in very dilute solution (5×10^{-5}M) does not give both isomers (3) and (7). The u.v. spectrum of the starting material (1) disappeared and was not replaced by the spectrum of (3). Instead a less conjugated product was formed; we hope to investigate this reaction further.

Cyclohexa-1,3-dienes are known to undergo other types of photochemical rearrangement. Two other reactions, reviewed by Dauben,[19] do not lead to a cyclopropane product and cannot explain the formation of a product which would undergo the reactions of α-photodypnopinacolone. Cyclohexa-1,3-dienes can undergo a π-methane rearrangement and this is sensitised by benzophenone triplets (in the terminology of Woodward and Hofmann [23] this is a $[_\pi 2_a + _\sigma 2_a]$ reaction).[24] This leads to a cyclopropane; application of the scheme to isodypnopinacolone (1) may give either compound (14) or a structural isomer in which Me rather than Ph has migrated. The reaction, if concerted, should be stereospecific, but Zimmerman [24] does record a stereoisomer ratio of 13·5 : 1 for a case where this point has been tested. Structure (14) can accommodate the ozonolysis reactions of α-photodypnopinacolone but it cannot accommodate the reaction with base to yield γ-photodypnopinacolone, which contains a CH=CH group.[6] Neither is there accommodation for β-photodypnopinacolone as the initial product which undergoes



conversion into the α-stereoisomer. Structure (14) is therefore discounted. Interestingly, the ring opening of a hexa-1,3-diene is not sensitised by a ketone triplet, in contrast to the π-methane rearrangement.[24]

We know that isodypnopinacolone is in equilibrium

[19] Reviewed by W. G. Dauben, *Pure Appl. Chem.*, 1964, **9**, 539.
[20] G. R. Evanega, W. Bergman, and J. English, *J. Org. Chem.*, 1962, **27**, 13.
[21] R. J. deKock, N. G. Minnard, and E. Havinga, *Rec. Trav. chim.*, 1960, **79**, 922; J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, 1966, **88**, 2850.
[22] A. Padwa and S. Clough, *J. Amer. Chem. Soc.*, 1970, **92**, 5803; A. Padwa, L. Brodsky, and S. C. Clough, *Chem. Comm.*, 1971, 417.
[23] R. B. Woodward and R. Hofmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.
[24] H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, 1970, **92**, 1411.

with its tautomer (15), so the phototransformation in a protic solvent such as ethanol may proceed through the latter species. In an aprotic solvent this proton-catalysed tautomerism could be replaced by a concerted 1,3-photomigration of hydrogen. The di-π-methane rearrangement [25] (again a $[_{\pi}2_a + {}_{\sigma}2_a]$ reaction) of (15) and its stereoisomer can give both α- and β-photodypnopinacolones if it is applied either to both stereoisomers of (15) or to both conformers of one stereoisomer. This reaction is sensitised by ketone triplets.[25] Irradiation of isodypnopinacolone in anhydrous ether gives α- and β-photodypnopinacolones, but in a markedly different ratio (95% α-isomer) to that obtained from solutions in ethanol.

EXPERIMENTAL

U.v. spectra were recorded for solutions in ethanol. ^{1}H N.m.r. spectra were obtained for solutions in deuteriochloroform, unless otherwise stated, with a Varian HA-100 spectrometer (tetramethylsilane as internal lock). Mass spectra was measured with an ionising beam voltage of 70 eV. A 125 W Hanovia medium-pressure mercury vapour lamp enclosed in a water-cooled Pyrex jacket was used for the photoreactions. Light petroleum had b.p. 40—60°.

