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PHOTOCYCLIZATION REACTIONS OF ARYL POLYENES—VI[1]

THE PHOTOCYCLIZATION OF 1,4-DIARYL-1,3-BUTADIENES*

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Abstract—Calculations by the Simple Hückel Molecular Orbital (SHMO) method of the sum of the free valence indices in the first excited state (ΣF^*) of the terminal atoms concerned in the photocyclizations of 1,4-diaryl-1,3-butadienes give values which are accurate guides in predicting the photoproducts obtained in the photocyclization–oxidation reactions of 1,4-diaryl-1,3-butadienes. Irradiation of 1,4-di-α-naphthyl-1,3-butadiene gave 1-α-naphthylphenanthrene. The photocyclization–oxidation of 1,4-di-β-naphthyl-1,3-butadiene gave a mixture of 4-β-naphthylphenanthrene and naphtho[1,2-e]pyrene. It was shown that the naphtho[1,2-e]pyrene arose from a subsequent photocyclization–oxidation reaction of the first-formed 4-β-naphthylphenanthrene. Irradiation of 1-α-naphthyl-4-β-naphthyl-1,3-butadiene gave 4-α-naphthylphenanthrene. The structures of the photoproducts were confirmed by independent syntheses. All the photoproducts obtained from the irradiation of 1,4-diaryl-1,3-butadienes were the ones predicted by the SHMO calculations.

THE PHOTOCYCLIZATION–OXIDATION reaction of stilbene-like molecules has been widely investigated[2,3,4] and in many cases has led to the synthesis of a variety of interesting polyaromatic compounds,[5,6] but some stilbene-like molecules are inert to irradiation and oxidation.[7] Scholz *et al.*[8] used Simple Hückel molecular orbital (SHMO) theory to calculate the free valence indices in the first excited state (F^*) of a large number of compounds containing the diphenyl-ethylenic moiety. Laarhoven *et al.*[7] showed that, only if the sum of free valence indices in the first excited state (ΣF^*) of the terminal atoms concerned in the photocyclization of stilbene-like compounds exceeds a critical value (unity in this case), will cyclization occur. In some stilbene-like molecules, photocyclization can occur in a number of possible ways. By use of the calculations of Laarhoven *et al.*,[7] one can predict the preferred mode of cyclization in these cases. When more than one mode of cyclization has a value of unity or greater for ΣF^* of the terminal atoms concerned in the photocyclization, then cyclization occurs for the highest calculated value as long as the difference in the values of ΣF^* is more than 0·1; otherwise both photocyclizations can occur.[7,9]

The photocyclization–oxidation reaction of 1,4-diphenyl-1,3-butadiene (I),[10] 1-substitutedphenyl-4-phenyl-1,3-butadienes[11] amd 1,4-substitutedphenyl-1,3-butadienes[12] gave the appropriate 1-arylnaphthalenes. The irradiations of 1-aryl-4-phenyl-1,3-butadienes, where the aryl group is a polyaromatic moiety, gave a variety of polyaromatic compounds,[13] but a single photo-product was generally observed for each reacting diene. For example, irradiation of 1-β-naphthyl-4-phenyl-1,3-butadiene (II) gave exclusively 4-phenylphenanthrene (III) as the primary photoproduct. Other possible modes of cyclization yielding 1-phenylanthracene (IV) and

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* Taken from the doctoral thesis of R. J. Hayward, York University (1971)

1,2′-binaphthyl (V) were not realized.[13] It thus became apparent that calculation of the ΣF^* of the terminal atoms involved in the cyclization of 1,4-diaryl-1,3-butadienes would yield useful information and aid us in predicting the direction of cyclization when multiple modes of cyclization are possible. Using the relation $F_r^* = \sqrt{3} - \Sigma_s p_{rs}^*$, in which p_{rs}^* is the π-bond order in the first excited state between the atom *r* and a neighbouring atom *s*,[14] the ΣF^* of the terminal atoms involved in the cyclization was calculated for a number of 1,4-diaryl-1,3-butadienes. All possible modes of cyclization are included in the calculations. The cyclization for which ΣF^* of the terminal atoms involved in the cyclization is maximal gives the predicted product.

The calculations for ΣF^* of the terminal atoms involved in the cyclization of a number of 1,4-diaryl-1,3-butadienes are outlined in Table 1. The different directions of cyclization are represented by the numbers of the terminal atoms involved in the photocyclization.

