PHOTOCYCLIZATION REACTIONS OF ARYL POLYENES—II[1]

THE PHOTOCYCLIZATION OF 1-ARYL-4-PHENYL-1,3-BUTADIENES

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Abstract—The photocyclization–oxidation reaction of 1-(β-naphthyl)-4-phenyl-1,3-butadiene gave 4-phenylphenanthrene and 1,2-benzopyrene. It was shown, however, that the 1,2-benzopyrene arose from a subsequent photochemical reaction of the first-formed 4-phenylphenanthrene. Irradiation of 1-(9'-phenanthryl)-4-phenyl-1,3-butadiene gave 1-phenyltriphenylene. The photocyclization-oxidation of 1-(9'-anthryl)-4-phenyl-1,3-butadiene yielded 3,4,8,9-dibenzopyrene. The formation of 3,4,8,9-dibenzopyrene is postulated to involve the intermediacy of a benzo-[10]-annulene.

THE photocyclization–oxidation reaction of stilbene-like molecules has received wide attention in recent years from both preparative[2] and mechanistic[3] points of view. The photocyclization–oxidation of 1,2-diarylethylenes. where one or both of the aryl groups represent polynuclear aromatic hydrocarbons has led to the synthesis of a wide variety of interesting polynuclear aromatic hydrocarbons, some of which would be tedious to synthesize by other routes.[4]

A similar type of photocyclization–oxidation reaction occurs when 1,4-diaryl-1,3-butadienes are irradiated in benzene or ether solution in the presence of oxygen or iodine to yield 1-phenylnaphthalenes.[1,5] In this paper we describe the results of the irradiations of 1,4-diaryl-1,3-butadienes in which one aryl group is a phenyl moiety and the other aryl group is a polynuclear aromatic hydrocarbon. It was of interest to determine the direction of cyclization of these compounds and to discuss the mechanisms of their photocyclization.
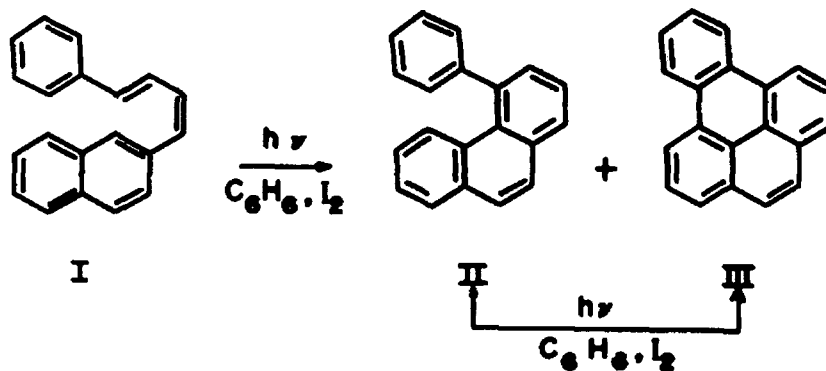

FIG 1

Irradiation of 3.9×10^{-3}M solutions of 1-(β-naphthyl)-4-phenyl-1,3-butadiene (I)[*] and 2×10^{-3}M iodine in dry C_6H_6 for 72 hr resulted in the disappearance of the absorption maxima of I at 332 nm, 345 nm and 364 nm. The crude reaction mixture was separated by T.L.C. to give 4-phenylphenanthrene (II) in 7% yield and 1,2-benzopyrene (III) in 4% yield. Although the formation of photo-dimers of I was noted, they were not purified or characterized.

The formation of 1,2-benzopyrene (III) in the photocyclization–oxidation of I was shown to arise from a further photocyclization–oxidation of the first-formed 4-phenylphenanthrene (II), as irradiation of pure II gave III in 46% yield.

Other possible monomeric products resulting from the photocyclization–oxidation of I, such as 1-phenylanthracene (IV) and 2,1'-binaphthyl (V) were not produced at least within the detection limits of TLC. Compounds II[6], III[7], IV[8], and V[9] were synthesized by known procedures and were shown to be well resolved using 2% $AgNO_3$-coated silica gel TLC plates. As shown above, compound II was unstable to the irradiation conditions and was slowly converted to III. Compound III, itself, slowly decomposed by about 10% under the irradiation conditions for 72 hr. Compounds IV and V were stable to the reaction conditions for 72 hr and hence would have been detected if formed from I.

