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PHOTOCYCLIZATION REACTIONS OF ARYL POLYENES – III[1]

THE PHOTOCYCLIZATION OF 1,8-DIPHENYL-1,3,5,7-OCTATETRAENE AND 1,10-DIPHENYL-1,3,5,7,9-DECAPENTAENE

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Abstract – The photocylization-oxidation reaction of 1,8-diphenyl-1,3,5,7-octatetraene gave 1-phenylphenanthrene and a trace of 9-phenylphenanthrene. It was shown that 1-(α-naphthyl)-4-phenyl-1,3-butadiene and *o*-phenylstilbene may be intermediates in the formation of the photoproducts of 1,8-diphenyl-1,3,5,7-octatetraene. The irradiation of 1,10-diphenyl-1,3,5,7,9-decapentaene yields picene. It was demonstrated that 1-(α-naphthyl)-6-phenyl-1,3,5-hexatriene, 1,2-di-(α-naphthyl)ethylene, and 1-styrylphenanthrene are likely intermediates involved in the formation of picene.

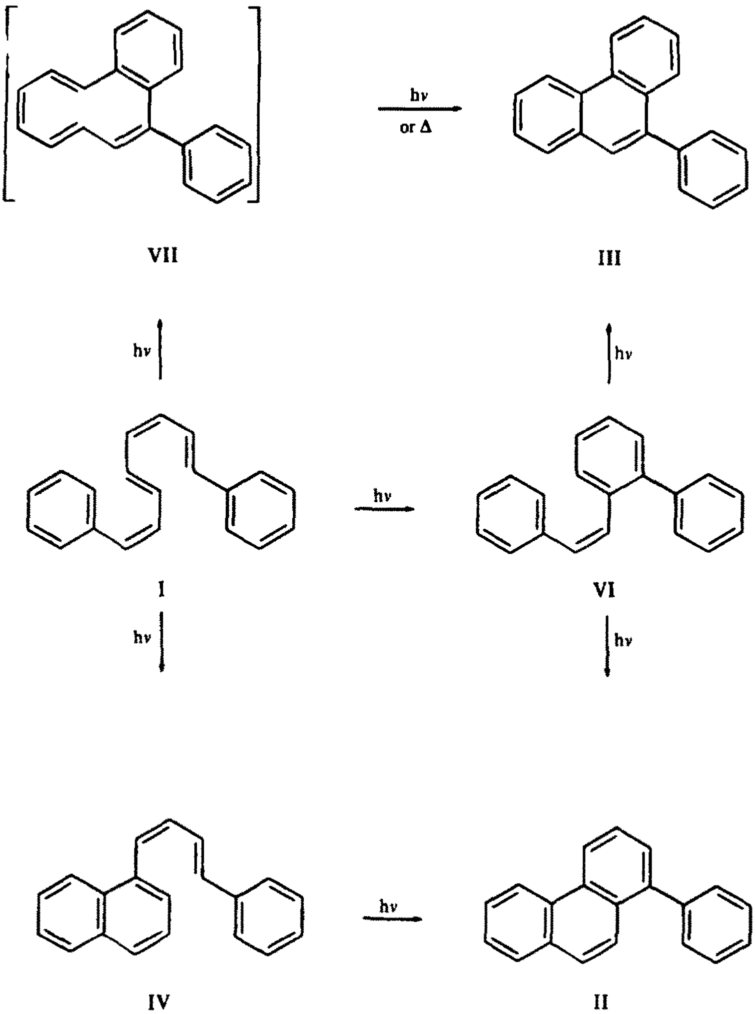
SOME years ago Fonken[2] reported that the photocyclization-oxidation reaction of 1,4-diphenyl-1,3-butadiene gave 1-phenylnaphthalene, and irradiation of 1,6-diphenyl-1,3,5-hexatriene gave chrysene. Recently, it was shown that a whole series of 1-aryl-4-phenyl-1,3-butadienes undergo similar photocyclization-oxidation reactions to give a wide variety of condensed aromatic systems.[1,3] It was decided to examine the photocyclization-oxidation reactions of some highly conjugated diphenyl polyenes with the view of studying the effect of conjugation on the mode and direction of photocyclization reactions.

Irradiation of $3{\cdot}8 \times 10^{-4}$M solutions of 1,8-diphenyl-1,3,5,7-octatetraene (I) and $7{\cdot}8 \times 10^{-4}$ M iodine in dry benzene for 120 hr resulted in the disappearance of the absorption maxima at 403 nm, 380 nm, 361·5 nm, and 347 nm. The reaction mixture was separated by TLC to give 2% 1-phenylphenanthrene (II)[4] and 22% of recovered starting material. VPC of the monomeric fraction obtained from TLC revealed the presence of a trace of 9-phenylphenanthrene (III) in 0·1% yield, based on I. The presence of III was proved by comparing the photo-products of I with an authentic sample of III, synthesized by another route.[5] Some dimeric and polymeric material was also separated by TLC. Irradiation of II and III, under conditions identical to that of I, showed no decomposition.

