Photocyclisation of 1,3,6-Triphenylhexa-1,3,5-triene

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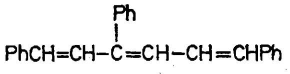
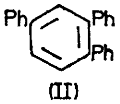
Summary Irradiation of 1,3,6-triphenylhexa-1,3,5-triene in the presence of iodine unexpectedly affords 1,2,4-triphenylbenzene; 3-methyl-1,6-diphenylhexa-1,3,5-triene, in contrast, gives chrysene.

Photocyclisation of 1,6-diarylhexa-1,3,5-trienes provides a convenient route to some polycyclic aromatic compounds. 1,6-Diphenylhexa-1,3,5-triene affords chrysene on irradiation in presence of an oxidant and a variety of substituted chrysenes has been prepared in the same way.[1] With 1,3,6-triphenylhexa-1,3,5-triene (I) (m.p. 132—133°, prepared by reaction of *trans*-chalcone with *trans*-cinnanmyltriphenylphosphonium bromide and ethanolic sodium ethoxide; stereochemistry of central double bond unknown) however, the reaction takes an unexpected course. Irradiation through Pyrex of a solution in benzene or cyclohexane at 20°, in presence of iodine, rapidly (1 h) leads to the formation of a crystalline product, $C_{24}H_{18}$, m.p. 99—100°, isolated after preparative layer chromatography (60%). This product



$PhCH{=}CH{-}\overset{\overset{Ph}{|}}{C}{=}CH{-}CH{=}CHPh$

(I)



(II)

is not the expected 6-phenylchrysene or 2-phenyl-1-styrylnaphthalene; its u.v. absorption [λ_{max} (cyclohexane) 248, infl. 270 nm; log ϵ 4·52, 4·38] indicates a simpler chromophore and, with the i.r. spectrum and the m.p. strongly suggests that the compound is 1,2,4-triphenylbenzene (II).[2] The same compound was readily obtained by heating[3] the hexatriene (50° in benzene) in the presence of iodine. Nevertheless, the product from the irradiation experiment appears to be formed mainly in a photoreaction; irradiation at 20° with iodine gave 90% conversion into 1,2,4-triphenylbenzene within 1 h (g.l.c.), but in the absence of light only about 10% triphenylbenzene was formed. In an attempt to isolate the initial cyclisation product the irradiation was conducted under non-oxidative conditions. The hexatriene was rapidly consumed but the product was an oily mixture (g.l.c., n.m.r.) from which no pure constituent has been isolated.

Since the photocyclisation product of 1,3,6-triphenylhexa-1,3,5-triene is surprising, the irradiation of 1,6-diphenylhexatriene was re-examined, but no more than a trace of product which might have been *o*-terphenyl was detected by g.l.c.; the main product, as before,[1] was chrysene. 3-Methyl-1,6-diphenylhexatriene was also mainly unchanged by irradiation under the same conditions as 1,3,6-triphenylhexatriene; more prolonged reaction gave chrysene by ejection of the methyl substituent.

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[3] *Cf.* A. Padwa, L. Brodsky, and S. Clough, *J. Amer. Chem. Soc.*, 1972, **94**, 6767.