

Photodehydrocyclizations in Stilbene-Like Compounds. X.¹ Rearrangements in the Photocyclization of 4,5-Diphenyltriphenylene and 4,5-Diphenylphenanthrene

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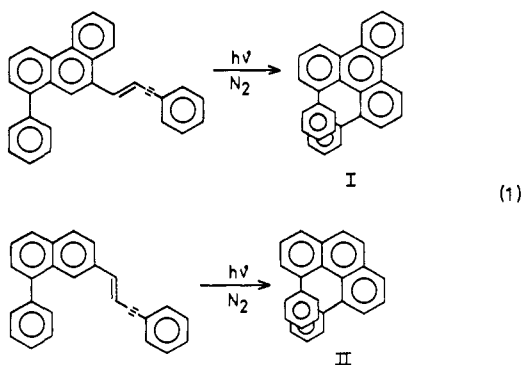
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Abstract: Photodehydrocyclizations of 4,5-diphenyltriphenylene (I) and 4,5-diphenylphenanthrene (II) are accompanied with a similar 1,2-phenyl shift as previously found in the photocyclization of 1-phenylpentahelicene. I gives 1-phenyldibenzo[*e,l*]pyrene (IIIa) and tribenzo[*e,ghi,k*]perylene (IV); the photoproducts of II are 1-phenylbenzo[*e*]pyrene (XVIIa) and dibenzo[*e,ghi*]perylene (XVIII). From I, however, a third photoproduct, benzo[*e*]naphtho[1,2,3,4-*ghi*]perylene (VI) can be isolated. It is suggested that its formation is due to a sigmatropic rearrangement in the same intermediate radical (XXII) which undergoes the phenyl shift.

In the preceding paper¹ we presented a first example of a photodehydrocyclization in which the ring closure is accompanied with a 1,2 shift of a phenyl residue, present at one of the ring positions concerned in the formation of the new C–C bond. In this paper the occurrence of this and another, more complex type of rearrangement will be described, found in the photocyclization of 4,5-diphenyltriphenylene (I) and 4,5-diphenylphenanthrene (II).

Results

The starting compounds were obtained from appropriate diarylbutenyne² *via* a novel photocyclization reaction² which already appeared to be a valuable synthetic tool in the preparation of such strongly overcrowded compounds (eq 1).



The spatial relationships between the phenyl substituents in I and II are probably similar to those between the pyridyl residues in 13,14-bis(2-pyridyl)pentaphene^{3a} and 3,6-dihydroxy-4,5-bis(2-pyridyl)phenanthrene.^{3b} X-Ray analysis of the 2,7-dibromo derivative of the latter compound⁴ has revealed that the pyridyl residues are almost parallel and have a nonbonded intramolecular distance of 2.81 Å between C₂ of one pyridine and C₂' of the other pyridine ring. The distortion of the phenanthrene moiety is evenly distributed

(1) Part IX: see A. H. A. Tinnemans and W. H. Laarhoven, *J. Amer. Chem. Soc.*, **96**, 4611 (1974).

(2) A. H. A. Tinnemans and W. H. Laarhoven, *Tetrahedron Lett.*, 817 (1973).

(3) (a) D. L. Fields and T. H. Regan, *J. Org. Chem.*, **36**, 2995 (1971); (b) *ibid.*, **36**, 2991 (1971).

(4) D. L. Smith and E. K. Barrett, *Acta Crystallogr., Sect. B*, **27**, 419 (1971).

over the entire framework. All individual rings, but no major segments, are approximately planar.

The overcrowding in I and II is apparent from spectroscopic data. The mass spectra of both compounds show M⁺ – C₆H₅ peaks of 90% relative abundance. This predominant loss of a phenyl group is unusual in phenyl-substituted aromatics, *e.g.*, 2% in 4-phenylphenanthrene, 20% in the more strained 3,4-diphenylphenanthrene.

In comparison with unstrained diphenylphenanthrenes and triphenylenes a bathochromic shift of the α and p band and loss of fine structure is observed in the uv spectra of I and II (see Figure 1). According to Murrell⁵ such a shift has to be expected in spectra of compounds in which a bond having a nodal plane in the highest occupied molecular orbital (*e.g.*, the 4a–4b bond in I or II) is twisted (insert of Figure 1).