The formation of II and III from the irradiation of I can occur via several pathways as indicated in Scheme 1.

In order to test the validity of the pathways outlined in Scheme 1, the possible intermediate compounds were synthesized and subjected to the photocyclization-oxidation reaction.

Thus irradiation of a $3{\cdot}9 \times 10^{-3}$ M C_6H_6 solution of 1-(α-naphthyl)-4-phenyl-1,3-butadiene (IV), under conditions identical to those used in the irradiation of I, gave II as the only monomeric product in 8·5% yield, showing that IV can indeed be an intermediate in the photocyclization-oxidation of I to give II. Diene IV could possibly undergo a photocylization-oxidation reaction to give 1,1'-binaphthyl (V), but as



SCHEME 1

described in a previous paper,[1] cyclization to the naphthalene ring of IV should be highly favoured over cyclization to the phenyl ring. In any case, an authentic sample of V was synthesized by another route[6] and was shown to be absent from the photomixture, obtained in the irradiation of IV.

Similarly, irradiation of a 9·0 × 10^{-4} M C_6H_6 solution of *o*-phenylstilbene (VI) gave a 36% yield of a 1:1 mixture of II and III. Since 9-phenylphenanthrene (III) is formed from VI, and is also present as a photoproduct in the irradiation of I, it is highly likely that VI is also an intermediate in the photocyclization-oxidation of I to give II and III. Since III is formed from I in only trace amounts, however, and since the intermediacy of VI requires *equal* amounts of II and III to be produced as shown from the separate irradiation of VI. then one can state that the pathway involving intermediate VI in the irradiation of I accounts for the formation of the trace amount of III but only for an equal trace amount of product II. The bulk of 1-phenylphenanthrene (II) must therefore arise through the diene IV.

It is possible that product II could arise through the formation of cyclobutane dimers of I. In a recent publication.[7] Laarhoven. *et al.* have shown that cyclobutane dimers are intermediates in the photocyclization reactions of distylrylbenzenes. and it is possible that similar dimers are operative in the photocyclization-oxidation of I. To test this possibility. the mixture of dimers obtained in the irradiation of I was isolated and this mixture was subjected to a further photocyclization-oxidation reaction. No 1-phenylphenanthrene (II) was formed showing that dimeric products are unlikely precursors to II in the irradiation of I*.

Although the formation of 9-phenylphnanthrene (III) can be readily explained through the irradiation of intermediate VI. product III can arise by an alternate route. The photocyclization-oxidation of I can give an unstable phenylbenzo [10] annulene (VII) which on thermal or photochemical cyclization and oxidation can give III.

Irradiation of $1{\cdot}2 \times 10^{-4}$ M solutions of 1.10-diphenyl-1.3.5.7.9-decapentaene (VIII) and $7{\cdot}8 \times 10^{-4}$ M iodine in dry C_6H_6 for 1 hr. with a 450 w high pressure mercury lamp. resulted in a rapid decrease of the absorption maxima of VIII at 426 nm. 401 nm. and 380 nm. The reaction mixture was separated by TLC to give a sole monomeric product. picene (IX) in 2·3% yield based on unrecovered starting material. Although some reactant VIII was obtained from the photo-mixture in 12% recovery and polymeric material was noted. no dimeric products were isolated. Some of the various pathways by which IX can be formed from XIII are outlined in Scheme 2.

One possible pathway that can occur in the photocyclization-oxidation of VIII to IX involves the intermediate compound. *o*-distyrylbenzene(X) which has already been shown[7] to undergo cyclization to picene (IX). It has veen postulated that X goes to 1-styrylphenanthrene (XI) on irradiation but only through cyclobutane dimers since the direct photocyclization-oxidation of X to XI is not favoured by the calculated excited state free valence indices of X.[7] Since no dimeric products of X were detected in the irradiation of VIII. it is suggested that the formation of IX does not involve X as an intermediate.

A more likely possibility for the formation of IX from VIII. under photochemical-oxidation conditions. involves the intermediacy of 1-(α-naphthyl)-6-phenyl-1.3.5-hexatriene (XII). Irradiation of a $7{\cdot}0 \times 10^{-4}$ M C_6H_6 solution of XII† and $3{\cdot}6 \times 10^{-3}$ M iodine showed after 72 hr a decrease in the ultraviolet absorption maxima of XII at 402 nm. 377 nm. and 359 nm. Separation of the photo-products by TLC gave a 2% yield of picene (IX). showing that XII may very well be an intermediate in the formation of IX from VIII. It is also possible that cyclobutane dimers of VIII can give XII on further irradiation but the lack of formation of dimers of VIII seems to exclude