As shown in Table 1, SHMO calculations on 1,4-diphenyl-1,3-butadiene (I) ($\Sigma F^* = 1{\cdot}1500$) confirm the experimental results of Fonken, who showed that I undergoes a photocyclization–oxidation to 1-phenylnaphthalene.[10] The SHMO calculations also show that our previous experimental results on the photocyclization–oxidation of 1-aryl-4-phenyl-1,3-butadienes all gave the predicted product.[13] Thus irradiation of 1-β-naphthyl-4-phenyl-1,3-butadiene (II) gave 4-phenylphenanthrene (III).[13]‡ Irradiation of 1-α-naphthyl-4-phenyl-1,3-butadiene (VI) gave 1-phenylphenanthrene (VII)[13] and the photocyclization–oxidation of 1-(9′-phenanthryl)-4-phenyl-1,3-butadiene (VIII) gave 1-phenyltriphenylene (IX).[13] In Part II of this series of papers, we postulated that the formation of 3,4,8,9-dibenzopyrene (X) from the irradiation of 1-(9′-anthryl)-4-phenyl-1,3-butadiene (XI) proceeds through a benzo-[10]-annulene intermediate.[13] SHMO calculations on XI actually favour the formation of the benzo-[10]-annulene intermediate over cyclization to form 9-(α-naphthyl)-anthracene (XII). Once again the calculations supported the experimental findings. The SHMO calculations show that a benzo-[10]-annulene intermediate is favoured in the photocyclization–oxidation of XI but possible benzo-[10]-annulene intermediates that can be drawn in the irradiation of II, VI and VIII, are not favoured (Table 1) and indeed were considered unlikely intermediates in the formation of the photoproducts.[13]

The successful correlation of the ΣF^* of the possible terminal atoms concerned in the photocyclization of known 1,4-diaryl-1,3-butadienes with experimental results obtained in the irradiation of 1-aryl-4-phenyl-1,3-butadienes,[13] prompted us to calculate the ΣF^* of the terminal atoms of possible cyclizations of a series of 1,4-diaryl-1,3-butadienes which had not been previously investigated. To this end the SHMO calculations of 1,4-di-α-naphthyl-1,3-butadiene (XIII), 1,4-di-β-naphthyl-1,3-butadiene (XIV), and 1-(α-naphthyl)-4-(β-naphthyl)-1,3-butadiene (XV) were done and are shown in Table 1. Subsequently, the 1,4-di-(naphthyl)-1,3-butadienes were irradiated and the products examined.

Thus, irradiation of a $6{\cdot}4 \times 10^{-4}$M solution of 1,4-di-(α-naphthyl)-1,3-butadiene (XIII) in dry C_6H_6 containing $1{\cdot}6 \times 10^{-3}$M iodine for 72 hours resulted in the gradual disappearance of the absorption maximum of XIII at 354 nm. The crude

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‡ Further irradiation of III gave 1,2-benzopyrene. SHMO calculations on III (Table 1) do not predict this cyclization to occur and at present this cyclization represents a major exception to the rule of Laarhoven *et al.*[7] who suggests that when $\Sigma F^* < 1$, photocyclization of stilbene-like compounds do not occur.

TABLE 1. RESULTS OF SHMO CALCULATIONS

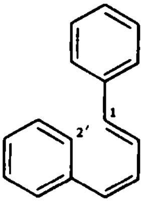
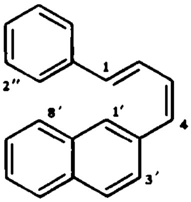
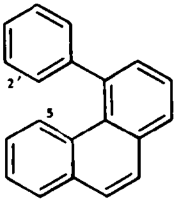
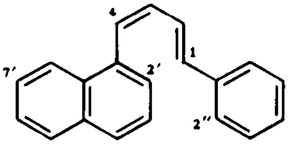
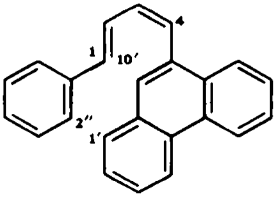
Compound	ΣF^*	Product	% Yield	Reference
1,4-Diphenyl-1,3-butadiene I				
	1,2′ = 1·1500	1-phenylnaphthalene	50	10
1-(β-Naphthyl)-4-phenyl-1,3-butadiene II				
	1,1′ = 1·2404	4-phenylphenanthrene III	7	13
	1,3′ = 1·0922	1-phenylanthracene IV	0	13
	2″,4 = 1·1133	1,2′-binaphthyl V	0	13
	2″,8′ = 0·9829	benzo-[10]-annulene	0	13
4-Phenylphenanthrene III				
	2′,5 = 0·9342	1,2-benzopyrene	46	13
1-(α-Naphthyl)-4-phenyl-1,3-butadiene VI				
	1,2′ = 1·1491	1-phenylphenanthrene VII	8·5	13
	2′,4 = 1·0700	1,1′-binaphthyl	0	13
	2″,7′ = 0·0173	benzo-[10]-annulene	0	13
1-(9′-Phenanthryl)-4-phenyl-1,3-butadiene VIII				
	1,10′ = 1·2381	1-phentyltriphenylene IX	13·5	13
	2′,4 = 1·0675	9-(α-naphthyl)-phenanthrene	0	13
	1′,2″ = 0·9738	benzo-[10]-annulene	0	13

