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PHOTODEHYDROCYCLIZATIONS IN STILBENE-LIKE COMPOUNDS—II

PHOTOCHEMISTRY OF DISTYRYLBENZENES

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Abstract—The photochemistry of distyrylbenzenes has been reinvestigated. It appears that formation of 1,12-benzperylene from the *para* isomer and picene from the *ortho* compound occur via an indirect route; the relevant cyclizations take place only in dimers of the parent compounds.

Other photoproducts from *ortho* distyrylbenzene are stilbene and phenanthrene, probably arising via 2,3-diphenyl-2,3-dihydronaphthalene.

These results show that the photoreactivity of the three isomers is entirely in accordance with the general rules previously formulated for photodehydrocyclizations in stilbene-like compounds.

IN PART I we showed[1] that photodehydrocyclizations of stilbene-like compounds appear to occur only if the sum of the free valence numbers in the excited state (ΣF^*_{rs}) of the atoms involved in the cyclization is larger than 1·0. Limiting values were also given for the localization energy (L*) and the superdelocalizability (ΣS^*): cyclizations are only possible if $L^* < 3{\cdot}45$ and $\Sigma S^* < 1{\cdot}44$. In a series of 29 compounds only one exception was found.

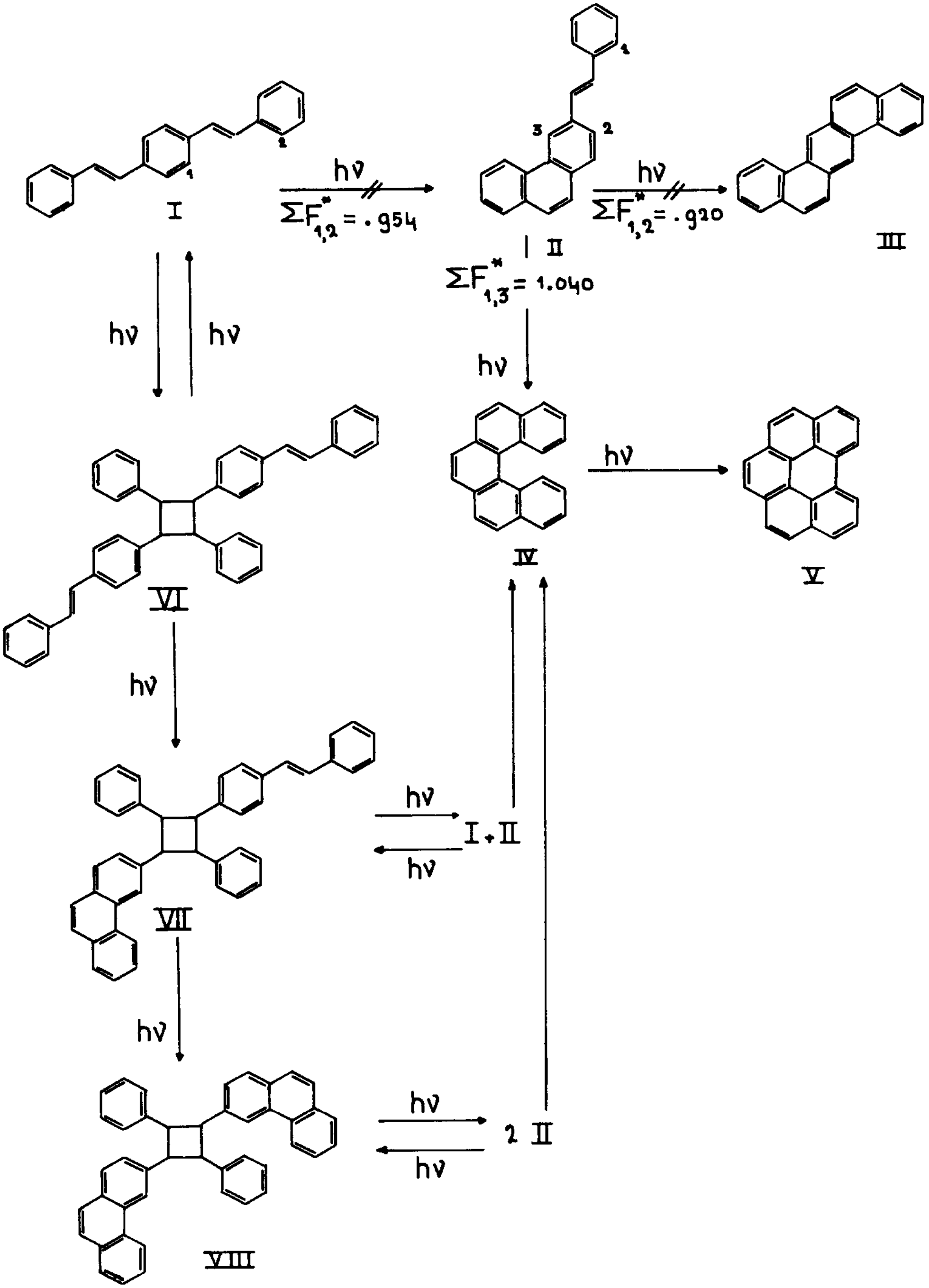
In this paper we justify this rule further by applying it to photoreactions in distyrylbenzenes containing two stilbenic parts.[2] Because of the different photochemical behaviour of the three isomers and the complexity of the phenomena observed the results and a discussion will be given separately for the various compounds.

p-Distyrylbenzene (I, Scheme 1)

In 1961 Misumi *et al.*[3] reported irradiation experiments of *p*-distyrylbenzene performed to determine the relative rates of photoisomerization. They irradiated the *cis,cis*, *cis,trans* and *trans,trans* isomers with a fluorescent tube in hexane solution for 240 hr, and observed that "some kind of photocyclization presumably accompanied by photodegradation occurs." The authors did not report concentrations and other experimental details but gave UV spectra of reaction mixtures after various times of irradiation.

In 1968 Dietz and Scholz[4] described the formation of 1:12-benzperylene (V) by irradiation of a ca. $3{\cdot}10^{-3}$ molar solution of *p*-distyrylbenzene in cyclohexane or benzene with added iodine. Irradiation by a high pressure Hg lamp for 20 hr yielded 11·5% of V.