The nmr spectra of I and II clearly show shielding of the aromatic protons in the phenyl substituents. At room temperature the para protons of II appear as an unresolved multiplet at δ 6.91, the meta protons as a triplet of multiplets at δ 6.85, and the ortho protons as a doublet at δ 6.40.

Irradiation of 4,5-Diphenyltriphenylene (I). Irradiation at 300 nm of I, dissolved in deaerated benzene, for 3 hr under nitrogen and in the presence of 3 equiv of iodine gave a rather complex reaction mixture. By column chromatography on Al₂O₃ the starting compound and three products (A, B, and C) could be isolated in 5, 29, 33, and 6% yield, respectively. A similar irradiation in hexane without added iodine did not lead to substantial photoconversion even after 14 hr. A slight amount of tarry products had been formed but 80% of the starting compound could be recovered.

B had the molecular formula C₃₀H₁₈ (*m/e* 378). A and C appeared to be isomers C₃₀H₁₆ (*m/e* 376). A purified sample of B could be converted into C by renewed irradiation in the presence of iodine. In view of the 1,2-phenyl shift occurring in the photocyclization of 1-phenylpentahelicene,¹ it could be supposed that B should be 1-phenyldibenzo[*e,l*]pyrene (IIIa) which can cyclize into tribenzo[*e,ghi,k*]perylene (IV). Identity of C with IV could be demonstrated by comparison of

(5) (a) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London, 1963; (b) R. I. T. Cromartie and J. N. Murrell, *J. Chem. Soc.*, 2063 (1961).

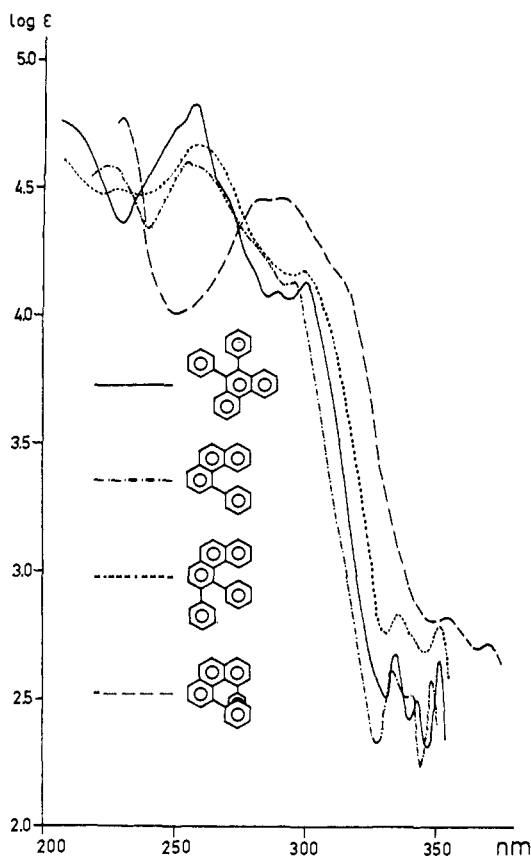
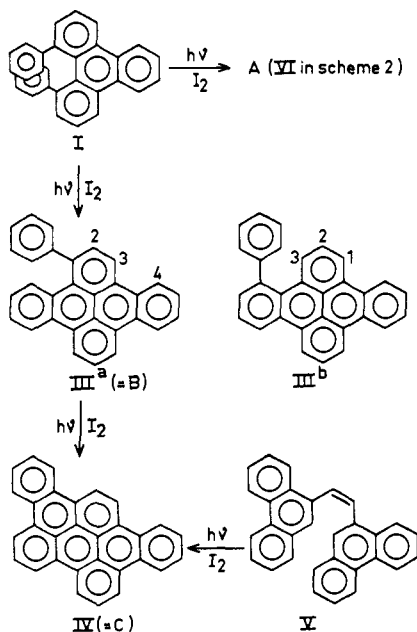


Figure 1. Uv spectra of some phenylphenanthrenes in methanol.

the melting point and uv spectrum of C with those of the irradiation product of bis(9-phenanthryl)ethylene (V) which is known⁶ to be IV (see Scheme I).