TABLE 1. (*Continued*)

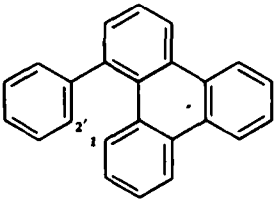
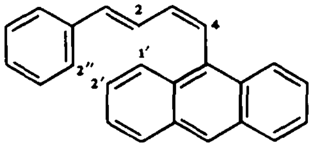
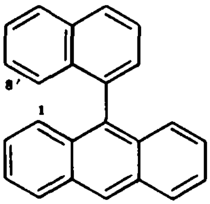
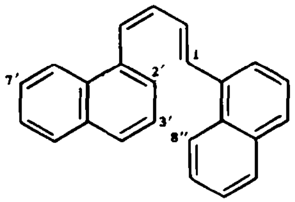
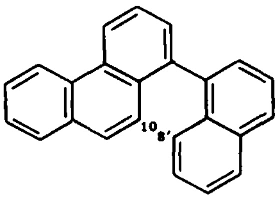
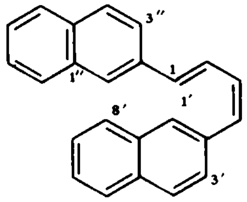
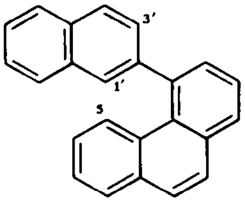
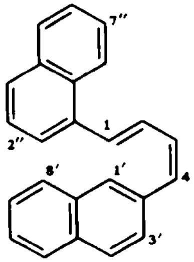
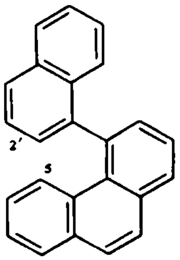
Compound	ΣF*	Product	% Yield	Reference
1-Phenyltriphenylene IX 	1,2′ = 0·9494	1,2,6,7-dibenzopyrene	0	13
1-(9-Anthryl)-4-phenyl-1,3-butadiene XI 	2″,2′ = 1·2167	Benzo-[10]-annulene [3,4,8,9-dibenzopyrene] X	7	13
	2″,4 = 1·1883	9-(α-naphthyl)-anthracene XII	0	13
	2,1′ = 1·0419		0	13
9-(α-Naphthyl)-anthracene XII 	1,8′ = 0·9343	1,2-benzoperylene	0	13
1,4-Di-(α-naphthyl)-1,3-butadiene XIII 	1,2′ = 1·091	1-(α-naphthyl)-phenanthrene XVI	10	[a]
	3′,8″ = 0·9512	dibenzo[fg,mn]naphthacene XVIII	0	[a]
	7′,8″ = 0·8754	naphtho-[10]-annulene	0	[a]
	2′,7″ =	dibenzo[def,j]chrysene XVII	0	[a]
1-(α-Naphthyl)-phenanthrene XVI 	8′,10 = 0·9788	dibenzo[fg,mn]naphthacene XVIII	0	[a]

TABLE 1. (*Continued*)