The authors argued that the intermediate 3-styrylphenanthrene (II) would give rise to the dibenzphenanthrene (IV) and benzperylene (V) and not to dibenzanthracene (III), on account of the ΣF^*-values (1·040 and 0·920, respectively) and localization energies. The low yield was ascribed to the low value of ΣF^* (0·954) for the first step, SCHEME 1 Photoreactions of *p*-distyrylbenzene



the formation of II. The authors stated that yields of cyclization products are only larger than 50% if $\Sigma F^* > 1{\cdot}0$.

According to our findings, however, this first step should not occur. We therefore repeated the irradiation experiments with the *para* isomer.

Results and discussion

Irradiation of a very dilute solution ($c = 5{\cdot}10^{-6}$) of *cis,cis* or *cis,trans* *p*-distyrylbenzene in methanol or benzene with or without added iodine resulted in a rapid isomerization to the *trans,trans* form. On prolonged irradiation all three isomers were destroyed as was concluded from the lowering of the extinction in the UV spectra; after about 6 hr only end absorption was left. In this respect the *para* compound is clearly distinguishable from the *meta* isomer (see further).

In more concentrated solutions ($5{\cdot}10^{-5}$–10^{-3} moles/l) all three *p*-distyrylbenzenes also behaved similarly due to very rapid isomerization to the *trans,trans* form. In experiments performed in a spectrophotometer cuvet in the absence of iodine it was seen that after 10 min the UV spectra of the solutions already seemed to be identical to those found by Misumi[3] after 240 hr. The broad absorption band at 340–380 nm of *trans,trans* I had disappeared and some inflections appeared at 250 and 300 nm. After 30 min the spectrum looked in all details like that of phenanthrene. Longer irradiation did not alter the spectrum significantly.

In a similar experiment but with added iodine, in the first instance the same spectral changes were observed but now continued irradiation resulted in the appearance of some new peaks at 367 and 387 nm, which may be attributed to benzo [*c,d,e*] perylene (V).

Finally, irradiation of solutions free from iodine and also in the absence of oxygen gave rise to spectra characteristic of stilbene (broad absorption band at 280–310 nm with fine structure).

It appeared that irradiation of *trans*-3-styrylphenanthrene (II) dissolved in benzene in a low concentration without iodine did not change the spectrum. In the presence of iodine, however, the spectrum of benzo [*c,d,e*] perylene was obtained in a few minutes.

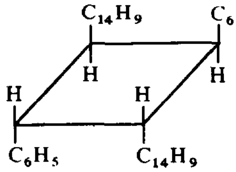
For a verification of these spectral data several irradiation experiments have been performed on a preparative scale under a wide variety of conditions as to solvent, concentration, irradiation time, presence of iodine and the use of filters.

They revealed that benzo [*c,d,e*] perylene (V) was only obtained from I in the presence of iodine and after long irradiation times. The yield never exceeded 10%. In most cases starting material (*trans,trans* I) was found in the reaction mixture, even after 20 hr in a quartz vessel and in the presence of iodine. In the presence of oxygen rather polar yellow-coloured compounds were formed, which according to the IR spectra, contained CO groups.

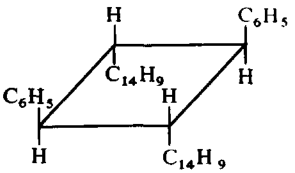
In all experiments the major part of the irradiation mixture consisted of dimerization products of the parent compound. Complete separation of the fractions containing such dimers appeared to be very difficult. Only two compounds could be isolated to which structures VII and VIII were tentatively assigned on account of physical and chemical properties.

On thermolysis of VII and VIII only the compounds I and/or II could be isolated, indicating that no vicinal stilbene or phenanthrene residues are present at the cyclobutane rings. In the NMR spectra the cyclobutane protons appear at $\tau = 5{\cdot}3$, comparable to the value (5·6) found by Shechter[5] for a stilbene dimer, the structure of which was 1, *trans*-2, *trans*-3, *cis*-4 tetraphenylcyclobutane. These results point to the configuration presented as **a** for compounds VII and VIII (e.g. 1-phenanthryl, *trans*-2-phenyl, *trans*-3-phenanthryl, *cis*-4-phenylcyclobutane).

The presence of dimeric products with another configuration **b** in irradiation mixtures was demonstrated by the NMR spectra of some dimer fractions, in which besides the peak at 5·3 a signal at $\tau = 6{\cdot}1$ was also observed. The latter value is comparable to that found[5] for 1, *trans*-2, *cis*-3, *trans*-4 tetraphenylcyclobutane ($\tau = 6{\cdot}37$).



a (VII, VIII)



