Photodehydrocyclizations in Stilbene-like Compounds.   Part V.[1]   Photochemistry of 2,2'-Distyrylbiphenyl

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The photochemistry of 2,2'-distyrylbiphenyl (I) has been investigated. Irradiation under nitrogen gives, as the kinetically controlled product, *trans,trans,trans*-1,2,2a,10b-tetrahydro-1,2-diphenylcyclobuta[*l*]phenanthrene (IIa), and as the thermodynamically-controlled product 4,5,9,10-tetrahydro-4,9-diphenylpyrene (IXa). Irradiation under nitrogen in the presence of iodine gives 7-phenylbenzo[*c*]chrysene (IV). The mechanisms are discussed. Heating (I) at 240° gives *cis,cis,cis*-1,2,2a,10b-tetrahydro-1,2-diphenylcyclobuta[*l*]phenanthrene (IIb) as the only primary product. The isomers (IIa) and (IIb) behave quite differently on heating and on irradiation. Under both conditions (IIa) is converted into (I) and (IIb) into stilbene and phenanthrene. The stereospecificity of the non-pericyclic conversions of (IIa and b) is remarked upon.

We have previously reported [2] that *o*-distyrylbenzene cannot be converted directly into 1-styrylphenanthrene by irradiation, because the relevant value [3] of ΣF_{rs}^{*} is too small.   Instead of photodehydrocyclization, inter- and intra-molecular cycloadditions between the olefinic substituents took place initially.

Meinwald found [4] that 1,8-distyrylnaphthalene, in which the styryl residues are separated by two aromatic bonds, also yields cycloaddition products.

We have now investigated the photochemistry of 2,2'-distyrylbiphenyl (I) in which the substituents are separated by three C–C bonds and some rotational freedom around the central bond is present.

During the course of our work, Tulloch and Kemp

published results [5] on the photolysis of the biphenyl (I). On irradiation in boiling cyclohexane under nitrogen, only one product, assumed to be a 1,2,2a,10b-tetrahydro-1,2-diphenylcyclobuta[*l*]phenanthrene (II) of unknown configuration, was isolated in 60% yield. However, this result is only partly in accordance with our findings.

Calculation of free valence numbers of the various carbon atoms of (I) in the excited state reveals that photocyclization into 2-(1-phenanthryl)stilbene (and further into 1,1'-biphenanthryl) is improbable ($\Sigma F_{ab}^{*} = 0.939$). Although the formation of a bond between C_c and C_d is not quite comparable with stilbene-like

[1] Part IV, W. H. Laarhoven and Th. J. H. M. Cuppen, *Tetrahedron Letters,* 1971, 163.
[2] W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Tetrahedron,* 1970, **26,** 1069.
[3] W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Rec. Trav. chim.,* 1968, **87,** 687.
[4] J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.,* 1971, **93,** 725.
[5] C. D. Tulloch and W. Kemp, *J. Chem. Soc. (C),* 1971, 2824.

photodehydrocyclizations, such ring closures seem to follow a rule similar to that found with 4-styrylphenanthrene[2] and 5-styrylbenzo[c]chrysene.[6] Because $\Sigma F_{cd}^* = 1.095$, the biphenyl (I) might cyclize into

(I) (II)
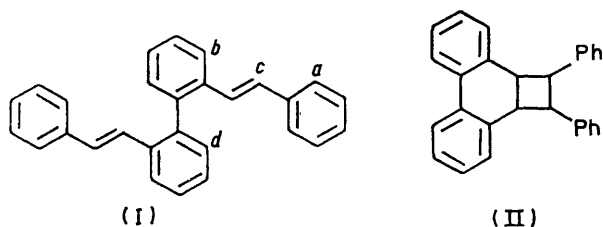
4-styryl-10-phenylphenanthrene (III), which by a second cyclization might give rise to 7-phenylbenzo[c]chrysene (IV) and 4,9-diphenylpyrene (V).