α- and β-Photodypnopinacolones.—Isodypnopinacolone [2] (2·0 g, 4·7 mmol) in ethanol (300 ml) containing pentan-2-one (0·02 g, 0·28 mmol) was irradiated at 20° for 48 h. The solid (0·73 g, 36%), m.p. 197—198°, which formed was filtered off and the filtrate irradiated for a further 12 h. More solid (0·17 g, 9%) formed and was collected. The combined solids were recrystallised from acetic acid (140 ml) and then from benzene (10 ml) to give α-photodypnopinacolone (3) (0·35 g, 18%), m.p. 200—201° (lit.,[3] 200°), $\nu_{max.}$ ($CHCl_3$) 1660 (C=O) and 1028 cm^{-1} (cyclopropane deformation), $\lambda_{max.}$ 200 (ε 29,000), 268 (21,000), and 355sh nm, τ ($CDCl_3$) 8·32 (3H, s, Me), 6·18 (1H, q, H_a), 7·12 (1H, d, H_b), 7·26 (1H, d, H_c), and 2·3—3·2 (*ca.* 20H, m, aromatic), J_{ab} 20, J_{ac} 8, J_{bc} 1 Hz (irradiation at τ 8·32 caused no change in the integral at τ 7·26), τ (C_6D_6) 8·20 (3H, s, Me), 6·04 (1H, q, H_a), 7·27 (1H, q, H_b), 7·41 (1H, q, H_c), and 2·0—2·3 (m, aromatic), J_{ab} 18, J_{ac} 7·5, J_{bc} 1 Hz, *m/e* 426 (30%, M^+), 411 (6, $M^+ - CH_3$), 322 (9), 321 (36, $M^+ -$ PhCO), 320 (9), 215 (4), 115 (5), 105 (100, $PhCO^+$), 91 (4), and 77 (35, Ph^+).

The acetic acid mother liquors from crystallisation of the α-isomer were concentrated to 20 ml, giving more α-isomer (0·21 g, 10%). Concentration of the filtrate to 5 ml afforded a solid (0·23 g, 11%) which was recrystallised from ethanol (20 ml) to yield β-photodypnopinacolone (7) (0·18 g, 9%), m.p. 180—181° (lit.,[3] 180—181°), $\nu_{max.}$ ($CHCl_3$) 1660 (CO) and 1028 cm^{-1} (cyclopropane ring deformation), $\lambda_{max.}$ 220 (ε 29,000), 269 (ε 20,500), and 335sh nm, τ 8·74 (3H, s, Me), 6·34 (1H, q, H_a), 7·33 (1H, d, H_b), 7·90 (1H, d, H_c), and 2·0—3·4 (20H, m, aromatic), J_{ab} 18·5, J_{ac} 7·5, J_{bc} 0·0 Hz (irradiation at τ 8·47 caused no change in the integral at τ 7·90), *m/e* 426 (32%, M^+). 411 (5, $M^+ - Me$), 321 (35, $M^+ - PhCO$), 215 (5), 115 (5), 105 (100, $PhCO^+$), 91 (5), and 77 (35, Ph^+).

Isodypnopinacolone (1·0 g) in ether (200 ml) was irradiated for 24 h at room temperature. Evaporation of the solvent left a solid (95% α-, 5% β- by n.m.r.) from which α-photodypnopinacolone, m.p. 200—201°, was obtained.

Determination of Yields.—(*a*) Isodypnopinacolone (2 g) was dissolved in ethanol (900 ml) and irradiated at 20° until precipitation of the products commenced. Samples (25 ml) were removed and the solvent evaporated. 1,4-Dimethoxybenzene (25 mg) was added to each as internal standard and the relative amounts of compounds (1), (3), and (7) determined by integrating the *C*-Me and *O*-Me n.m.r. signals (see Figure).

(*b*) A solution of α-photodypnopinacolone (0·20 g) in ethanol (400 ml) was irradiated at 20°. Samples were taken for n.m.r. analysis until a constant ratio of α- to β-isomer was obtained (7 h). A solution of the β-isomer (0·02 g) in ethanol (40 ml) was irradiated for the same length of time to give the same equilibrium mixture (80% α- and 20% β-isomer).