b

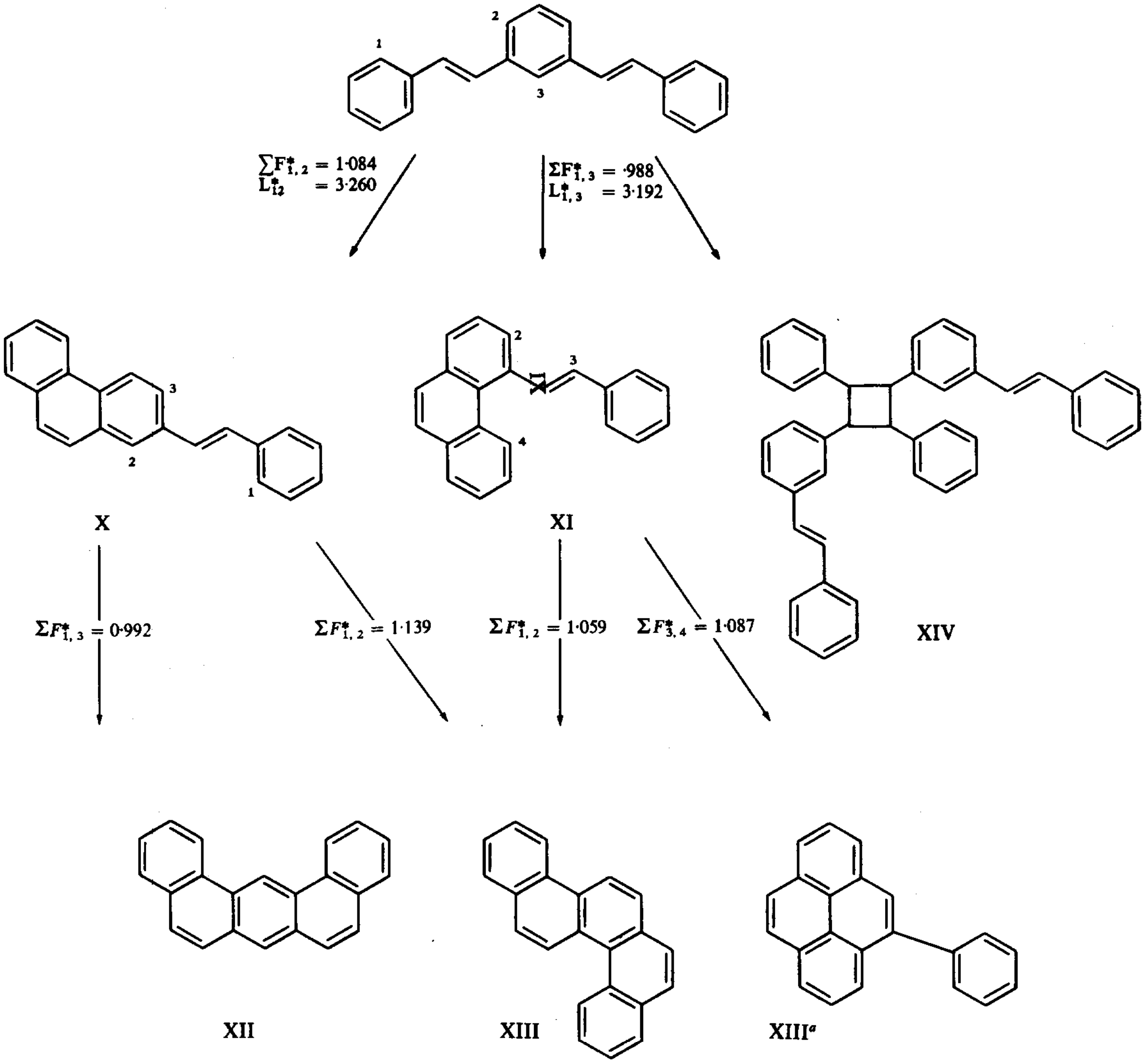
Irradiation of a solution of VIII in methanol in the absence of iodine resulted in an equilibrium between VIII and II (isosbestic points at 262 and 241 nm), reached in ca. 30 min. After that time the spectrum did not change much in appearance, but the extinction diminished slowly. The equilibrium mixture contained about 30% of 3-styrylphenanthrene (II). In the presence of iodine the irradiation of solutions of VII, VIII or "dimer" mixtures resulted in the formation of V as indicated by the appearance of the characteristic UV maxima at 363 and 378 nm; intermediate formation of II could not be observed in these experiments.

In a final experiment equimolar solutions of I, II and VIII ($0{\cdot}5.10^{-5}$ moles/l) in benzene with added iodine were simultaneously irradiated in pyrex or quartz vessels under identical conditions. II was almost completely converted into V in half an hr; from VIII about 40% V was formed in 2 hr; in that time conversion of I into V could not be observed.

From these experiments the following conclusions can be drawn. The formation of benzperylene (V) from *p*-distyrylbenzene (I) under the influence of light takes place via II (and undoubtedly via IV which obviously undergoes more rapid cyclization than II). Cyclization of II to III does not occur due to the low ΣF^*-value for this reaction.

The intermediate 3-styrylphenanthrene (II) only arises from the parent compound via an indirect route, namely dimerization of I; in very dilute solutions this reaction could not be observed. In the primarily formed product (VI) photodehydrocyclizations are possible in the presence of oxygen. In this way mono- and di-phenanthrylcyclobutane derivatives like VII and VIII arise. The ΣF^*-values of these reactions must be comparable to those for the dehydrocyclization of stilbene, as VI can be conceived as a *para* alkylated stilbene derivative.

Under the influence of light compounds such as VI, VII and VIII are in equilibrium with their "monomeric" forms I and/or II (scheme 1).



SCHEME 2 Photoreactions of *m*-distyrylbenzene

m-Distyrylbenzene (IX, Scheme 2)

In scheme 2 the possible photoreactions starting with *m*-distyrylbenzene are given. According to ΣF^*-values benzchrysene (XIII) should be expected as the end product (via X). According to L^*-values photocyclizations of IX can also proceed via XI giving rise to 4-phenylpyrene (XIIIa) as a second end product.

Benzchrysene was obtained by Dietz and Scholz[4] in 80% yield by irradiation of a 3.10^{-3} molar solution of IX in hexane or benzene. Apparently they did not take into account the possible formation of XIIIa.

It may be noted that the contradiction between indications based on ΣF^*- and L^*-values should not arise if photocyclizations take place in a vibrationally excited ground state as argued by Güsten and Klasinc.[6] Calculations of ΣF and L for all compounds previously investigated by us revealed that the barrier for the occurence or otherwise of photocyclizations should then be $\Sigma F > 0{\cdot}9$ or $L < 4{\cdot}30$, although with more exceptions. For *m*-distyrylbenzene we found $\Sigma F_{1,2} = 0{\cdot}917$, $\Sigma F_{1,3} = 0{\cdot}953$, $L_{1,2} = 4{\cdot}22$ and $L_{1,3} = 4{\cdot}13$. Therefore, cyclization in the ground state should be possible via X as well as XI, with a preference for the latter.

Results and discussion

On irradiation of a very dilute methanolic solution ($c = 5.10^{-6}$) of IX rapid cyclization to XIII took place as indicated by the appearance of the benzo[*e*]chrysene spectrum.

Spectra traced at different time intervals from a solution irradiated in a spectrometer cuvet showed similar alterations after a short time. The set of spectra did not show real isosbestic points but a small "isosbestic area" at 328–330 nm and at 280–290 nm. After about 40 min there was no further significant change in the spectrum. It was concluded that the second cyclization step in the formation of XIII is faster than the first one.

Several irradiations on a preparative scale were performed with the intention of isolating an expected intermediate (X or XI). Unfortunately, however, we did not succeed in the isolation or detection of any styrylphenanthrene (X or XI).

Besides benzchrysene (XIII), obtained in 70% yield, and minor amounts of dimers like XIV, we isolated in 2% yield a compound with m.p. 129–130·5°. Its UV spectrum appeared to be identical to that reported by Lang and Buffleb[7] and identified as belonging to 4-phenylpyrene (XIIIa) by Dickerman and Feigenbaum.[8] In accordance with expectations no trace of dibenzo[*a,j*]anthracene (XII) has been found in any experiment.