(III)

(IV) (V)
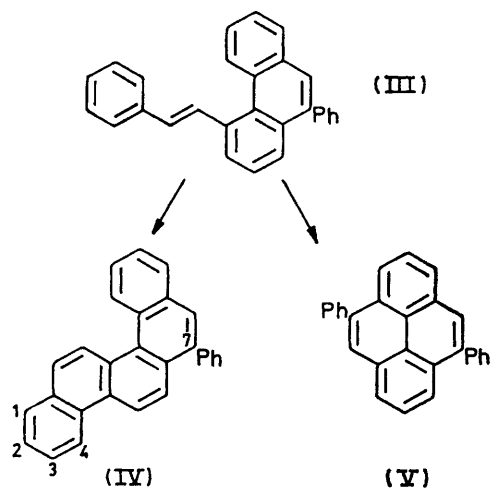
RESULTS

We found that the nature and yields of the irradiation products of (I) varied considerably with the conditions. Depending on the wavelength used, the presence of iodine as an oxidant, and the time of irradiation, one of three different compounds could be obtained as the main product, whereas in the presence of oxygen (air) various oxidation products were formed (see Table).

Irradiation experiments with solutions of 2,2'-distyryl-biphenyl in hexane (10^{-4}—10^{-2} molar) [a]

	Vessel	Atmo-sphere	Oxidant	t	Products [c]
1	Quartz	N_2		15 min	A (B)
2	Quartz	N_2		6 h	B (A)
3	Glass	N_2		15 min	A (B)
4	Glass	N_2		6 h	A (B)
5 [b]	Quartz	N_2		15 min	A
6 [b]	Quartz	N_2		4 h	A (B)
7	Quartz	N_2	I_2	6 h	B (A)
8	Quartz	N_2	I_2	6 h	C
9	Quartz	Air		15 min	Oxidation product (A) (B)
10	Quartz	Air		6 h	Oxidation product (B) (C)
11	Quartz	Air	I_2	6 h	Oxidation product

[a] Light source was a Philips high-pressure mercury lamp (see Experimental) except where indicated. [b] λ <300 nm. [c] Products mentioned in parentheses are only isolated in small amounts. The main product is always formed in >50% yield.

Generally, the irradiations were carried out with solutions of the *trans,trans*-isomer of (I), which could be obtained pure more easily than the other isomers. Due to photo-isomerization (followed by n.m.r.), however, the *cis,trans*- and *cis,cis*-isomers give the same results, although at a slower rate: product A was formed from all three isomers on simultaneous irradiation at 300 nm under identical conditions (experiment 5).

Experiments 1—5 reveal that in the absence of an oxidant two products A and B can be formed. Apparently A is not photostable, because on longer irradiation, especially at shorter wavelength, B becomes predominant.

In experiment 6, conditions were identical with those used by Tulloch and Kemp,[5] who isolated a product with m.p. 202—203° [probably B (m.p. 213—215°) contaminated with A (m.p. 136°)]. The reported u.v. and n.m.r. data differ from those found by us for A and B.

In the presence of oxygen (experiments 8—10) mainly oxidation occurs; in view of broad i.r. absorptions at 3400, 1730 and 1280 cm^{-1}, the irradiated mixture must contain several oxygen-containing polar products (>70%). However, with iodine as an oxidant (experiment 7), a third hydrocarbon (C), a dehydrocyclization product, could be isolated.

The Structure of the Products.—Compound A has an u.v. spectrum similar to that of 9,10-dihydrophenanthrene.[7] Its i.r. spectrum does not show absorptions due to olefinic bonds. The n.m.r. spectrum consists of several multiplets integrating for 22 protons in all, and an AA'BB' pattern (18 lines). Two multiplets at δ 3·67—3·33 and 3·29—2·95 p.p.m. (2H each) are mirror images except for some broadening of lines in the signal at higher field, which disappears, however, on decoupling at the phenyl absorption.

In the mass spectrum, the parent peak at 358 ($C_{28}H_{22}$) is of low abundance (1%), and large peaks are at 180 (92%, $C_{14}H_{12}$, stilbene?) and 178 (100%, $C_{14}H_{10}$, phenanthrene?). Measurements of metastable ions in the field-free section of the mass spectrometer proved that both ions were formed directly from the parent ion at 358.