From similar studies involving the photocyclization of styryl naphthalenes, it is not surprising that photocyclization of I occurs to the 1-position of the naphthalene nucleus to give II rather than to the 3-position to give IV as the free valence index at the 1-position of naphthalene is greater than that at the 3-position.[10]

The lack of formation of 2,1'-binaphthyl is expected as the energy required to form a dihydroderivative leading to V is much greater than the energy required to form the dihydroderivative leading to II. The formation of V thus requires the disruption of the resonance energy of a benzene ring, while the formation of II only disrupts the resonance energy of one of the rings of the naphthalene nucleus.

Irradiation of 3.3×10^{-3}M solutions of 1-(9'-phenanthryl)-4-phenyl-1,3-butadiene (VI) and 2×10^{-3}M iodine in dry C_6H_6 for 84 hr resulted in a 40% reduction of the absorption maximum of VI at 346 nm. The crude reaction mixture was separated on TLC to give 1-phenyltriphenylene (VII)[11] in 13.5% conversion. About 60% of the starting material was recovered from the photo-reaction. Although some dimeric photo products of VI were detected, compound VII was the sole monomeric product detected in the reaction mixture. Specifically, no 9-(α-naphthyl)phenanthrene (VIII) was isolated.[12] It is possible that 1-phenyltriphenylene (VII) can undergo a further photocyclization–oxidation reaction to give 1,2,6,7-dibenzopyrene (IX), but prolonged irradiation of VII resulted in no further reaction.

The product VII, obtained in the irradiation of VI is the expected product as there is only one position on the phenanthrene nucleus of VI available to take part in a photocyclization–oxidation reaction. For reasons identical to those discussed above for the irradiation of I, the formation of product VIII was neither predicted nor obtained.

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[*] It is assumed that the *trans-trans* butadienes are formed from the method of preparation. The IR spectral data for I, VI and X also show absorption peaks for *trans* double bonds. The *trans-trans* forms of these readily form equilibrium mixtures with cis-trans and cis-cis forms under the irradiation conditions and these stereoisomers give the observed photo-products.
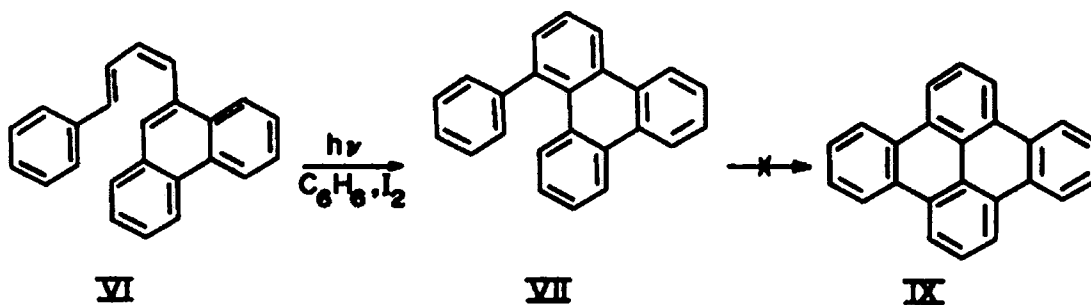
Fig 2