Scheme I

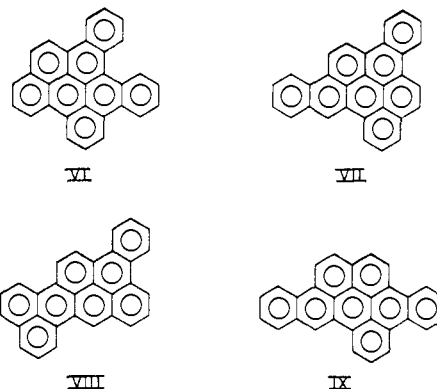


The ultimate formation of IV might also have occurred *via* 4-phenyldibenzo[*e,l*]pyrene (IIIb) which should arise if ring closure of I were accompanied with a 1,9-phenyl shift. The nmr spectrum of B points,

(6) W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **87**, 687 (1968).

however, clearly to structure IIIa. It contains a one-proton signal at rather high field (δ 7.66) in comparison with the remainder of the spectrum. It consists of a triplet of multiplets pointing to coupling with two ortho protons and one meta proton. The δ value and splitting pattern are consistent with H_{13} in IIIa but with none of the protons in IIIb. The other nmr data, a six-proton multiplet at 9.08–9.43 (bay protons 3, 4, 7, 8, 10, and 11), a triplet at 8.58 (H_9), a quartet of signals with equal intensity at 8.29 as is also found in triphenylene (H_5 and H_6), and a multiplet of the five phenyl protons at 7.9–8.1 substantiate the supposed structure.

The third irradiation product of I had mp 256–258°. It showed strong blue fluorescence in organic solvents. Its uv spectrum in benzene consisted of a series of bands at 328, 357, 374, 394, and 416 nm which are characteristic for a benzo[*b*]pyrene or a perylene moiety.⁷ Its nmr spectrum showed only aromatic protons, present in two clearly separated multiplets of equal intensity at δ 7.82–8.47 and 8.86–9.36. The δ value of the latter group of protons is found for α_3 protons⁸ (e.g., in phenanthrene) or α_4 protons (e.g., in benzo[*c*]phenanthrene). The nmr spectrum points to a polycyclic aromatic compound without phenyl substituents; this in accordance with the molecular formula $C_{30}H_{16}$ which affirms that two dehydrogenations had occurred in the formation of A from I. These data leave, however, four possible structures, VI–IX. IX could be excluded because of its known melting point (391°) and uv spectrum.⁹



From a compound like VIII uv absorptions between 400 and 470 nm may be expected.⁷ Therefore, this structure could also be rejected. Clar¹⁰ mentioned a melting point 243–244° for VI, only slightly lower than that found for product A. Therefore, we decided to synthesize VI and to compare its physical properties with those of A (Scheme II).

Phenyl-9-(9-allylfluorenyl)carbinol (X) was heated with P_2O_5 . In this way Bavin¹¹ obtained 9,10-dihydro-10-methylbenzo[*g*]chrysene (XIII) in 90% yield. We isolated mainly 9-allyl-10-phenylphenanthrene (XI) (82%) and small amounts of the isomers XII (5%) and XIII (13%). The allyl derivative XI could, however, be isomerized into the propenyl derivative XII by refluxing with KOH in butanol, and XII gave XIII on irradiation

(7) E. Clar, "Polycyclic Hydrocarbons," Vol. I, Academic Press, London, 1964, Chapter 9.

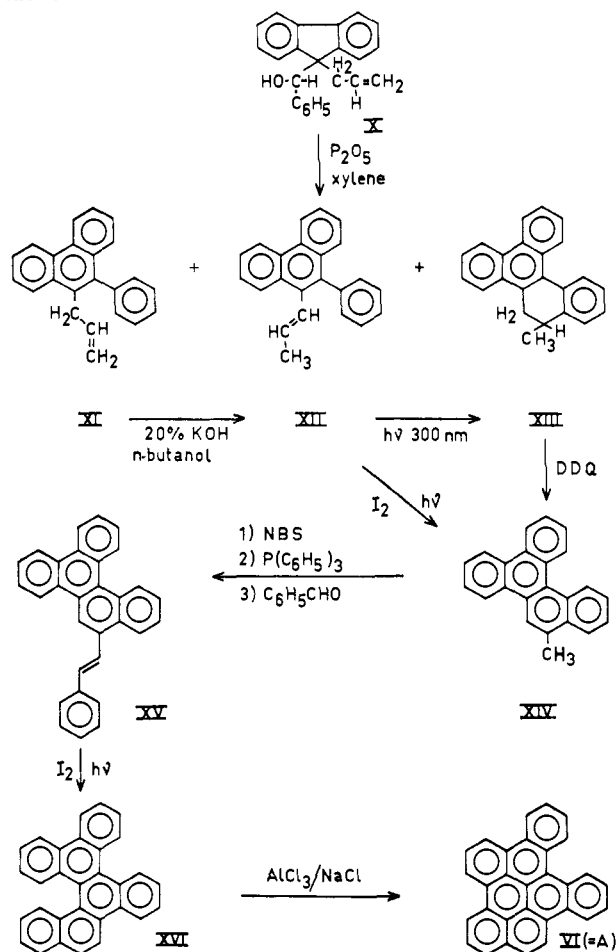
(8) The symbols $H-\alpha_3$, $H-\alpha_4$, H_7 , etc., are used to differentiate the several aromatic protons to their specific positions as was done first by R. H. Martin, *Tetrahedron*, **20**, 897 (1964).