From these results it is sure that 4-styrylphenanthrene (XI) must be an intermediate in the photocyclization of IX, because XI is a precursor of XIIIa.*

p-Distyrylbenzene (XV, Schemes 3 and 4)

ΣF^*- as well as L^*-values given in scheme 3 predict that under the influence of light XV will be converted into 2,3-diphenylnaphthalene (XVIII). Further cyclization to dibenzo[*a,c*]anthracene (XIX) seems improbable ($\Sigma F^* = 0{\cdot}918$).

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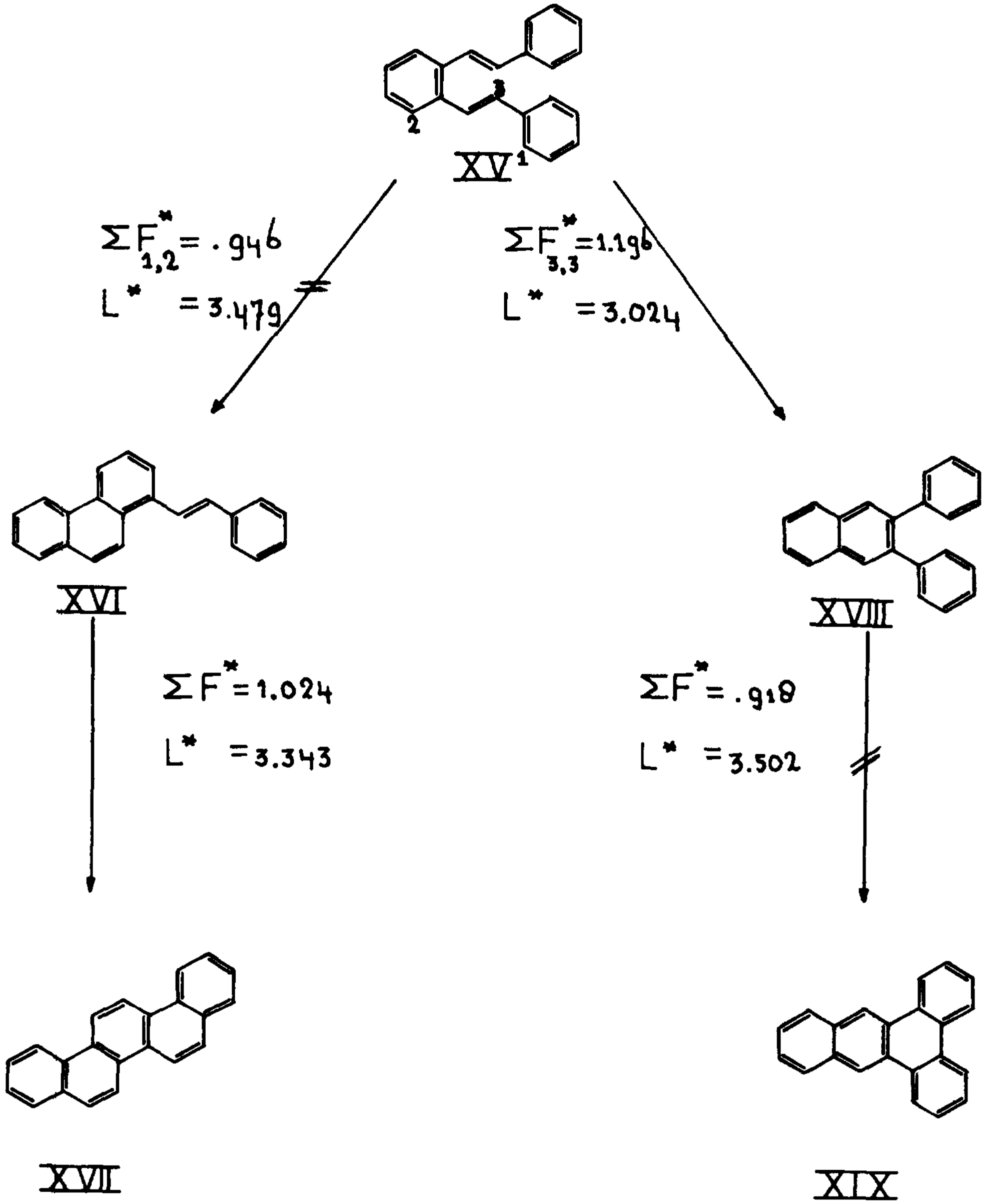
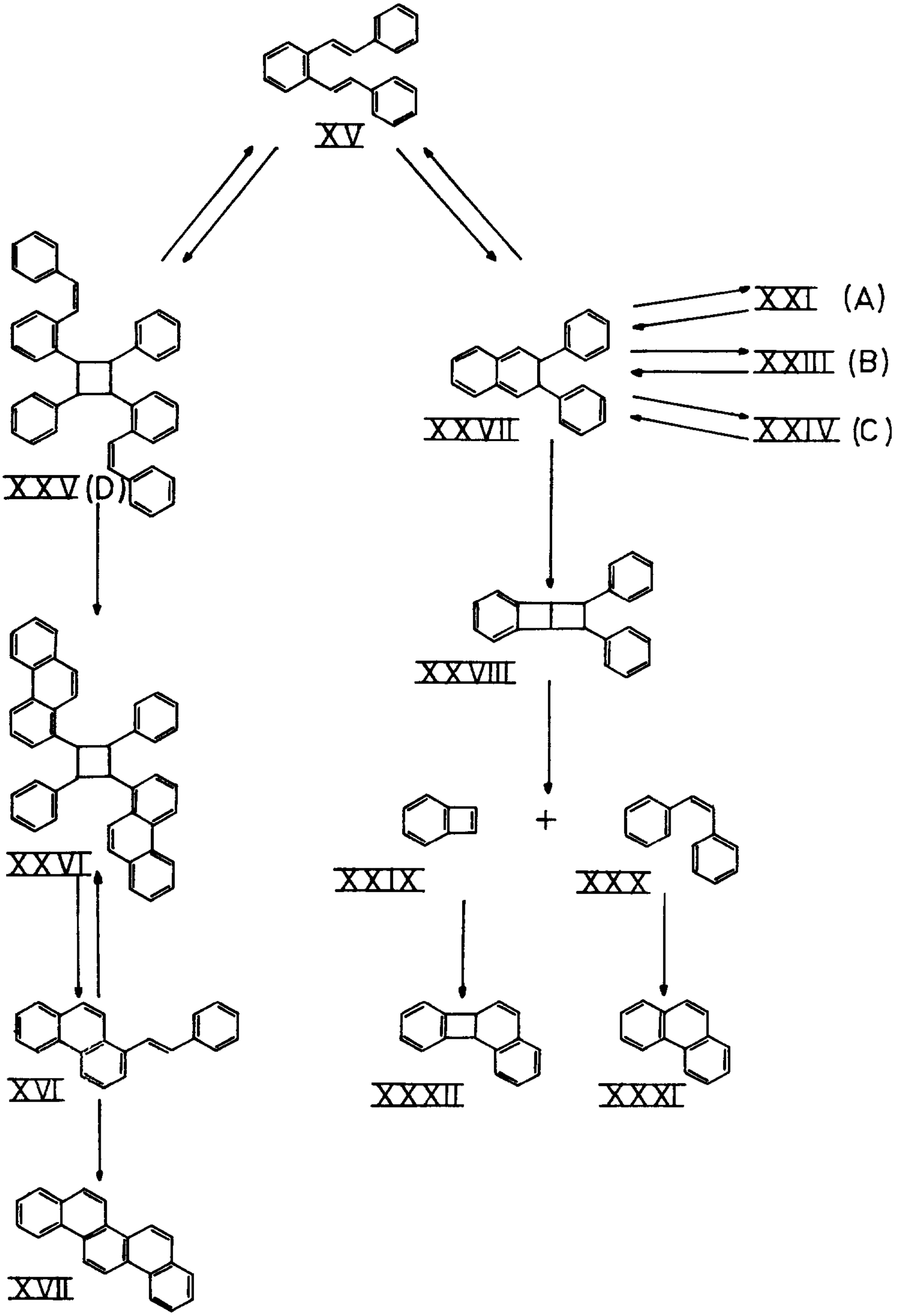
* *Note added in proof*—Compound XI has been synthesized by a Wittig reaction from 4-bromomethylphenanthrene and benzaldehyde. Irradiation of XI yielded besides XIII as the main product, about 2% of XIIIa.