From these data, it can be concluded that A is a cyclo-butane derivative. Two basic structures are possible: (II) with six stereoisomers and (VI) with three different configurations (a, b, and c).

(VI)
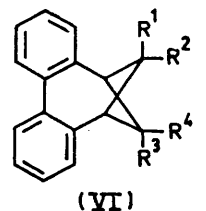
a; $R^1 = R^3 = H$, $R^2 = R^4 = Ph$

b; $R^1 = R^3 = Ph$, $R^2 = R^4 = H$

c; $R^1 = R^4 = H$, $R^2 = R^3 = Ph$

The fragmentation pattern of A (with the possible formation of stilbene and phenanthrene) in the mass spectrometer points to structure (II). However, the fragmentation might also proceed *via* a thermal process such as A $\longrightarrow$ (I) $\longrightarrow$ (II), because heating A at *ca.* 250° yields

[6] W. H. Laarhoven and J. A. M. van Broekhoven, *Tetrahedron Letters*, 1970, 73.

[7] DMS atlas of u.v. spectra; spectrum D10/43.

not only stilbene and phenanthrene, but also (IIb) and some of the starting compound (I).

Ozonolysis of A during 12 h, followed by oxidation and esterification gave the *trans,trans,trans*-tetraester (VII), identified by comparison with an authentic sample. Therefore compound A must be (IIa) or (VIa).

Models of (VIa), (IIa), and the *cis*-isomer (IIb) show that (VIa) has a planar, rigid biphenyl portion in which the 2,2'-protons are closer than the 4,5-protons in phenanthrene. The isomer (IIa) is also rigid, but the biphenyl portion is not planar and the distance between the *ortho*-protons is larger than in (VIa), while (IIb) is less rigid, and the *ortho*-protons fluctuate between two nearly planar conformations. The models suggest that the n.m.r. signal of the *ortho*-protons in (VIa) should be at lower field than in (IIb), because of

(IIa) (IIb)

(VII)
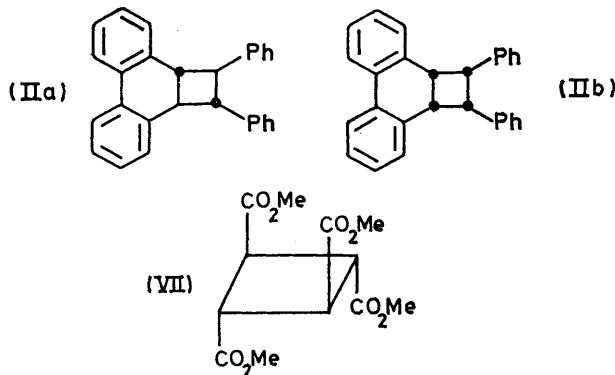
strong van der Waals interaction in the former,* and that that of (IIa) should be at higher field than in (IIb). In compound A the signal was found at δ 7·69—7·54 p.p.m.; that of (IIb) (see later) at 7·85—7·72. Therefore, structure (IIa) is more probable for A. The high-field multiplet (3·29—2·95) belongs to the 2a- and 10b-protons, which are shielded by the phenyl rings of the biphenyl structure, and slightly broadened by allyl coupling.

To obtain more evidence about the structure of A, an attempt was made to oxidize the compound into the known dihydroderivative (VIII). With dicyanodichloroquinone (DDQ) in benzene for a week, no conversion could be achieved. Bromination with *N*-bromosuccinimide gave a mixture of very labile bromides. An attempt to purify the bromides on alumina caused dehydrobromination, but in
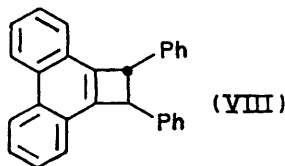

(VIII)

the resulting mixture (VIII) could be detected (g.l.c. and n.m.r. and mass spectroscopy). Thus it is clear that A is *trans,trans,trans*-1,2,2a,10b-tetrahydro-1,2-diphenylcyclobuta[*l*]phenanthrene (IIa).