Compound	ΣF^*	Product	% Yield	Reference
1,4-Di(β-naphthyl)-1,3-butadiene XIV 	1,1′ = 1·1249	4-(β-naphthyl)-phenanthrene XIX	2	a
	1″,8′ = 1·0779	naphtho[1,2-e]pyrene XX	9	a
	1,3′ = 0·9889	1-(β-naphthyl)-anthracene XXII	0	a
	3″,8′ = 0·9429	naphtho[2,3-e]pyrene XXI	0	a
4-(β-Naphthyl)-phenanthrene XIX 	1′,5 = 1·0998	naphtho[1,2-e]pyrene XX	35	a
	3′,5 = 0·8822	naphtho[2,3-e]pyrene XXI	0	a
1-(α-Naphthyl)-4-(β-naphthyl), 1,3-butadiene XV 	1,1′ = 1·1958	4-(α-naphthyl)-phenanthrene XXIV	11	a
	1′,7″ = 1·0447	naphtho-[10]-annulene	0	a
	1,3′ = 1·0367	1-(α-naphthyl)-anthracene XXV	0	a
	2″,4 = 0·9896	1-(β-naphthyl)-phenanthrene XXVI	0	a
	2″,8′ = 1·0017	naphtho-[10]-annulene	0	a
4-(α-Naphthyl)-phenanthrene XXIV 	2′,5 = 0·9795	naphtho[2,1-e]pyrene XXVII	0	a

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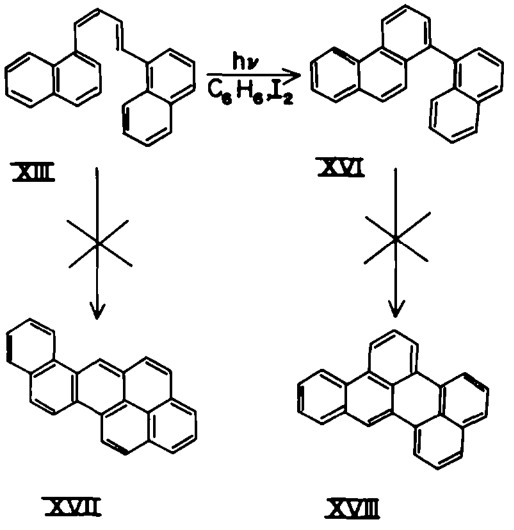
[a] This work

reaction mixture was separated by TLC to give 1-(α-naphthyl)-phenanthrene (XVI) in a 10% yield as the sole monomeric product (Scheme 1).

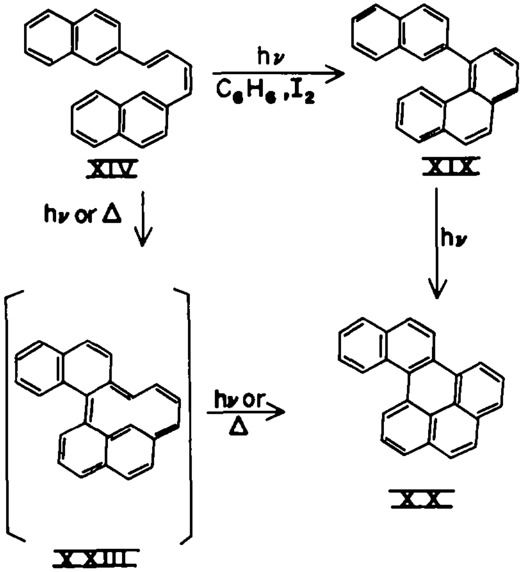


SCHEME 1

Photocyclization of XIII at the $2'$ and $7''$ positions (Table 1) to give dibenzo[def,j]-chrysene (XVII) was predicted not to occur as ΣF^* for these positions is less than unity and only the predicted product XVI was obtained. Compound XVI was synthesized by an alternate route[15] and shown to be stable to irradiation. The photocyclization–oxidation of XIII or XVI to give dibenzo[fg,mn]naphthacene (XVIII) was also predicted not to occur and experiment confirms these findings.

Similarly, irradiation of 1,4-di-(β-naphthyl)-1,3-butadiene (XIV) yielded 2% of 4-β-naphthylphenanthrene (XIX) and 9% of naphtho[1,2-e]pyrene (XX) (Scheme 2). Synthesis of XIX by an alternate route[16] confirmed the structure of the photo-product XIX. Irradiation of XIX under conditions identical to those of XIV gave XX in 35% yield showing that XX is probably obtained from the diene XIV by a further photo-cyclization–oxidation reaction of the first formed XIX. Naphtho[1,2-e]pyrene (XX) is inert to the irradiation conditions.