(9) E. Clar, "Polycyclic Hydrocarbons," Vol. II, Academic Press, London, 1964, p 65.

(10) Reference 9, p 75.

(11) P. M. G. Bavin, *Can. J. Chem.*, **37**, 2023 (1959).

Scheme II



in hexane. Irradiation of XII in the presence of iodine gave a mixture of XIII and its dehydrogenation product, 10-methylbenzo[*g*]chrysene.¹² This compound (XIV) could also be obtained from XIII by treatment with dicyanodichloroquinone (DDQ). By bromination followed by a Wittig reaction with benzaldehyde XIV was converted into 10-styrylbenzo[*g*]chrysene, which underwent dehydrocyclization on irradiation in benzene yielding tribenzo[*c,g,p*]chrysene (XVI). Unlike pentahelicene, XVI appeared to be stable on irradiation.¹³ Cyclization leading to benzo[*e*]naphtho[1,2,3,4-*ghi*]perylene (VI) could, however, be achieved by melting with AlCl_3 and NaCl. Melting point and spectroscopic data of this product appeared to be identical with those of compound A, and the melting point of a mixture of A and VI was not lowered.

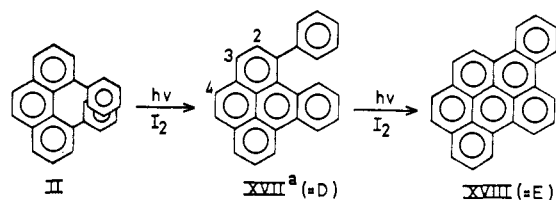
Irradiation of 4,5-Diphenylphenanthrene (II). In the hope to get insight into the nature of the new type of rearrangement occurring in the formation of VI from I, 4,5-diphenylphenanthrene (II) was irradiated under similar conditions as used in the irradiation experiments

(12) See for comparable cyclizations: W. H. Laarhoven and Th. J. H. M. Cuppen, *J. Chem. Soc., Perkin Trans. 1*, 2075 (1972); S. W. Horgan, D. D. Morgan, and M. Orchin, *J. Org. Chem.*, 38, 3801 (1973).

(13) Previously we demonstrated⁶ that photodehydrocyclizations of stilbene-like compounds appear to occur only if the sum of the free valence numbers of the proper atoms in the excited state exceeds a critical barrier ($\Sigma F^* > 1.0$). Formally this value is not valid for pentahelicene derivatives. In a series of five pentahelicene compounds which do all photocyclize the range of ΣF^* is 0.899–0.984; e.g., for dibenzo[*c,g*]phenanthrene (XXI) and dibenzo[*f,j*]picene the ΣF^* values are 0.911 and 0.899. However, tribenzo[*c,g,p*]chrysene (XVI) is photostable ($\Sigma F^* = 0.901$). This fact had to be explained by other reasons than these ΣF^* values.