From its spectral properties (u.v., n.m.r., and mass; see experimental section) compound B is likely to be a tetrahydrodiphenylpyrene (IXa or b); the 4,9-diphenyl-isomer (IXa) is the most conceivable photoproduct of (I).

* An analogous difference is found in the n.m.r. spectra of *trans,trans*-(I) and *cis,cis*-(I). The peaks of the *ortho*-protons in the former are at distinctly lower field than those of the latter (see Experimental section).

To support this suggested structure, compound B was treated with DDQ. The expected dehydrogenation product, 4,9-diphenylpyrene (V) is unknown. The product


(IXa) (IXb)
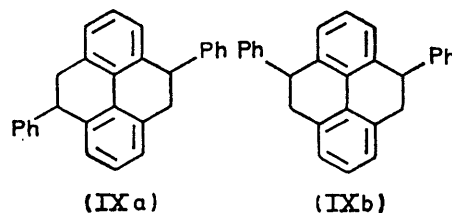
obtained had, however, a characteristic pyrene u.v. spectrum with clearly separated p, β, and β' bands (all with fine structure), mass peaks at 354 ($C_{28}H_{18}$), 276 ($M^+ - C_6H_6$), and 177 ($1/2\ M^+$), and only aromatic signals in the n.m.r. spectrum. The i.r. spectrum contained strong peaks characteristic of a mono-substituted benzene, two peaks indicative of three adjacent aromatic hydrogens, and a peak due to an isolated aromatic hydrogen atom (see Experimental section), in accordance with the suggested structure.

Compound C had a parent peak in the mass spectrum at 354 ($C_{28}H_{18}$). In comparison with (I) four protons have been lost, which suggests that C arises by two dehydrocyclizations. Its u.v. spectrum is very similar to that of benzo[*c*]chrysene.[8] That and the n.m.r. spectrum lead to the conclusion that the structure must be 7-phenylbenzo[*c*]chrysene (IV).

Thermal Reactions of the Biphenyl (I).—Because of the apparent stereospecificity of the photochemical conversion of (I) into (II) [of six possible isomers only one, (IIa), is obtained] it seemed worthwhile to investigate potential thermal reactions of (I). A thermal cycloaddition seemed to be probable, because the mass spectrum of (I), being quite similar to that of the cyclobutaphenanthrene (IIa), had a very low parent peak (358, only observed at low energy, 40 eV), but large peaks at 180 (stilbene) and 178 (phenanthrene).
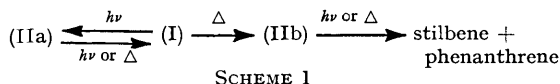
Below 220°, the biphenyl (I) was stable, while above 300° only phenanthrene and stilbene could be detected. However, on heating at 240° in an evacuated tube for 1 h, ca. 20% of the expected cyclobutaphenanthrene (II) could be isolated. Its mass spectrum was similar to that of (I) and (IIa) (A), and its u.v. spectrum almost identical with that of (IIa). The n.m.r. spectrum contained an AA'BB' pattern as well as signals for aromatic protons (see Experimental section). The low-field multiplet and the small couplings constants of the cyclobutane protons point to the configurations (IIb) or (IIc) with a *cis*-9,10-fused dihydrophenanthrenic part and *cis*-substitution of the phenyl groups.