Reduction of α-Photodypnopinacolone with Lithium Aluminium Hydride.—α-Photodypnopinacolone (0·30 g, 0·7 mmol) in ether (15 ml) was added dropwise during 20 min to a solution of lithium aluminium hydride (70 mg, 2·0 mmol) in ether (10 ml) and the mixture was refluxed for 2 h. Ethyl acetate (10 ml) was added and the cold mixture was filtered and evaporated to dryness. The residual secondary alcohol related to (3) crystallised from ether–light petroleum as rectangles (0·27 g, 87%), m.p. 148—150° (Found: C, 89·5; H, 6·6. Calc. for $C_{32}H_{28}O$: C, 89·7; H, 6·6%), $\nu_{max.}$ (KBr) 3560 (OH) and 1020 cm^{-1} (cyclopropane ring), $\lambda_{max.}$ 208 (ε 13,000) and 260 nm (ε 4900), τ 8·67 (3H, s, Me), 4·38 (1H, d, collapsed to s on shaking with D_2O, *J* 9 Hz, PhC*H*), 6·66 (1H, q, H_a), 7·20 (1H, q, H_b), 7·53 (1H, q, H_c), 8·55 (1H, d, disappears on shaking with D_2O, OH), and 2·5—3·2 (20H, m, aromatic), J_{ab} 18, J_{ac} 7, J_{bc} 1·5 Hz, *m/e* 428 (40%, M^+), 410 (25, $M^+ - H_2O$), 395 (10), and 105 (21).

Oxidation of the Foregoing Alcohol.—(*a*) A solution of chromium trioxide (2 g, 20 mmol) in water (9 ml) and concentrated sulphuric acid (1·75 ml) was added dropwise to the alcohol (0·90 g, 2·1 mmol) in acetone (20 ml) at 0°. After 10 min, water was added; the products were isolated with ether, washed with sodium hydrogen carbonate solution and water, and dried ($MgSO_4$), and the solvent was removed. The residue was chromatographed on neutral alumina (activity I). Light petroleum–ether (10 : 1) eluted 2,3-*epoxy*-6-*methyl*-1,3,6-*triphenylbicyclo*[3,1,0]*hexan*-2-*yl phenyl ketone* (11) (87 mg, 10%), m.p. 162—164° (from ether–light petroleum) (Found: C, 86·7; H, 6·1. $C_{32}H_{26}O_2$ requires C, 86·9; H, 5·9%), $\nu_{max.}$ ($CHCl_3$) 1675 (C=O), 1260 and 870 (epoxide), and 1025 cm^{-1} (cyclopropane ring), $\lambda_{max.}$ 216 (ε 67,500), 253 (ε 32,400), and 290 nm (ε 4500), τ 7·92 (3H, s, Me), 7·68 (1H, complex, H_c), 7·19 (2H, m, $H_a + H_b$), and 2·6—3·4 (*ca.* 20H, m, aromatic), *m/e* 442 (12%, M^+), 426 (10), 337 (8, $M^+ - PhCO$), 322 (24), 218 (8), 105 (100, $PhCO^+$), and 77 (32, Ph^+). Light petroleum–ether (10 : 2) eluted α-photodypnopinacolone, m.p. and mixed m.p. 200—201° (0·63 g, 70%).

(*b*) Chromium trioxide (1 g) was added to pyridine (10 ml) with the temperature kept below 30°. The alcohol (0·30 g) was then added and the mixture stirred for 3 days at 15°. The mixture was then poured into water and filtered, and the filtrate was extracted with ether. The ether extracts were washed with dilute hydrochloric acid and water, dried

[25] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, 1968, **90**, 6097; H. E. Zimmerman and C. O. Bender, *ibid.*, 1969, **91**, 7516.

($MgSO_4$), and evaporated. Chromatography of the residue as before yielded only α-photodypnopinacolone, m.p. and mixed m.p. 200—201° (0·25 g, 82%).

Ozonolysis of α-Photodypnopinacolone.—α-Photodypnopinacolone (1 g) was dissolved in chloroform (20 ml) and methanol (25 ml) and treated at −30° with a stream of ozonised oxygen (1 l min^{-1}; 65 mg ozone per l) for 12 h. While still at −30°, the system was flushed with nitrogen, and dimethyl sulphide (3 ml) in methanol (10 ml) was added. The mixture was allowed to warm slowly to room temperature during 4 h and the solvents were then removed *in vacuo*. The residue in light petroleum was washed with water and dried ($MgSO_4$). Evaporation left a yellow-brown oil (0·8 g) which was chromatographed on basic alumina. Elution with light petroleum–ether (1 : 1) afforded 4-*benzoyl*-6-*methyl*-1,3,6-*triphenylbicyclo*[3,1,0]*hex*-3-*en*-2-*one* (4) as plates (0·33 g, 32%), m.p. 193—194° (from methanol) (Found: C, 87·0; H, 5·8. $C_{32}H_{24}O_2$ requires C, 87·2; H, 5·5%), $\nu_{max.}$ 1730 (C=O), 1640 (C=O), and 1029 cm^{-1} (cyclopropane ring), $\lambda_{max.}$ 225 (ε 3330), 262 (ε 1260), and 309 nm (ε 3780), τ 8·63 (3H, s, Me), 7·09 (1H, s), and 2·3—2·5 (20H, m, aromatic), *m/e* 440 (60%, M^+), 335 (6, M^+ − PhCO), 293 (10), 229 (10), 215 (7), 105 (100, PhCO), and 77 (18, Ph^+).