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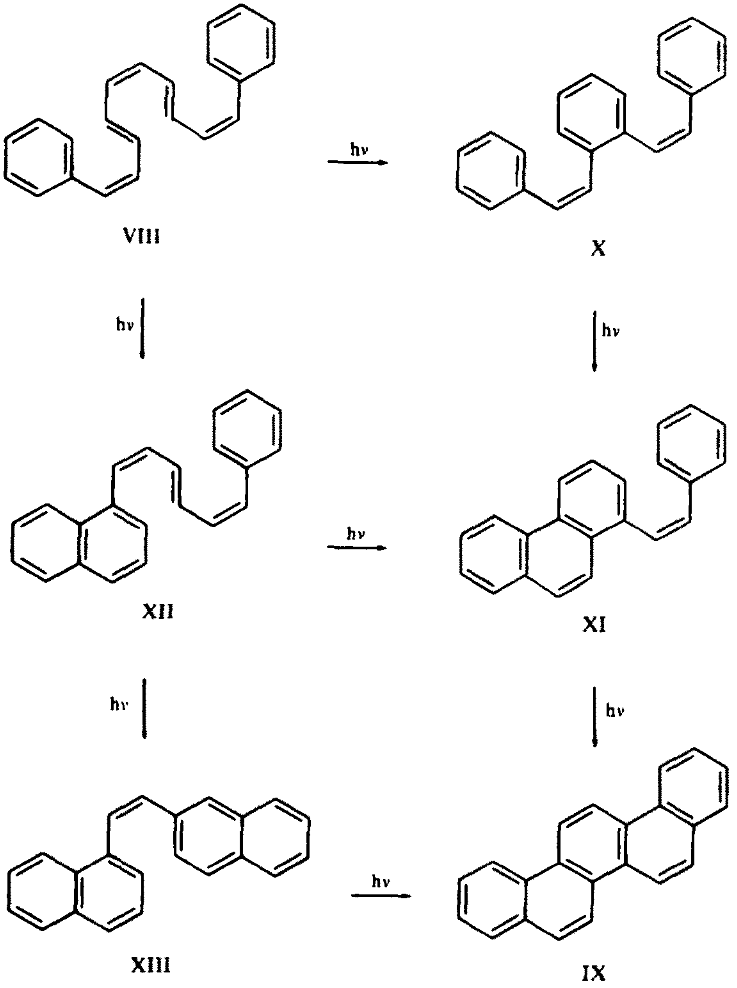
[*] It is possible of course. that the specific dimer that might lead to II was totally converted to II in the initial photo-reaction and hence the formation of II via cyclobutane dimers can not be entirely dismissed.

[†] Compounds I. IV. VI. VIII. XI and XII exist as the *all-trans* isomers from the method of preparation. The I.R. spectral data also show absorption peaks for *trans* double bonds. The *all-trans* forms of these compounds readily form equilibrium mixtures with *cis-trans* froms under the irradiation conditions and these isomers give the observed photoproducts.



Scheme 2

this possibility. The triene XII does not go directly to IX, but in turn can undergo a photocyclization-oxidation reaction to give XI or 1,2-di-(α-naphthyl)ethylene (XIII). It has been shown by other workers that irradiation of XIII gives picene (IX) in 30–100% yield.[8] Thus the intermediacy of XIII in the photocyclization-oxidation of VIII to IX is highly likely.

Irradiation of a $1{\cdot}4 \times 10^{-3}$ M C_6H_6 solution of XI gave picene (IX) in 61% yield. Thus it is not possible to say at the present time whether XII goes to IX via XI or XIII, as both XI and XIII give IX in high yield.

The irradiation reactions of I and VIII most likely begin with a *cis-trans* photoisomerization of all-*trans* I and all-*trans* VIII to give a complex mixture of *cis-trans* isomers. It is suggested that the photocylization-oxidation of I gives II mostly through intermediate IV. The formation of a trace of III in the irradiation of I can be accounted for by the intermediacy of VI or VII.

The irradiation of VIII to give IX is even more complex than the irradiation of I to II and III. The intermediate compounds XI, XII, and XIII can all account for the formation of picene (IX). The possible formation of X from VIII is in doubt since X gives isolable dimers on irradiation and no dimers of VIII or X were obtained in the photocyclization-oxidation of VIII. Since picene was obtained from VIII in only 2% yield, however, it is possible that any dimers of X that could lead to IX were simply not present in sufficient yield to be detected.

EXPERIMENTAL

UV spectra were recorded in C_6H_6 soln on a Cary 15 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-6 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, unless otherwise indicated.

All m'ps were determined on a Kofler hot stage and are uncorrected.