(IIc) (X)
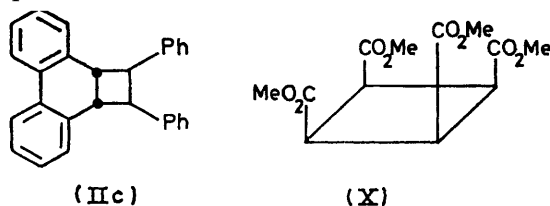
By ozonolysis, oxidation, and methylation as for the isomer (IIa), the product could be converted into the *cis,cis,cis*-tetraester (X). Therefore, structure (IIb) is
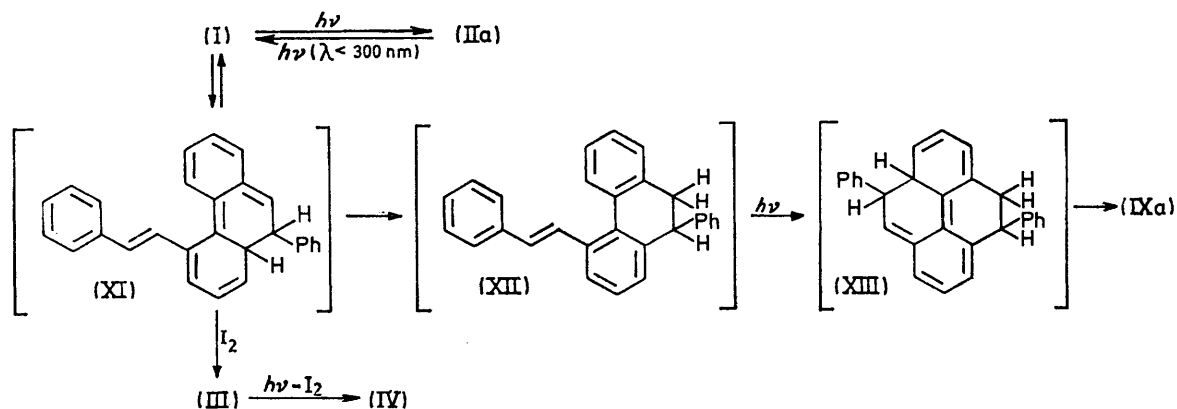
[8] E. Clar, 'Polycyclic Hydrocarbons,' vol. I, Academic Press, London, 1964, p. 277.

assigned to the thermolysis product of the biphenyl (I). The higher field signals for the aromatic protons in the *cis*-isomer (IIb) by comparison with (IIa) (δ 7·26—6·70 and 7·35—6·95 p.p.m., respectively) and the lower field signals for the cyclobutane protons (4·14—3·92 and 3·67—2·95,

$$(IIa) \underset{hv \text{ or } \Delta}{\overset{hv}{\rightleftarrows}} (I) \overset{\Delta}{\longrightarrow} (IIb) \overset{hv \text{ or } \Delta}{\longrightarrow} \text{stilbene} + \text{phenanthrene}$$

<center>SCHEME 1</center>

respectively) can be ascribed to stronger mutual shielding between the phenyl residues and the aromatic rings of the biphenyl group, and less shielding between aromatic rings and cyclobutane protons.

Photo- and Thermal Stability of the Cyclobutaphenanthrenes, (IIa) *and* (IIb).—The isomers (IIa) and (IIb) behave quite differently on heating and on irradiation. Irradiation with a HPK125 light source of a 10^{-4} molar solution of the *trans*-isomer (IIa) in hexane for 6 h under nitrogen in a quartz vessel gave the tetrahydropyrene

phenanthrene (XI) isomerizes by a 1,5-sigmatropic hydrogen shift into the intermediate (XII) which gives the pyrene (IXa) by similar processes.

The rapid and stereospecific cyclization of the biphenyl (I) into the cyclobutane (IIa) might proceed by two successive electrocyclic reactions, an internal cycloaddition, or in a non-concerted way.

If the lower velocity of the conversions of the *cis,trans*- and *cis,cis*-isomers of (I) in comparison with the *trans,trans*-compound means that the cyclobutane (IIa) mainly arises from the last isomer, electrocyclic reactions in the excited state obeying the Woodward–Hoffmann rules should proceed according to Scheme 3. But this is not found.

An internal concerted cycloaddition of (I) might be compared with the photodimerization of *trans*-stilbene [9] which yields *trans,trans,trans*- and *trans,cis,trans*-tetraphenylcyclobutane (XIVa and b).

<center>SCHEME 2</center>

(IXa) (B) in good yield. A similar experiment with iodine added yielded the benzo[c]chrysene (IV). Apparently the photoconversion of the biphenyl (I) into the *trans*-isomer (IIa) is reversible under these conditions. The same reaction [(IIa) $\longrightarrow$ (I)] also proceeded on heating (IIa) at 240—300° (see before).