The diketone (4) (0·30 g) was dissolved in chloroform (38 ml) and methanol (12 ml) and ozonised as just described. The mixture was then decomposed with dimethyl sulphide. The red-brown oily product was chromatographed on neutral alumina. Elution with light petroleum–ether afforded the yellow oily 1-*methyl*-1,2-*diphenyl*-2,3-*bisphenylglyoxyloylcyclopropane* (5) (75 mg, 23%) (Found: C, 81·0; H, 5·5. $C_{32}H_{24}O_4$ requires C, 81·3; H, 5·1%), $\nu_{max.}$ (KBr) 1720, 1670 (C=O), and 1032 cm^{-1} (cyclopropane ring), $\lambda_{max.}$ 256 (ε 16,500) and 390 nm (ε 270), τ 8·78 (3H, s, Me), 8·16 (1H, s), and 2·3—3·3 (20H, m, aromatic), *m/e* 472 (5%, M^+), 440 (35), 412 (8), 367 (18), 291 (18), 289 (18), 229 (24), 221 (20), 215 (24), 202 (24), 191 (30), 189 (24), 178 (36), 165 (24), 105 (100, $PhCO^+$), 91 (40), and 77 (95, Ph^+).

Hydrogenation of α-Photodypnopinacolone.—α-Photodypnopinacolone (0·30 g) in ethyl acetate (50 ml) was hydrogenated at atmospheric temperature and pressure in the presence of 5% palladium–charcoal (0·05 g) (uptake 60 ml, 3·8 mol. equiv.). Filtration and evaporation left an oily hydrocarbon (Found: C, 92·1; H, 8·0. Calc. for $C_{32}H_{32}$: C, 92·3; H, 7·7%), τ 8·95 (3H, d, *J* 7 Hz, CH_3·CH), 6·60 (1H, q, *J* 7 Hz, PhC*H*Me), 7·5—8·5 (8H, m, aliphatic), and 2·5—3·5 (*ca.* 20H, m, aromatic), *m/e* 416 (55%, M^+), 233 (18), 219 (24), 207 (25), 193 (25), 143 (20), 129 (20), 119 (18), 117 (18), 115 (18), 105 (66, $PhCHMe^+$), 91 (100, $PhCH_2^+$), 86 (24), 85 (30), 84 (30), and 77 (50, Ph^+). G.l.c. analysis (F11 instrument; 2 m 2·5% silicone gum rubber column; *t* 130°) showed the presence of two major components in the ratio 1 : 1.

Dehydrogenation of α-Photodypnopinacolone.—α-Photodypnopinacolone (1 g) and sulphur (1 g) were heated at 250° for 2 h. The mixture was then extracted with dichloromethane and the extract washed with water and dried ($MgSO_4$). Evaporation gave a yellow-brown solid which was chromatographed on neutral alumina. Elution with light petroleum–ether (10 : 2) gave 2,4,6-triphenylbenzophenone (0·63 g, 60%), m.p. and mixed m.p. 166—168° (lit.,[17] 167—168°). Elution with ether gave a compound (0·10 g, 9%) which crystallised from ether–light petroleum as needles, m.p. 219—220° (Found: C, 80·1; H, 4·8%), $\nu_{max.}$ 1678 cm^{-1} (C=O), $\lambda_{max.}$ 250 (ε 18,340) and 370 nm (ε 5100), τ 2·5—3·0 (*ca.* 20H, m, aromatic), 4·52 (1H, s), and 8·46 (1H, s), *m/e* 454 (18%, M^+), 422 (9), 349 (16), 331 (15), 105 (100, $PhCO^+$), and 77 (80, Ph^+).

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