The photocyclization–oxidation reactions of I and VI led exclusively to products resulting from cyclization to the polynuclear aromatic substituent. A general rule can thus be formulated which states that *in photocyclization–oxidation reactions of 1-aryl-4-phenyl-1,3-butadienes the direction of photocyclization always occurs to the aryl group when the aryl group is a polynuclear hydrocarbon*. It is necessary, of course, for the polynuclear hydrocarbon to have a position ortho to the phenyldienyl group free for photocyclization. It was thus decided to attempt a photocyclization–oxidation reaction in which both positions ortho to the phenyl-dienyl substituent of the poly-nuclear aromatic hydrocarbon would be unavailable for photocyclization. To this end a 3.3×10^{-3}M solution of 1-(9'-anthryl)-4-phenyl-1,3-butadiene (X) containing 2×10^{-3}M iodine was irradiated as before. After 84 hr irradiation, the absorption maxima of X at 325 nm and 394 nm only decreased by 20%. From the reaction mixture 80% of the starting material could be recovered along with a new monomeric product shown to be 3,4,8,9-dibenzopyrene (XI) by comparison with a commercially available sample. Product XI was obtained in a 7% conversion from X. along with
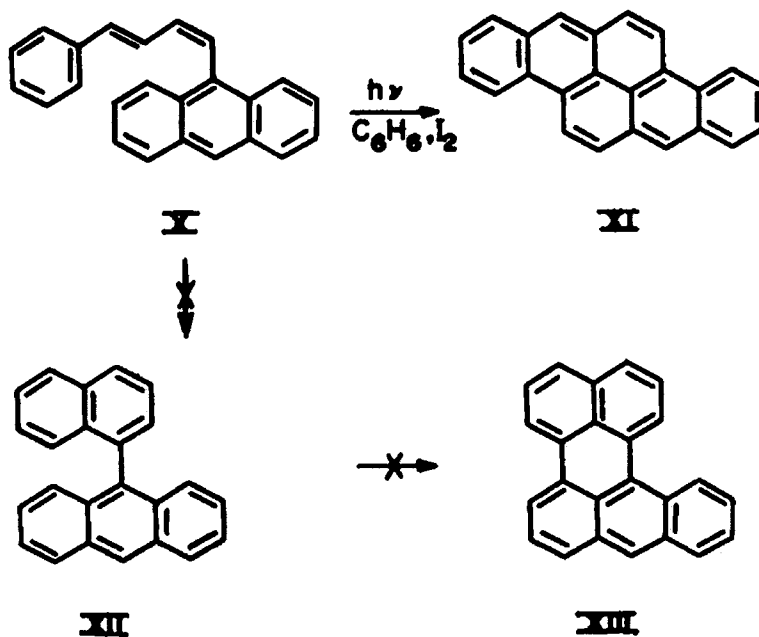

Fig 3

dimeric products which were not separated or characterized. The only other possible monomeric product that is likely to be formed is 9-(α-naphthyl)-anthracene (XII) which was synthesized by a known procedure[13] and proven to be absent from the photoproducts within the limits of TLC examination. The very slow photoreaction of X and the absence of XII in the photoproducts show that photocyclization to the phenyl ring of 1-aryl-4-phenyl-1,3-butadienes, where the aryl group is a polynuclear hydrocarbon, is a highly unfavoured process and does not occur even when alternative pathways are of very high energy. Compound XII was stable to prolonged exposure to light and hence the unlikely[10] photocyclization of XII to XIII could be definitely discounted.