SCHEME 3 Expected photoreactivity of *o*-distyrylbenzene



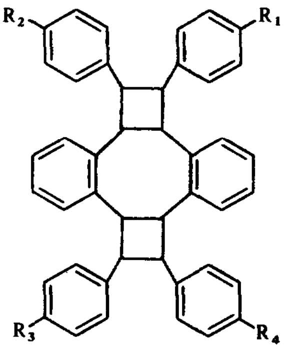
SCHEME 4 Photoreactions of *o*-distyrylbenzene



Picene (XVII) cannot be formed although XVI → XVII seems to be possible, since XVI will not arise ($\Sigma F^* = 0{\cdot}946$).

Irradiation experiments with *o*-distyrylbenzene reported in literature give, however, quite different results. Müller *et al.*,[9] irradiating a 10% solution of XV in cyclohexane for 6 hr with an S81 high pressure lamp, obtained a product melting at 64–70°. It had mol. wt. 564 (parent compound 282) and showed NMR peaks at 3·08, 5·45, 8·65, 8·83 and 9·11. On thermolysis above 150° *in vacuo* the starting compound was quantitatively re-obtained. From these data and comparable results on irradiation of *o*-bis (phenylethinyl)benzene the authors concluded that the "compound" might be a mixture of stereoisomers with structure XXa.

Dietz and Scholz[4] isolated picene (XVII) in 14·5% yield on irradiation of a ca. 3.10^{-3} molar solution of XV for 2 hr in the presence of traces of iodine. They argued that hampering of the more probable reaction (XV → XVIII) may be due to factors which also govern the cyclization of the related 1,2-diphenylbenzene.[10]



XXa: $R_1 = R_2 = R_3 = R_4 = H$
XXb: $R_1 = R_3 = CH_3$
$R_2 = R_4 = H$
XXc: $R_1 = R_2 = CH_3$
$R_3 = R_4 = H$

Our first results appeared to be quite different from those of both of these authors. However, by repetition of our experiments under a variety of circumstances most of the conflicting results were brought into agreement.

Results and discussion

We could not reproduce Müller's experiment. Irradiation of a 10% solution of XV ($c = 0{\cdot}4$ moles/l) in cyclohexane appeared only to be possible near the b.p. of the solution. After 6 hr only a part of the parent compound had disappeared. Thermolysis of about 50 mg of the product mixture at 170° resulted in the parent compound again, but a residue consisting of dimers with considerably higher m.p. than that given by Müller was left.

Spectra taken from a 10^{-5} molar solution of *trans,trans*-XV in methanol showed a rapid decrease of extinction with increasing irradiation time. When the extinctions at 280 and 310 nm had been reduced to 10% new maxima at ca. 250, 270 and 290 nm began to arise and a spectrum analogous to that of phenanthrene appeared. The *cis,cis* isomer rapidly isomerized into the *trans,trans* form and gave then similar results. Addition of iodine to the solutions did not alter the phenomena.

In irradiation experiments on a preparative scale ($c = 5.10^{-3}$–10^{-2}) in benzene without iodine for 8–24 hr phenanthrene, *cis*- and *trans*-stilbene, and the three isomers of XV were found in the reaction mixtures by gas chromatography. In addition to these compounds four other products (A, B, C and D) could be isolated by column chromatography (Table 1). Moreover, more polar compounds containing CO groups as shown by IR appeared to be present.

TABLE I. PHYSICAL DATA OF COMPOUNDS A, B, C AND D

	M.p.	M	UV λ_{max}	NMR τ-value
A	337°	564	261 (benzene-like fine structure)	2·15 5·45–5·60 (in $AsCl_3$)
B	293°	564	261 (log ε = 3·25)	2·25 (s) 4·85 (s) (in $AsCl_3$) 2·60 (s) 5·2 (s) (in CCl_4)
C	230°	564	261 (benzene-like fine structure)	2·60 (s) 5·2 (s) (in CCl_4)
D	133°	564	260–280 (log ε = 4·93)	2·0 (s) 3·4 (s) 5·5 (m) (in CCl_4)

Thermolysis of D at 250° produced *trans,trans*-XV. On irradiation of a solution of D its *cis*-stilbene-like spectrum became analogous to that of phenanthrene. D must, therefore, be a dimer like XXV. Several stereoisomers of the compound seemed to be present in the reaction mixture (Experimental) but only one could be isolated. On simultaneous irradiation of ca. 6.10^{-4} molar solutions of XV and XXV (D) in benzene with added iodine about 30 % of picene (XVII) was obtained from XXV in 1½ hr; in that time only very small amounts of XVII had been formed from XV. The results in quartz and pyrex were identical.