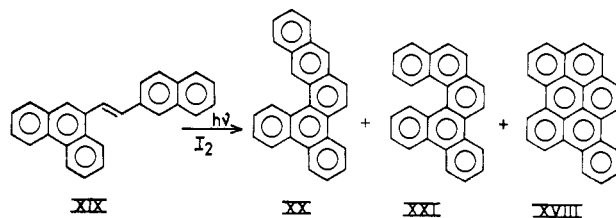
with I. Also in this case a rather complex reaction mixture was obtained when iodine was present. A similar irradiation in hexane without added iodine did not lead to substantial photoconversion. Even with longer reaction times, the starting compound could be recovered for the larger part. The reaction mixture of the former experiment was separated by column chromatography on Al_2O_3 . In this way 12% of the starting compound and two products, D and E, could be isolated (40 and 6%, respectively, after purification). In one experiment a fraction containing a third product F was eluted, but the compound could not be completely separated from D. E had the molecular formula $\text{C}_{26}\text{H}_{14}$ (m/e 326) pointing to a formation *via* two photodehydrocyclizations. It arose also in 85% yield from D on irradiation. On the analogy of the photoproducts IIIa and IV obtained from I, D, and E might be 1-phenylbenzo[*e*]perylene (XVIIa) and dibenzo[*e,ghi*]perylene (XVIII), respectively (Scheme III). The uv spec-

Scheme III

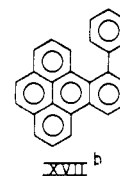


trum of E showed indeed absorptions characteristic for perylene derivatives. Furthermore, the compound appeared to be identical with that photoproduct from 1-(β -naphthyl)-2-(9-phenanthryl)ethylene (XIX) which has the same molecular weight as E (Scheme IV). A

Scheme IV



structural formula XVIIb for D, isomeric with XVIIa, could be excluded in a similar way as in the corresponding case of the photoproduct B from I. The nmr spectrum of D contains a triplet of multiplets centered at 7.00 ppm and corresponding with one proton, which must be H_{11} in XVIIa. The other signals, two one-



proton multiplets at 8.58 and 8.69 (H_8 and H_9 , respectively), an AB pattern between 7.75 and 8.02 with $J_{AB} = 7.8$ Hz (H_2 and H_3), and a nearly collapsed AB pattern at 7.90 (H_4 and H_5) are consistent with this structure.

The composition of F remained unknown because it could not be separated from D. The nmr spectrum of the impure sample showed, apart from signals due to D and a lot of additional peaks due to aromatic protons (6.77–6.97), weak signals at 6.33 and 6.43 with the characteristic pattern of an allylic residue.

336 nm (4.49); nmr (CS₂, TMS) δ 2.65 (s, 3 H CH₃), 6.28 and 7.66 (AB, ethylene, J_{AB} = 15.9 Hz), 7.11–7.53 (m, 9 H), 7.87 (m, 1 H α), 8.02 (m, 1 H α).

9-Methyl-1-phenylphenanthrene. A 10⁻³ M solution of the above arylbutenyne in methanol was irradiated for 8 hr at 300 nm in a Rayonet reactor. The solution was then concentrated and passed over a column of silica, to remove polymeric products, and subsequently over Al₂O₃. 9-Methyl-1-phenylphenanthrene was eluted with benzene/hexane (1:9) and crystallized from methanol: yield 54%; mp 96–98°; *m/e* 268; uv_{max} (CH₃OH) [220 (log ϵ 4.58)], 258 (4.76), [277 (4.32)], [290 (4.16)], 301.5 (4.16), 3.36 (2.71), 3.41 (2.52), 3.52 nm (2.66); nmr (CS₂, TMS) δ 2.57 (s, 3 H, CH₃), 7.36 (s, 5 H, C₆H₅), 7.26–7.62 (m, 5 H), 7.89 (m, 1 H α), 8.52 (m, 1 H- α_3), 8.59 (m, 1 H- α_3).

1-(1-Phenyl-9-phenanthryl)-4-phenylbut-1-en-3-yne. By bromination of the previous compound with *N*-bromosuccinimide, 9-bromomethyl-1-phenylphenanthrene was obtained in 70% yield. The bromide, mp 140.5–141.5° from tetra, was converted into its triphenylphosphonium salt (mp 257–261°) by treatment with triphenylphosphine in boiling xylene. To a solution of equivalent amounts of the salt and of phenylpropargylaldehyde in DMF an excess of sodium methoxide was added. After several hours, when the red color had disappeared, the solvent was evaporated and water added. After extracting with benzene, washing the organic layer with water, and drying over magnesium sulfate the mixture of *cis* and *trans* isomers was obtained by column chromatography on silica (yield 83%). The *trans* isomer was isolated in pure form as described in a foregoing preparation: mp 120–124°; *m/e* 380; uv_{max} (CH₃OH) 222.5 (log ϵ 4.64), [250 (4.50)], 260 (4.57), 286 (4.58), 341 nm (4.43); nmr (CS₂, TMS) δ 6.08 and 6.24 (part of an AB pattern, J_{AB} = 15.9 Hz), 7.14–7.72 (m, 10 H), 7.43 (s, 5 H, C₆H₅), 7.88 (s, 1 H), 8.08 (m, 1 H α), 8.56 (m, 1 H- α_3), 8.64 (m, 1 H- α_3).