The formation of XI in the photocyclization–oxidation reaction of X can be visualized as a photocyclization involving a 10π electron system to give the dihydro-intermediate XIV, which on dehydrogenation gives the intermediate [10]-annulene compound XV. Numerous syntheses of unbridged [10]-annulenes and its derivatives
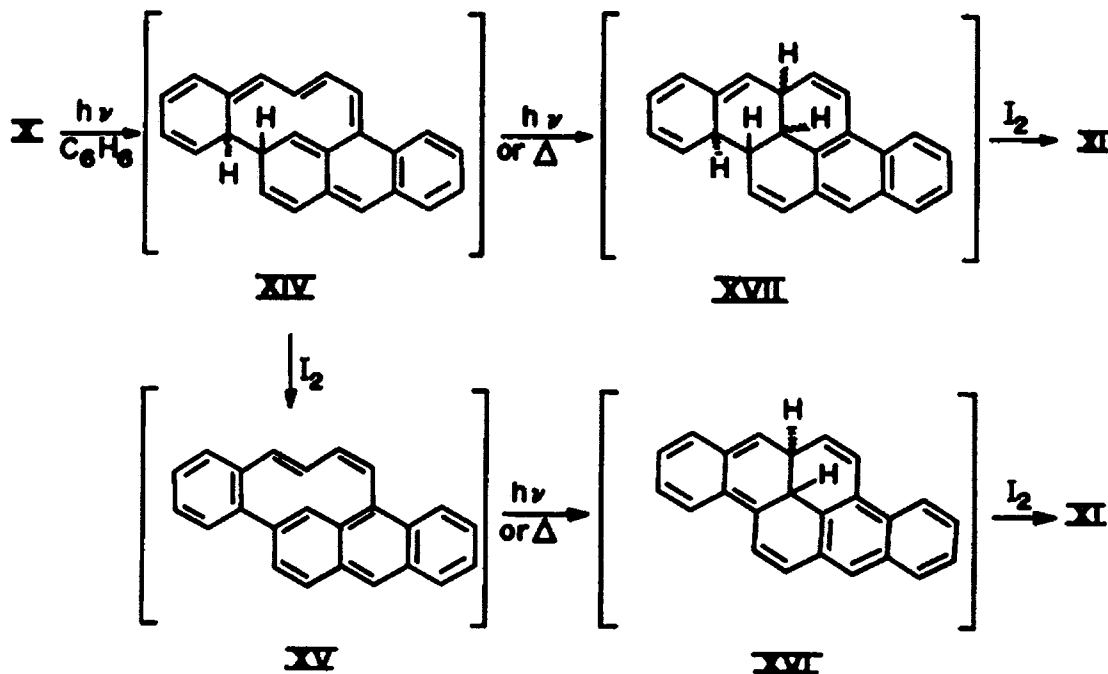

FIG 4

have been attempted but invariably any [10]-annulenes that have been sythesized undergo further thermal or photochemical cyclization and oxidation to naphthalene derivatives.[14] Thus, further thermal or photochemical cyclization of XV can give the dihydrointermediate XVI, which is readily oxidized to XI.

In an alternative scheme, the dihydrointermediate XIV, could undergo further thermal or photochemical cyclization prior to oxidation to give XVII, followed by the loss of 4 hydrogen atoms to give XI. This latter scheme is less favoured by the authors as the rate of the oxidation step under similar photo-cyclization–oxidation reaction conditions is known to be rapid.[15]

It is also possible that a benzo-[10]-annulene-type derivative is formed as an intermediate in the photo-cyclization–oxidation of I to give III, however, the formation of II from I and the further photo-conversion of II to III, seems to be the more likely pathway for the formation of III.
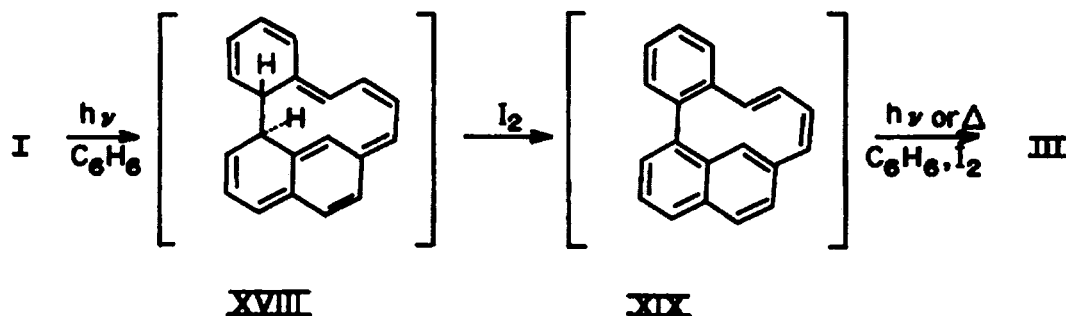

FIG 5

EXPERIMENTAL

UV spectra were recorded in 95% EtOH solution on a Cary 14 UV spectrometer. Data have only been presented where deviating or no results were found in the literature.

IR spectra were run in KBr discs on a Perkin–Elmer 257 spectrophotometer.

Mass spectra were obtained on a Hitachi–Perkin–Elmer RMU-6D mass spectrometer. The number in brackets after a given peak represents the % of the base peak of that ion.

Silica gel was used for thin- and thick-layer chromatography.

All photochemical reactions were carried out in a Rayonet photoreactor using RPR 3500°A lamps in a Pyrex vessel.