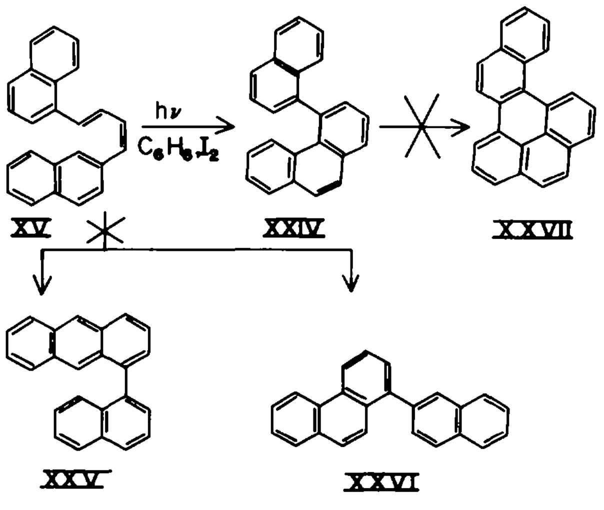
Naphtho[1,2-e]pyrene (XX) was identified by its parent ion in the mass spectrum and its UV spectrum which was characteristic of polyaromatic hydrocarbons.[17] Calculation of ΣF^* for positions $1',5$ of 4-β-naphthylphenanthrene (XIX) gives a value which is greater than unity and hence the formation of XX from XIX is predicted. In addition, cyclization of XIV to the 3-position of the naphthalene nucleus to form the known naphtho[2,3-e]pyrene (XXI)[18] is calculated not to occur and indeed the isolated naphtho[1,2-e]pyrene is different from the known XXI. One other possible product that could be formed in this photocyclization of XIV, namely, 1-(β-naphthyl)-anthracene (XXII) was not produced within the limits of detection by TLC. SHMO calculations on the various modes of cyclization of XIV (Table 1) strongly predict the



SCHEME 2

sole formation of XIX. The formation of XX *via* the naphtho[10]annulene intermediate (XXIII) (Scheme 2) is allowed by the value of the ΣF^* of the appropriate atoms but is probably unlikely due to the facile formation of XX from XIX.

The photocyclization–oxidation of 1-(α-naphthyl)-4-(β-naphthyl)-1,3-butadiene (XV) gave 4-(α-naphthyl)phenanthrene (XXIV) as the sole monomeric product (Scheme 3). Synthesis of XXIV by an alternate route[16] supported the assigned structure. Photocyclization–oxidation of XV to give 1-(α-naphthyl)anthracene (XXV) or 1-(β-naphthyl)phenanthrene (XXVI) did not occur as the value of ΣF^* of the atoms



SCHEME 3

concerned in the cyclization leading to these products were much less than the corresponding value leading to XXIV.

The 1-(β-naphthyl)phenanthrene (XXVI) was synthesized by an alternate route[15] and shown to be absent from the photoproducts within the limits of detection by TLC. Compound XXIV was stable to the irradiation conditions and was not transformed into naphtho[2,1-e]pyrene (XXVII). Again, experiment agrees with the SHMO calculations as ΣF^* of the terminal atoms involved in the cyclization of XXIV to give XXVII is less than unity.

Although photodimers and polymeric-type compounds were formed in the irradiation of XIII, XIV, and XV, they were not purified or characterized.

The results of the calculations by the SHMO method on F^* of some 1,4-diaryl-1,3-butadienes parallel similar results obtained for 1,2-diaryl-ethylenes by Laarhoven *et al.*[7]

Thus a similar rule can be formulated which states that *in photocyclization–oxidation reactions of* 1,4-*diaryl*-1,3-*butadienes, cyclization will occur only if the* ΣF^* *of the terminal atoms involved in the cyclization is greater than unity. If two or more cyclizations are possible, both can occur if the difference between* ΣF^* *of the proper atoms is small, but for larger differences only the one with the highest value will occur.*

The calculations for 1,4-diaryl-1,3-butadienes show that the F^* for the 1-position on the naphthalene ring is always greater than that at the 2- or 3-position. Hence it can be predicted that when photocyclization is possible to a naphthalene ring the 1-position will be the most likely to participate in such a reaction.

EXPERIMENTAL

UV spectra were recorded in 95% EtOH 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-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. All m.ps were determined on a Kofler hot stage and are uncorrected. The bond orders for the first excited states of the molecules were obtained by solution of the appropriate Hückel secular equations on an IBM-7094-II computer.