Irradiation of the *cis*-isomer (IIb) in a quartz tube with a high-pressure mercury lamp or at 300 nm rapidly yielded *cis*-stilbene and phenanthrene in high yield. The biphenyl (I) or its photoproducts could not be detected. Heating (IIb) (300°) had the same results in this case (see Scheme 1).

DISCUSSION

The photoreactions are summarized in Scheme 2. Apparently the formation of the phenanthrene (XI) is slow in comparison with the formation of the cyclobutane (IIa). Because the former reaction is followed by irreversible steps leading to the benzochrysene (IV) or pyrene (IXa), and the formation of the cyclobutane (IIa) is reversible at lower wavelength, the benzochrysene (IV) and the pyrene (IXa) are only obtained as the main products after longer irradiation. In the presence of an oxidant (iodine), mainly the benzochrysene (IV) is formed, undoubtedly *via* the phenanthrene (III). Under nitrogen, however, the dihydro-

However, the biphenyl (I) cannot occur in a conformation suitable for the formation of a cycloaddition
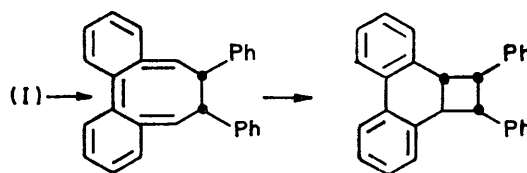
<center>SCHEME 3</center>

product (IIc) comparable to (XIVb). The only product found, (IIa), is stereochemically equivalent to (XIVa).

The remarkable stereospecificity of the thermal and photolytic reactions of the isomers (IIa) and (IIb), (Scheme 1) cannot be due to concerted mechanisms, because with both compounds the conversions in the ground and excited state are identical. A pericyclic pathway in the thermal reactions should be indeed improbable in view of the high temperature (*ca.* 300°).

The stereospecificity, at first sight surprising in non-concerted reactions, has already been found earlier in

[9] H. Shechter, W. J. Link, and G. V. D. Tiers, *J. Amer. Chem. Soc.*, 1963, **85**, 1601.

similar reactions [10] with *rigid* compounds. Hoffmann [11] showed that in such cases the intermediate biradicals do not represent true energy minima, and called them 'twixtyls'. From Dreiding models it appears that the unpaired electrons in the twixtyl formed from (IIb) by
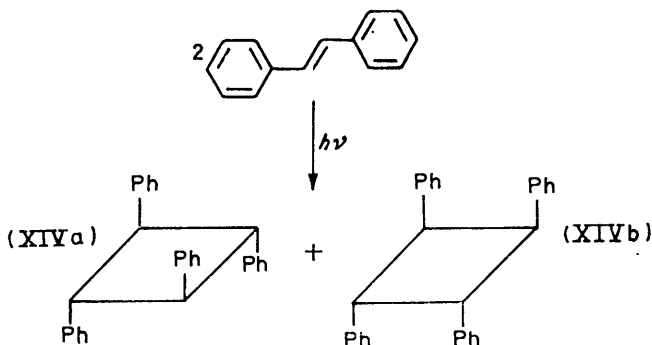
homolytic fission of C(3)–C(4) overlap less well with aromatic rings than those in the biradical formed by splitting of C(2)–C(3). In (IIa) no preference can be given on this ground, but its twixtyl apparently has a different structure from that from (IIb). It is noteworthy that the stilbene formed from the isomer (IIb) has a *cis*-configuration, which is a consequence of a mechanism *via* an intermediate with a short life time but without an energy minimum corresponding to a rigid conformation.

EXPERIMENTAL

For spectral data the following instruments were used: a Varian-SM2B mass spectrometer, a Beckman DK2A or a Cary 15 spectrophotometer, a Perkin-Elmer 257 apparatus, and a Varian HA100 or T60 instrument.

Irradiations were carried out in a cooled quartz tube surrounding a Philips HPK125 high-pressure mercury lamp,[3] or in a Rayonet Reactor fitted with 300 or 360 nm lamps.