The formation of picene. Obviously compound D is an intermediate in the photochemical conversion of XV into XVII, which is unlikely via the direct route XV → XVI → XVII. The formation of picene from the *o*-distyrylbenzene is then quite analogous to the formation of benzperylene from the *para* isomer (scheme 1). The analogy is found again in the related structures of compounds VII and VIII on the one hand, and XXV (and undoubtedly XXVI) on the other. They correspond in their NMR spectra, their chemical and photochemical properties.

The formation of stilbene and phenanthrene. Stilbene and its photocyclization product phenanthrene might arise by photolysis from dimers like XXa. However, dibenzocyclooctatetraene should be a second product but was not found.

The improbability of stilbene formation via XXa was more convincingly demonstrated in an experiment with 4'-methyl-*o*-distyrylbenzene. Dimerization in the suggested way should lead to XXb as well as XXc, from which on photolysis unsubstituted, 4-methyl- and 4,4'-dimethylstilbene should arise. On photocyclization of these compounds three phenanthrenes with one, two or no Me substituents, respectively, should also be obtained. Careful analysis of the irradiation mixture demonstrated that only monomethyl derivatives (4-methylstilbene and 3-methylphenanthrene) had been formed. This experiment also excludes isomers of XXV with vicinal phenyl substituents on the cyclobutane ring as intermediates in the formation of stilbene.

Our results indicate that stilbene and phenanthrene formation proceed in a monomolecular reaction, since in contrast to picene, phenanthrene arises even in very dilute solutions of XV. A possible route is via the intermediates XXVII and XXVIII as indicated in Scheme 4. The conversion of XV to XXVII is the expected photocyclization route. The primary formed 2,3-dihydronaphthalene derivative (XXVII) will then undergo a second cyclization instead of dehydrogenation. Such a photocyclization of a cyclohexadiene derivative has been described in literature among others by van Tamelen.[11] The second step is the normal photolysis of a cyclobutane derivative.

Formation of stilbene and phenanthrene along the proposed pathway should lead to benzocyclobutadiene (XXIX) as a side-product. It is known, however, that XXIX is a very unstable compound;[12, 13] it has only been isolated as a dimer, benzobiphenylene (XXXII), and appeared a very reactive dienophile.[14] In the presence of compounds like XXVII further conversion to other products might be expected. Moreover, we showed by irradiation of a solution of XXXII in benzene that the compound photolyses into a great number of products.

Considering that the yield of stilbenes and phenanthrene and consequently also the amount of all various side-products arising from XXIX in our experiments never exceeded 5 %, it seems understandable that none of the side-products have been found in the complex reaction mixture.

Unfortunately, the intermediates XXVII and XXVIII too, have not been detected. There is, however, another argument for the occurrence of XXVII, which will be given in the next paragraph.

The structures of the compounds A, B and C (Table 1). As can be seen from the Table B and C have very similar properties; we found differences only in m.p. and in solubility in carbon disulphide. The solubility of A is very low in all common solvents; its NMR spectrum could only be traced in arsenic trichloride.

The ratio of aromatic to methine protons in all three compounds appeared to be 7:2. The mass spectra pointed to the elemental formula $C_{44}H_{36}$ for all of them; so, 28 aromatic and 8 methine protons must be present. The UV spectra were like those of simple substituted benzene derivatives with extinctions about six times that of toluene. As no double bonds appeared to be present the compounds contain apart from six aromatic rings three other saturated rings.

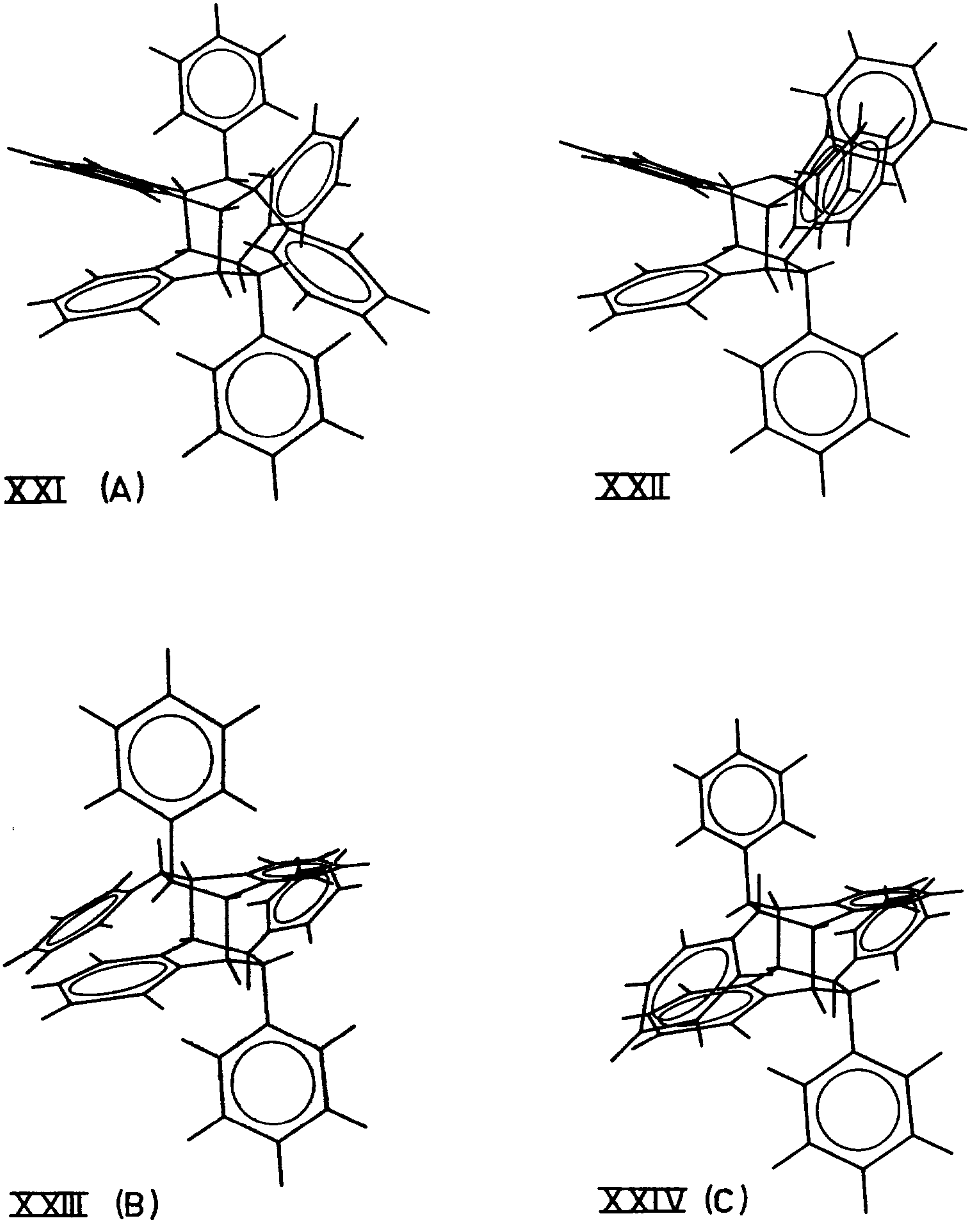
Thermolysis of A, B and C at 10^{-4} mm Hg pressure and ca. 400° or 500° for 3–5 hr gave results identical to those obtained on thermolysis of the parent compound under the same conditions; no stilbene nor phenanthrene was formed.