All m.p.s were determined on a Kofler hot stage and are corrected.

Starting materials. All the compounds were prepared by Wittig reactions. A typical example is given for the preparation of 1-(β-*naphthyl*)-4-*phenyl*-1,3-*butadiene* (I). To a mixture of 2-naphthaldehyde (2·95 g, 0·019 moles) and triphenylcinnamylphosphonium bromide (8·5 g, 0·019 moles) in MeOH, was added LiOMe (95 ml, 0·2M). The mixture was allowed to crystallize overnight afer which crystals of 1-(β-naphthyl)-4-phenyl-1,3-butadiene were filtered off in 41% yield, m.p. 181–183° (lit.[16] 172°); MS m/e: parent ion at 256 (100).

1-(9′-*Phenanthryl*)-4-*phenyl*-1,3-*butadiene* (VI). M.p. 161–162°; Yield: 35%; MS m/e: parent peak at 306 (39); UV (C₆H₆) λ max nm (ε): 279 (37,900), 292 (40,100), 346 (38,900); IR (KBr) νcm⁻¹: 1618, 980; Calc. for C₂₄H₁₈: C, 94·13; H, 5·86. Found: C, 93·94; H, 5·90%.

1-(9′-*Anthryl*)-4-*phenyl*-1,3-*butadiene* (X). M.p. 153–154° (lit.[17] 152–153°); Yield: 60%; MS m/e: parent peak at 306 (100).

Irradiation of 1-*Aryl*-4-*phenyl*-1,3-*butadienes.* The general techniques of irradiation on preparative scale have been described previously.[1] The photocyclization–oxidation reaction products were isolated by preparative thick layer chromatography (TLC) using 90% n-hexane : 10% C₆H₆ as eluant. All photocyclization–oxidation monmeric products moved faster than the starting 1,3-butadiene on TLC. Compounds moving slower than the starting material invariably turned out to be dimeric products as shown by MS. Since, in general, the results have already been mentioned only details of identification of the various reaction products will be given here.

Irradiation products of 1-(β-*napthyl*)-4-*phenyl*-1,3-*butadiene.* 4-Phenylphenanthrene was identified by its m.p. 72–73° (lit.[6] 80·5–81·5°); MS m/e: parent peak at 254 (100); UV spectrum and mixed m.p. with an authentic sample, synthesized according to reference 6, m.p. 72–73°. Both the photo-product and authentic sample were purified by preparative TLC and their m.p.'s taken on a corrected melting point apparatus. The UV spectra of the two samples were identical with the published spectrum.[6]

1,2-Benzopyrene was identified by its m.p. 177° (lit.[7] 175·5–176·5°); MS m/e: parent peak at 252 (100); UV spectrum and m.p. with an authentic sample.

Irradiation product of 4-phenylphenanthrene. Irradiation of 8.7×10^{-4}M solution of pure 4-phenylphenanthrene (II) and 4×10^{-4}M iodine in dry C_6H_6 for 72 hr resulted in the disappearance of absorption maximum of II at 297 nm and the appearance of absorption maxima characteristic of 1,2-benzopyrene at 366 nm, 348 nm, 331·5 nm, 316 nm and 306 nm. The crude reaction mixture was separated by preparative TLC to give 1,2-benzopyrene in 46% conversion and recovered 4-phenylphenanthrene (21%). 1,2-benzopyrene was identified as described above.

Irradiation product of 1-(9'-phenanthryl)-4-phenyl-1,3-butadiene. 1-Phenyltriphenylene was identified by its m.p. 161–162° (lit.[11] 162°); MS m/e: parent ion at 304 (100) and UV spectrum $\lambda_{max}(\varepsilon)$; 284 nm (4,830), 273 nm (5,640), 273 nm (5,640), 257·5 nm (41,300), 248·5 nm (22,700).

Irradiation product of 1-(9'-anthryl)-4-phenyl-1,3-butadiene. 3,4,8,9-Dibenzopyrene was identified by its m.p. 311–312° (lit.[18] 315°); MS m/e: parent peak at 302 (100); UV spectra, MS and mixed m.p. with an authentic sample.

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