2,2'-Distyrylbiphenyl (I).—This was synthesized by the method of Hall *et al.*[12] The last step, a Wittig synthesis, was performed in boiling ethanol with sodium methylate, and benzaldehyde in two-fold excess. The *trans,trans*-isomer of (I) (25%) crystallized out from the mixture. Because the unknown *cis,trans*- and *cis,cis*-isomers could be detected in the mother liquor, separation was effected by column chromatography. The separation was not complete, but the isomers were purified by recrystallization: *trans,trans*-2,2'-distyrylbiphenyl, m.p. 148—149° (from methanol), $\lambda_{max.}$ (MeOH) 327 (log ε 4·39), 313 (4·59), 295 (4·65), 225 (4·63), and 207 nm (4·67), δ (CS$_2$) 7·75—7·6 (2H, *o*-biphenyl), 7·6—7·0 (16H, m, Ph), and 6·85 p.p.m. (4H, d), m/e 358 (3%, M^+), 267 (16), 265 (16, $M - C_7H_7$), 252 (13, $M - C_8H_8$), 213 (14), 202 (7), 180 (90, $1/2M + 1$), 178 (100, $1/2M - 1$), and 140 (21); *cis,trans*-isomer, m.p. 73—76° (from methanol) $\lambda_{max.}$ (MeOH) 327 (log ε 4·13), 311 (4·40),

292 (4·47), 223 (4·52), and 207 nm (4·52), δ (CS$_2$) 7·8—7·6 (2H, m), 7·4—7·0 (16H, m), 6·85 (2H, s), and 6·30 p.p.m. (2H, s); *cis,cis*-isomer, m.p. 92—102° (from methanol), $\lambda_{max.}$ (MeOH) 282 (log ε 4·34) and 220 nm (4·57), δ (CS$_2$) 7·15 (18H, s) and 6·30 p.p.m. (4H, s), mass spec. as for *trans,trans*-isomer.

trans-1,2-*Dihydro*-1,2-*diphenylcyclobuta*[l]*phenanthrene* (VIII).—This was prepared by photolysis [13] of dihydrophencyclone. In contrast with the analogous synthesis of dihydrodiphenylcyclobutabenzene from the corresponding ketone,[14] only the *trans*-isomer was obtained, m.p. 192°, $\lambda_{max.}$ (MeOH) 356 (log ε 3·42), 301 (4·23), 289 (4·16), 278 (4·21), 270 (4·32), 254 (4·86), 247 (4·78), 222 (4·72), and 211 nm (4·75), δ (CCl$_4$) 9·2—9·0 (2H, m), 8·0—7·8 (6H, m), 7·6 (10H, s), and 4·9 p.p.m. (2H, s).

*Tetramethyl trans,trans,trans-Cyclobutane-*1,2,3,4-*tetracarboxylate* (VII).—The ester, m.p. 127°, was obtained by isomerization with sodium methylate of the *cis,trans,cis*-isomer. The latter compound, m.p. 145°, was obtained [15] by irradiation of dimethyl fumarate.

The *cis,cis,cis*-tetracarboxylate (X), m.p. 200—203°, was obtained by ozonolysis of the *cis*-photo-dimer [16] of acenaphthylene, followed by oxidation and methylation as described by Griffin.[17]

trans,trans,trans-1,2,2a,10b-*Tetrahydro*-1,2-*diphenylcyclobuta*[l]*phenanthrene* (IIa).—*trans,trans*-2,2'-Distyrylbiphenyl in deaerated hexane was irradiated in a quartz vessel under nitrogen with a 300 nm lamp for *ca.* 15 min. The product was purified by column chromatography, m.p. 136° (from methanol), $\lambda_{max.}$ (MeOH) 297 (log ε 3·71), 265 (4·19), and 212 nm (4·69), δ (CS$_2$) 7·69—7·54 (2H, m), 7·35—6·95 (16H), 3·67—3·33 (2H, m), and 3·29—2·95 p.p.m. (2H, m), m/e 358 (1%, M^+), 279 (3, $M - C_6H_7$), 267 (14, $M - C_7H_7$), 265 (10), 253 (10), 180 (92, $1/2M + 1$), 178 (100, $1/2M - 1$).