Likewise, the irradiation of A, B and C led to a mixture similar to that found on irradiation of *o*-distyrylbenzene. Photolysis of A appeared to be slower than that of B or C, in agreement with the fact that the amount of A relative to that of B and C increased when the time of irradiation of XV was prolonged.

Apart from the fact that for compounds like XXa physical properties as given by Müller[9] are very improbable, such structures cannot be considered for compounds A, B or C since they would give rise to stilbenes (and other products) on thermolysis. The supposition that A, B and C are dimerization products of 2,3-diphenyl-2,3-dihydronaphthalene (XXVII) fits the given physical and chemical data much better.

Photocyclization of *trans,trans* XV in the excited state should lead to a *trans* substituted dihydronaphthalene according to the Woodward-Hoffmann rules. By dimerization two racemic (XXI and XXIII) and two meso compounds (XXII and XXIV) may be formed. However, for steric reasons XXII should be very unfavourable as can be seen from molecular models; thus three dimers can be expected (Fig. 1).

In XXI two protons lie very close to a benzene ring and their shielding should be apparent in the NMR spectrum. This is found for compound A. Compounds B and C should then be XXIII and XXIV. This tentative assignment of structures corresponds



XXI (A)

XXII

XXIII (B)

XXIV (C)

FIG. 1 Stereoisomeric structures for dimers of 2,3-diphenyl-2,3-dihydronaphthalene to the greater stability of A, already mentioned; inspection of molecular models reveals that steric strain is less in the "head to head" dimer than in the "head to tail" dimers.

EXPERIMENTAL

UV spectra were recorded in MeOH soln on a Beckman DK 2A spectrophotometer. Data have only been presented where deviating or no results were to be found in literature.

IR spectra were run in KBr discs on a Beckman IR 4 or a Perkin–Elmer 254 instrument. Proton NMR spectra were taken in CCl_4 soln at 100 Mc/s on a Varian HA100 spectrometer and the chemical shifts were recorded against TMS as internal standard. In two cases (Table 1) arsenic trichloride was used as solvent.

Mass spectra were obtained on a Varian Matt MS 1a mass spectrometer if need be coupled with a gas chromatograph packed with 5% SE30.

Calculations of free valence numbers and localization energies were carried out on an IBM 360/50 computer.

M.ps are uncorrected.

Starting materials. All compounds investigated were prepared by known methods. For the *p-distyrylbenzene* (I) obtained according to Campbell[15] m.ps 266° (*trans,trans*), 114° (*cis,trans*) and 78–80° (*cis,cis*) were found. As distinct from the *trans,trans* and *cis,cis* isomers the *cis,trans* compound presents two equally intense signals of olefinic protons in the NMR spectrum.

m-Distyrylbenzene (IX) was synthesized according to Nakaya.[16] Separation of the products of the Wittig reaction by column chromatography gave the three isomers: *trans,trans*-IX, m.p. 171° (lit.[18] 167–168°); UV λ_{max} nm (log ε); 223·5 (4·33), 294·5 (4·80), 306·5 (4·77), 321·5 (4·54); *cis,trans*-IX, m.p. 55–56°; UV λ_{max} nm (log ε): 220·5 (4·40), 286·5 (4·62), 306·5 (4·52), 321 (4·26); *cis,cis*-IX was isolated as an oil.

For the synthesis of *o-distyrylbenzene* (XV) Griffin's method[17] was used. He isolated only the *trans,trans* isomer, according to him due to thermodynamic control of the reaction. Under identical conditions we obtained all three isomers, the *cis,trans* compound, indeed, as an oil contaminated with the other isomers. *trans,trans*-XV, m.p. 119–120°; *cis,cis*-XV, m.p. 90–91°; UV λ_{max} nm (log ε): 268–283 (4·23).

3-*Styrylphenanthrene* (II) was prepared via a Wittig reaction from 3-phenanthraldehyde and benzyltriphenylphosphonium bromide under conventional conditions. Only the *trans* isomer was isolated, m.p. 154°; UV λ_{max} nm (log ε): 205·9 (4·49), 228 (4·36), 241 (4·45), 248·4 (4·51), 268 (4·40), 278 (4·35), 317·5 (4·43), 330 (4·51), 344 (4·42).

4'-*Methyl-o-distyrylbenzene. o*-Carboxystilbene[18] was reduced with LAH and the alcohol obtained (m.p. 100°) treated with HBr in benzene. The bromide was converted into the corresponding phosphonium bromide with triphenylphosphine and the product subjected to a Wittig reaction with *p*-tolualdehyde. 4'-methyl-*o*-distyrylbenzene was obtained in 60% yield, m.p. 99–101°; UV λ_{max} nm (log ε): 205 (4·50), 224 (4·29), 280·5 (4·84), 319·3 (4·47).