Starting materials. All of the starting 1,4-dinaphthyl-1,3-butadienes were prepared according to the procedures of Israelashvili *et al.*[19]

Preparation of naphthylphenanthrenes. A typical example is given for the preparation of 1-(*α-naphthyl-phenanthrene* (XVI). To the ice cold Grignard-reagent from 1·6 g (0·008M) of 1-bromonaphthalene and 0·18 g (0·080M) of Mg in 15 ml of dry ether was added 1·5 g (0·0076M) of 1-oxo-1,2,3,4-tetrahydrophenanthrene[20] (or 4-oxo-1,2,3,4-tetrahydrophenanthrene[20] for the synthesis of XIX and XXIV) in 15 ml of ether. After the addition had been completed the mixture was stirred for 1 hr at room temp, then cooled with ice. To this mixture was added 35 ml of a 25% solution of dilute H_2SO_4. The mixture was then heated under reflux, cooled, and extracted with ether. The ether fraction was then evaporated and the residue dissolved in 50 ml of benzene. To this solution was added 3 g of DDQ and the mixture was heated under reflux overnight, then purified by TLC. M.p. 112–114° (lit.[21] 113–115°): Yield: 35%: MS *m/e*: parent ion at 304 (100%).

4-(β-*Napthyl*)-*phenanthrene* (XIX). M.p. 105–106° (lit.[16] 105–106°): Yield: 27%, MS *m/e*: parent ion at 304 (100%).

4-(α-*Naphthyl*)-*phenanthrene* (XXIV). M.p. 108–110°: Yield: 40%: MS *m/e*: parent ion at 304 (100%): UV (95%, EtOH) λ_{max} nm (ε): 327 (16,300), 300 (24,000), 288 (26,200), 279 (39,300), 252 (53,000), 223 (49,000): (Calc. for $C_{24}H_{16}$: C, 94·70: H, 5·30. Found: C, 94·70: H, 5·51%).

1-(β-*Naphthyl*)-*phenanthrene* (XXVI). M.p. 137–139°: Yield: 24%, MS *m/e*: parent ion at 304 (100%):

UV (95%, EtOH) λ_{max} nm (ε): 301 (17,200), 255 (54,200), 221·5 (52,800); (Calc. for $C_{24}H_{16}$: C, 94·70, H, 5·30. Found: C, 94·35; H, 4·96%).

Irradiation of starting materials. The general techniques of irradiation on a preparative scale have been described previously.[11] The photocyclization–oxidation reaction products were isolated by prep. TLC using hexane:C_6H_6 (3:1) as eluant. All photocyclization–oxidation monomeric 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 mass spectroscopy. Since, in general, the results have already been mentioned only details of identification of the various reaction products will be given here.

Irradiation product of 1,4-*di*-(α-*naphthyl*)-1,3-*butadiene* (XIII). 1-(α-Naphthyl)-phenanthrene (XVI) was identified by its m.p. 112–113° (lit.[21] 113–115°); MS *m/e*: parent ion at 304 (100%); UV spectrum and m.m.p. with an authentic sample.

Irradiation products of 1,4-*di*-(β-*naphthyl*)-1,3-*butadiene* (XIV). 4-(β-Naphthyl)-phenanthrene (XIX) was identified by its m.p. 104–105° (lit.[16] 105–106°); MS *m/e*: parent ion at 304 (100%); UV spectra and m.m.p. with an authentic sample.

Naphtho(1,2-e)pyrene (XX) was identified by its m.p. 278–280°; MS *m/e*: parent ion at 302 (100%); UV spectrum (95% EtOH) λ_{max} nm (ε): 423 (1800), 400 (2100), 311 (35,200), 298 (24,000), 287 (17,200), 269 (12,300), 255 (11,800), 248 (11,200), 239 (11,300), 219 (38,200). (Calc. for $C_{24}H_{14}$: C, 95·68; H, 4·32. Found: C, 95·29; H, 4·30%).

Irradiation products of 1-(α-*naphthyl*)-4-(β-*naphthyl*)-1,3-*butadiene* (XV). 4-(α-Naphthyl)- phenanthrene (XXIV) was identified by its m.p. 109–110°; MS *m/e*: parent ion at 304 (100%); UV spectrum and m.m.p. with an authentic sample.

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