A New Reaction Pathway ($_6\pi + _2\pi$) for the Intramolecular Photocycloaddition of a Carbonyl Substituted Hexatriene[1]

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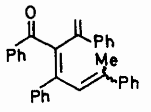
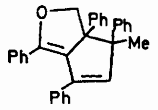
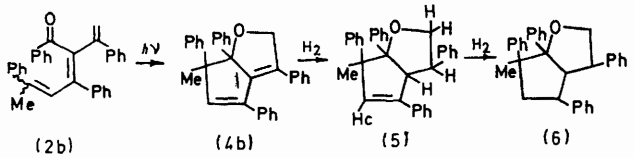
Summary The trienic primary product formed in the photochemical ring opening of the cyclohexadienic isodypnopinacolone follows two different photoreaction pathways: a [$_4\pi + _2\pi$] cycloaddition and a [$_6\pi + _2\pi$] reaction involving the conjugated carbonyl group.

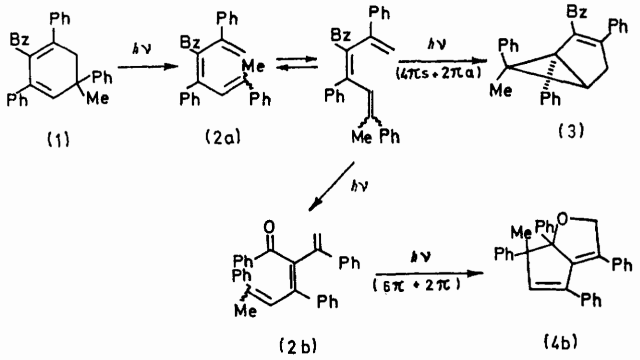


(2a)



(4a)





The results of Alexander and Grimshaw[2] on the irradiation in ethanolic and ethereal solutions of isodypnopinacolone (**1**)[3-5] prompt us to report our findings on the photochemical behaviour of this compound when irradiated in ether solution.

It appears that the presence of a benzoyl group on the cyclohexadiene ring does not alter the usual ring opening photoreaction[6] but a difference is found in the behaviour of the primary trienic photoproduct. Whereas Alexander and Grimshaw[2] isolated in ethanolic solution and identified in ethereal solution only one type of photoproduct, *i.e.* both isomers of the bicyclo[3,1,0]hex-2-enic derivative (**3**) α- and β-photodypnopinacolones[4], we isolated another photoproduct (**4**), with an unexpected structure. The irradiation of a $1\cdot5 \times 10^{-3}$M-ether solution of 4-methyl-2,4,6-triphenylcyclohexa-1,5-dienyl phenyl ketone, isodypnopinacolone (**1**), for 3 h with a medium-pressure mercury arc (Hanau Q 81, Pyrex filter), yields two main products (n.m.r. analysis), which were separated by liquid–solid column chromatography on 10% silver nitrate-silica gel. The first compound (35%) corresponds to the α-photodypnopinacolone (**3**), previously isolated and identified by Alexander and Grimshaw.[2]† We isolated a second compound ($C_{32}H_{26}O$, 35% yield), with m.p. 151°; λ_{max} (EtOH) 302 (16,800) and 267 nm (14,150); no carbonyl band in the i.r. spectrum, but strong bands near 1020—1070 cm^{-1} indicative of C–O–C deformation vibration. The n.m.r. spectrum ($CDCl_3$) shows a methyl singlet at τ 8·24, two aliphatic protons forming an AB system (J 12 Hz) centred at τ 4·74, and a multiplet at τ 2·35—3·33 corresponding to the four phenyl groups plus one vinylic proton (21H). These data and the hydrogena-

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† These authors used a longer irradiation period, 24 h, of a $1\cdot2 \times 10^{-2}$ M-ethereal solution of (**1**), in the same spectral region, but they used a crystallisation technique to obtain a 95–5 mixture (n.m.r. analysis) of (**3**) and of its *exo*-phenyl stereoisomer, the total yield not being mentioned.

tion results allow us to choose (**4b**) of the two possible structures (**4a** and **4b**) originating from the *cis* and *trans* isomeric primary trienes.

The photoproduct (**4**) can be selectively hydrogenated to a dihydro-photoproduct for which we suggest the structure (**5**) from n.m.r. data. Further hydrogenation yields a tetrahydro-photoproduct (**6**) identified by its n.m.r. spectrum. The occurrence of the methylene signal in the dihydro-photoproduct (**5**) at τ 5·65—6·06 supports structure (**4b**) in which the methylene is strongly deshielded by the allylic double bond (τ 4·74). We were not able to identify the presence of trienic compounds even in the first stages of irradiation, but the formation of (**3**) and (**4b**) can be rationalized only by assuming that ring opening has taken place in (**1**). In many cases[6,8,9] it was impossible to isolate the primary triene because of its high photochemical reactivity. The presence of a carbonyl group in (**1**) may enhance this reactivity through internal energy-transfer and we think that the following sequence fits the results: the ring opening of diene (**1**) yields the *Z*-central triene (**2a**) which is photocyclized to (**3**) through a $[{}_{4}\pi_{s} + {}_{2}\pi_{a}]$ allowed concerted mode.[1,6–9] This triene can be easily *cis–trans* photoisomerized (possibly through intramolecular triplet energy transfer) to the *E*-central triene (**2b**), which yields the bicyclic compound (**4b**) through a $[{}_{6}\pi + {}_{2}\pi]$ photocycloaddition.

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