4,5-Diphenyltriphenylene (I). A 3.7 \times 10⁻⁴ M solution of the previous butenyne in dry oxygen-free benzene was irradiated for 1.5 hr at 360 nm. After concentration of the solution the reaction mixture was chromatographed on Al₂O₃, and I was eluted with CCl₄. The product was crystallized from methanol (yield 60%) and had mp 150–152°; *m/e* 380 (100%, M⁺), 379 (29%, M⁺ - 1), 303 (53%, M⁺ - C₆H₅), 302 (78%), 190 (6%); uv_{max} (CH₃OH) [225 (log ϵ 4.56)], [260 (4.69)], 267 (4.76), 287 nm (4.60); nmr (CS₂, TMS) δ 6.40 (d, 4 H), 6.85 (t, 4 H), 6.91 (m, 2 H), 6.95 (d, 2 H), 7.44 (t, 2 H), 7.51 (q, 2 H), 8.34 (d, 2 H- α_3), 8.43 (q, 2 H- α_3).

9-Allyl-10-phenylphenanthrene (XI). Starting from 9-benzoylfluorene,¹⁹ (9-allyl-9-fluorenyl)benzyl alcohol (X) was synthesized in an overall yield of 40% as described by Bavin:¹¹ mp 130–132° from hexane (lit.¹¹ 132–134°); nmr (CS₂, TMS) δ 1.90 (s, OH), 2.95 (d, 2 H, CH₂), 4.51–4.72 (m, 1 H, vinyl), 4.80–5.34 (m, 2 H, vinyl), 4.92 (s, CH), 6.46–6.94 (m, 5 H), 7.02–7.60 (m, 8 H). To a solution of 4.4 g of X in 60 ml of xylene 8.0 g of P₂O₅ were added under vigorous stirring, and the mixture was refluxed for 16 hr. Water was then added, the layers were separated, and the water layer was extracted with benzene. The combined organic layers were washed with water until neutral and dried over magnesium sulfate. According to nmr analysis the crude product obtained after evaporation of the solvents contained 82% of XI, 13% of XIII, and a small amount of XII. By column chromatography on alumina and elution with pentane/benzene (20:1) XI could be separated from the side products. It crystallized from methanol as colorless needles with mp 99–101°; *m/e* 294; uv_{max} (CH₃OH) [222.5 (log ϵ 4.39)], [249 (4.70)], 255.5 (4.80), [270 (4.29)], 277 (4.15), 288 (4.05), 299.5 (4.10), 326 (2.77), 334 (2.85), 341.5 (2.72), 350 nm (2.85); nmr (CS₂, TMS) δ 3.48–3.64 (m, CH₂), 4.62–5.03 (m, 2 H, vinyl), 5.69–6.09 (m, 1 H, vinyl), 7.07–7.56 (m, 10 H), 7.98 (m, 1 H α) 8.45–8.61 (m, 2 H- α_3); ν 1645 cm⁻¹ (C=C stretch), 915 (CH₂).

trans-9-Propenyl-10-phenylphenanthrene (XII). XI (3.4 g) was refluxed for 20 hr with 100 ml of a 20% potassium hydroxide solution in 1-butanol. The solvent was evaporated and the residue added to a dilute solution of hydrochloric acid. The mixture was extracted with benzene, and the organic phase was washed with a sodium bicarbonate solution and then dried over magnesium sulfate. The resulting solution was concentrated to a small volume, and the residue was chromatographed over alumina and eluted with hexane/benzene (9:1). The product (XII) crystallized in 83% yield (2.8 g) as colorless needles from methanol: mp 163–164°; *m/e* 294; uv_{max} (CH₃OH) 212 (log ϵ 4.52), [250 (4.65)], 257 (4.72), [270 (4.38)], 301 (4.09), [332 (3.14)], 351 nm (2.69); nmr (CS₂, TMS) δ 1.72 (d, 3

H, CH₃), 5.56–6.31 (AB, 2 H, ethylene, J_{AB} = 16 Hz), 7.09–7.62 (m, 10 H), 8.17 (m, 1 H α), 8.55 (m, 2 H- α_3); ν 970 cm⁻¹ (C=C trans).