4,5,9,10-*Tetrahydro*-4,9-*diphenylpyrene* (IXa).—This is best obtained in 70% yield by irradiation for 6 h of a solution of the *trans,trans*-biphenyl (I) in a quartz vessel under nitrogen with a high-pressure mercury lamp in deaerated hexane. The product (70%) can be purified by column chromatography, m.p. 213—215° (from methanol), $\lambda_{max.}$ (MeOH) 292 (log ε 4·08), 281 (4·22), 270 (4·13), and 216 nm (4·69), δ (CS$_2$) 7·2—6·6 (16H, m, ArH), 4·15 (2H, t, J 7 Hz), and 3·16 p.p.m. (4H, d, J 7 Hz), m/e 3·58 [100%, M^+ ($C_{28}H_{22}$)], 280 (18, $M - C_6H_6$), 279 (33), 203 (29), and 202 (33, $M - 2C_6H_6$).

4,9-*Diphenylpyrene* (V).—This was obtained in nearly quantitative yield by treatment of the foregoing compound in benzene with dichlorodicyanoquinone during 12 h, m.p. 256—257° (from methanol), $\lambda_{max.}$ (MeOH) 346 (log ε 4·45), 331 (4·33), 315 (4·01), 280 (4·69), 271 (4·46), 2·46 (4·77), 235 (4·62), 221 (4·72), and 207 nm (4·67), $\nu_{max.}$ 898 (isolated ArH), 806 and 782 (3 adjacent ArH), and 732 and 708 cm^{-1} (monosubstituted benzene), δ (ArH only), m/e 354 (M), 276 ($M - C_6H_6$), 177 ($1/2M$).

7-*Phenylbenzo*[c]*chrysene* (IV).—A solution of the biphenyl (I) in oxygen-free hexane was irradiated for 8 h in the presence of an equivalent amount of iodine. Work-up gave the benzochrysene (60%), m.p. 184—185° (from methanol), $\lambda_{max.}$ (MeOH) 323 (log ε 4·47), 295 (4·88), 284

[10] L. A. Paquette and G. L. Thomson, *J. Amer. Chem. Soc.*, 1971, **93**, 4920.

[11] R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, 1970, **92**, 7091.

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(4·75), 271 (4·65), 254 (4·50), 234 (4·54), and 210 nm (4·83), δ (CS$_2$) 8·7—8·5 (2H, m, 12- and 13-H), 8·35—8·18 (2H, m, 4- and 5-H), 7·75—7·4 (4H, m, 1-, 6-, 9-, and 14-H), 7·38 (1H, s, OH), 7·30—7·05 p.p.m. (9H, m, 2-, 3-, 10-, and 11-H and Ph).

Ozonolysis of the isomers (IIa) and (IIb) was performed by bubbling an oxygen–ozone mixture [from a Fischer ozongenerator (3% ozone)] for 15 h through a suspension of (II) in 80% acetic acid. The resulting solution was treated with 30% hydrogen peroxide for 36 h. The solvent was evaporated at low temperature, the residue was dissolved in methanol and esterified with a diazomethane solution by a conventional procedure.

The *trans*-tetracarboxylate (VII) and the *cis*-tetracarboxylate (X) were readily identified by their different retention volumes of those of the isomeric tetramethyl cyclobutanetetracarboxylates.

Thermolysis of trans,trans-*Biphenyl* (I).—The thermolysis was performed in an evacuated tube at 240—250° for 2 h. After cooling, the mixture was sublimed at 100° and 1 mmHg to remove phenanthrene and stilbene. The residue, cis,cis,cis-1,2,2a,10b-*tetrahydro*-1,2-*diphenylcyclobuta*[l]*phenanthrene* (IIb) was crystallized from methanol, m.p. 177—178°, $\lambda_{max.}$ (MeOH) 310 (log ε 3·49), 298 (3·57), 280 (4·09), 272 (4·13), and 211 nm (4·85), δ (CS$_2$) 7·85—7·72 (2H), 7·26—6·70 (16H), 4·14—4·06 (2H), and 4·00—3·92 p.p.m. (2H).

Thermolysis of the other isomers of (I) and of (IIa) was carried out under the same conditions and gave the same results.