Benzobiphenylene (XXXII) was prepared as described by Menitzescu and Avram,[14] m.p. 76°.

Irradiation experiments

The general techniques of irradiations in a spectrophotometer cuvet and on a preparative scale have been described previously.[1] Since in general the results have already been mentioned only some details concerning isolation and identification of the various reaction products will be given here.

Irradiation products of p-distyrylbenzene

Benzo[*c,d,e*]perylene (V) was isolated by column chromatography, preferentially on silica gel; on an alumina column the compound remains spread over several fractions of dimers. It was identified by its m.p. (283°) and UV spectrum (in accordance with that reported by Clar[19]).

Complete separation of all dimers present seemed to be impossible by column chromatography. For several fractions further purification was attempted by TLC on a preparative scale followed by crystallizations. By these methods two relatively pure compounds were obtained:

(a) 1-Phenanthryl, *trans*-2-phenyl, *trans*-3-(*p*-stilbenyl), *cis*-4-phenylcyclobutane (VII), m.p. 113–115° (from ligroin) UV λ_{max} nm: 252, 272, 280, 288, 300; IR ν_{max}: 840, 740, 700 cm^{-1}; NMR τ_{ppm}: methine protons at 5·3; MS m/e: main peaks at 562, 384, 382, 282, 280. Thermolysis *in vacuo* at 250° gave *trans,trans*-p-distyrylbenzene and 3-styrylphenanthrene, both identified by their spectra and mixed m.ps with authentic samples.

(b) 1-Phenanthryl, *trans*-2-phenyl, *trans*-3-phenanthryl, *cis*-4-phenylcyclobutane (VIII), m.p. 100–103° (from ligroin) UV λ_{max} nm: 212, 256, 270, 277, 286, 290; NMR τ_{ppm}: methine protons at 5·3; MS *m/e*: main peaks at 560, 386, 280. Thermolysis *in vacuo* yielded only 3-styrylphenanthrene identified by its UV spectrum and mixed m.p. with a pure sample.

Several dimer fractions, apparently containing compounds VI, VII and VIII on account of parent peaks at 564, 562 and 560 in the mass spectrum and corresponding peaks of thermally formed monomers at 282 and 280, showed methine proton signals in the NMR spectra at 5·3 as well as 6·1. The ratio of the added intensities of these signals to that of all aromatic and olefinic protons was about 1:8.

In one experiment we isolated *p*-styryldibenzyl from an irradiation mixture although in very low yield (< 1%); m.p. 154°; UV λ_{max} nm (log ε): 206·5 (4·50), 229 (4·24), 297·8 (4·32), 311 (4·29), 326·3 (4·07); MS *m/e*: main peaks at 284, 193, 178. The presence of this reduction product of the parent compound might be ascribed to an activity of p-distyrylbenzene as an oxidans in dehydrocyclizations.*

Irradiation products of m-*distyrylbenzene*

Column chromatography of the reaction mixture gave benzo[e]chrysene in about 70% yield; the compound was identified by its m.p. (127–128°) and UV spectrum (see Clar[19]). Two other compounds were isolated in minor amounts:

(a) A compound with m.p. 334–335°; UV: broad band between 280 and 340 nm (in CH_2Cl_2); MS *m/e*: 564 and 282.

(b) A compound with m.p. 336–337°; UV λ_{max} in CH_2Cl_2: 262, 270, 297, 310 and 320 nm; MS *m/e*: parent peak at 564.

Because of the high m.ps polymeric forms degraded by thermolysis in the mass spectrometer cannot be excluded.

Irradiation products of o-*distyrylbenzene*

cis and *trans*-Stilbene (XXX) and phenanthrene were detected in the irradiation mixture by GLC and mass spectrometry. The compounds could be isolated from the pentane–benzene (80/20) eluate of column chromatography on alumina.

Compound A was isolated from the pentane–benzene (70/30) fraction. The compound was also obtained from the crude reaction mixture by washing the solid with $CHCl_3$ and MeOH and crystallization of the residue from a large volume of CCl_4. The compound could be sublimated without destruction and melted at 337–338°. Because of very low solubility in common solvents the NMR spectrum (Table 1) was measured in a pale violet coloured soln in arsenic trichloride. The colour must be ascribed to complex formation since the compound was recovered unchanged from the soln.

Compounds B and C were obtained as a mixture (melting traject 220–290°) from the pentane–benzene (50/50) fraction or directly from the crude mixture left after separation from compound A. A small amount of C could be separated from B by extraction with CS_2 in which C was sparingly soluble. On TLC (silica gel H, Merck, dried at 100°) with CCl_4 as eluant R_f values of both compounds appeared to be 0·45. Under the same conditions $R_f = 0{\cdot}60$ was found for compound A.

In several fractions obtained by column chromatography on alumina various clearly related dimers but different from A, B and C appeared to be present. One of them (compound D) was isolated in pure form by TLC.

The mass spectra of the compounds A, B, C and D were very similar. In all of them the following main peaks were present: 564 (M^+), 473 (M^+-benzyl), 384 (M^+-stilbene), 293 (384-benzyl), 282 (1/2 M^+), 204 (M^+-2 stilbene), 191 (1/2 M^+-benzyl), 178 (1/2 M^+-styrene), 167 (?). In the mass spectra of some unresolved dimer fractions M^+ peaks at 560, 562 and 564 were found in different ratios. On photolysis they gave a result similar to compound D. The NMR spectra were quite analogous to those of dimers of the para isomer.

A useful procedure for the isolation of picene (XVII) was by column chromatography of the reaction mixture on alumina with benzene–MeOH or by preparative TLC.

Thermolysis experiments

Thermolysis of *o*-distyrylbenzene and of the compounds A, B and C was performed at 10^{-4} mm Hg and about 350° (A at 450°) for 3–5 hr. The residue was subjected to GLC. The gas chromatogram was quite

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* A similar observation has been made in irradiation experiments with some naphthylphenanthryl and diphenanthryl ethylenes, to be published.

similar in all cases; apart from many small peaks three main components appeared to be present, representing 70, 14 and 6% of the reaction mixture. The first one could be isolated by distillation, m.p. 102–104°; mol. wt. 280; NMR: only aromatic protons. A mixture containing both the other compounds exhibited also only aromatic protons in the NMR spectrum and mass numbers of 280 and 356. Although the data point to phenylated naphthalenes determination of the exact structures requires further investigations.

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