VPC measurements were made on a Hewlett-Packard 700 gas chromatograph equipped with a 6 ft stainless steel column packed with silicone rubber SE-30 810. The column temperature was maintained at 250° throughout all analyses. Flow rate was kept constant at 34 ml per min of helium. All analyses were run in diethyl ether soln and retention times were measured with reference to the ether peak. The number in brackets after the retention time represents % relative yield.

Starting materials. All compounds were prepared by Wittig reactions (for procedure see previous paper[1]) except XI and VI.

1-(α-*Naphthyl*)-4-*phenyl*-1.3-*butadiene* (IV). m.p. 108–109° (lit.[9] 109°); yield: 35%; MS *m/e*: parent ion at 256 (100%).

1.10-*Diphenyl*-1.3.5.7.9-*decapentaene* (VIII). m.p. 253° (lit.[10] 253°); yield: 20%; MS *m/e*: parent ion at 284 (42·5%).

1-(α-*Naphthyl*)-6-*phenyl*-1.3.5-*hexatriene* (XII). m.p. 159–160° (lit.[11] 159–160°); yield: 56%; MS *m/e*: parent ion at 282 (100%): UV λ_{max}nm (ε): 359 (49.000). 377 (49.000). 402 (25.200).

o-Phenylstilbene (VI). This compound was prepared as described.[12] b.p.$_{(0\ 1)}$ 142–144 (lit.[12] b.p.$_{(4\cdot5)}$ 190–210°); MS *m/e*: parent ion at 256 (100%).

1-*Styrylphenanthrene* (XI). To the ice cold Grignard-reagent from 2-bromoethylbenzene (3 g, 0·016 M) and Mg (0·42 g, 0·017 M) in 50 ml dry ether was added 1-keto-2,3,4-tetrahydrophenanthrene[13] (3·0 g, 0·015 M) in 25 ml ether. After the addition was complete the mixture was stirred for 1 hr at room temp then cooled with ice. To this mixture was added 100 ml sat NH_4Cl aq. The mixture was then boiled under reflux, cooled, and extracted with ether. The ether fraction was then evaporated and the residue dissolved in 75 ml C_6H_6. To this soln was added excess DDQ and the mixture was heated under reflux for 24 hrs. The mixture was then purified by preparative TLC. m.p. 173–174°; yield: 31%; MS *m/e*: parent ion at 280 (100%); UV λ_{max}nm (ε): 290·5 (34.200). 303 (33.000); IR (KBr) ν cm^{-1}: 1603. 963. (Found: C. 94·02; H. 5·36. Calc. for $C_{22}H_{16}$: C. 94·27; H. 5·71.

Irradiation of starting materials. The general techniques of irradiation on preparative scale have been described.[3] The photocyclization-oxidation products were isolated by preparative TLC using 90% n-hexane—10% C_6H_6 as eluant. All photocylization oxidation monomeric products moved faster than the starting material 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 1,8-*diphenyl*-1.3.5.7-*octatetraene* (I). The mixture of 1-phenylphenanthrene and 9-phenylphenanthrene produced in the irradiation of I were resolved by VPC into 2 peaks: 1-phenylphenanthrene (II): 7·20 mins (95%); 9-phenylphenanthrene (III): 7·16 mins (5%). Authentic samples of II and III synthesized by known methods (Ref 4 and 14 respectively) were shown to have identical retention times to the mixture obtained from the irradiation of 1.8-diphenyl-1.3.5.7-octatetraene.

Irradiation product of 1-(*α-naphthyl*)-4-*phenyl*-1.3-*butadiene* (IV). 1-Phenylphenanthrene (II) was identified by its m.p. 78–79° (lit.[4] 79–79·5°); MS *m/e*: parent ion at 254 (100%); UV spectrum and mixed m.p. with an authentic sample. synthesized according to Ref. 4. The UV spectra of the photo-product and authentic sample were identical with the published spectrum.[15]

Irradiation products of o-phenylstilbene (VI). The mixture of 1-phenylphenanthrene and 9-phenylphenanthrene produced in the irradiation of VI were resolved by VPC into 2 peaks as in the case of the identification of the products from the irradiation of 1.8-diphenyl-1.3.5.7-octatetraene: 1-phenylphenanthrene (II): 7·20 min (50%). 9-phenylphenanthrene (III): 7·16 min (50%)

Irradiation product of 1.10-*diphenyl*-1.3.5.7.9-*decapentaene* (VIII). Picene (IX) was identified by its m.p. >350° (lit.[16] 366–366·5°); MS *m/e*: parent ion at 278 (82·0%); UV spectrum and mixed m.p. with an authentic sample. The UV spectrum of the photo-product and authentic sample were identical with the published spectrum.[17]

Irradiation product of 1-(*α-naphthyl*)-6-*phenyl*-1.3.5-*hexatriene* (XII) *and* 1-*styrylphenanthrene* (XI). Picene (IX) was identified in the same manner as described above as the product from the irradiation of VIII.

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