9,10-Dihydro-10-methylbenzo[g]chryse (XIII). A 10⁻³ M solution of the previous compound (XII) in deaerated hexane was irradiated in a quartz vessel under nitrogen with 300-nm lamps for 80 min. By column chromatography of the irradiation mixture on alumina, XIII was obtained as a pale-yellow oil¹¹ in nearly quantitative yield: *m/e* 294; uv_{max} (CH₃OH) 258, [267], [276], 306, 317, and 331 nm; nmr (CS₂, TMS) δ 1.25 (d, 3 H, CH₃), 2.53–3.22 (m, 3 H), 7.05–7.50 (m, 7 H), 7.58–7.74 (m, 1 H), 7.80–8.00 (m, 1 H), 8.31–8.58 (m, 3 H).

10-Methylbenzo[g]chryse (XIV). Equivalent amounts of XIII and dicyanodichloroquinone were refluxed in benzene for 72 hr. The reaction mixture was passed through a column of silica gel. After evaporation of the solvent the remaining product was crystallized from methanol: yield 76%; mp 119–121° (lit.¹¹ 115–116°, and lit.²⁰ 150–151°); *m/e* 292; uv_{max} (CH₃OH) 210.5 (log ϵ 4.58), 260 (4.65), 268 (4.69), 277 (4.82), 287.5 (4.84), 310 (4.04), 322 (4.10), 336 (4.02), [351 (3.25)], 372 nm (2.81); nmr (CS₂, TMS) δ 2.82 (s, 3 H, CH₃), 7.40–7.65 (m, 6 H), 8.01 (m, 1 H α), 8.27 (s, 1 H- α_3), 8.40–8.60 (m, 3 H- α_3), 8.67 (m, 1 H- α_4), 8.77 (m, 1 H- α_4).

10-Styrylbenzo[g]chryse (XV). The above product XIV was treated with *N*-bromosuccinimide in carbon tetrachloride giving 82% of the 10-bromomethylbenzo[g]chryse (mp 184–186°). Equivalent amounts of this compound and triphenylphosphine were refluxed for 4 hr in xylene. The triphenylphosphonium salt, thus obtained, was dissolved in ethanol and supplied with an equivalent amount of benzaldehyde and then with an excess of sodium methoxide. After concentration a mixture of *cis*- and *trans*-XV could be separated from the solution in 88% yield. The *trans* isomer was obtained in pure form by column chromatography over alumina and crystallization from methanol. It melted at 146–148°, solidified between 150 and 160°, and melted again at 172–174°; *m/e* 380; uv_{max} 253 (log ϵ 4.72), 272 (4.71), 291 (4.70), 360 nm (4.42); nmr (CS₂, TMS) δ 7.81–7.22 (AB, J_{AB} = 15.8 Hz), 7.09–7.44 (m, 3 H), 7.44–7.65 (m, 8 H), 8.23 (m, 1 H α), 8.42–8.62 (m, 4 H- α_3), 8.66 (m, 1 H- α_4), 8.78 (m, 1 H- α_4).

Tribenzo[*c,g,p*]chryse (XVI). A 4 \times 10⁻⁴ M solution of XV in deaerated benzene was irradiated for 10 hr at 360 nm in the presence of 2 equiv of iodine. By column chromatography on alumina, elution with pentane/benzene (8:1), and crystallization from ethanol, XVI was obtained in 52% yield; mp 226–230°; *m/e* 378; uv_{max} (CH₃OH) [215 (log ϵ 4.66)], 233 (4.61), 255 (4.86), [265 (4.71)], [278 (4.61)], 295.5 (4.56), 303.5 (4.60), 320 (4.55), 347 (4.25), 360 (4.21), [384 (3.35)], 406 nm (3.01); nmr (CS₂, TMS) δ 7.04 (t, 1 H), 7.11 (t, 1 H), 7.31 (t, 1 H), 7.39 (t, 1 H), 7.44–7.66 (m, 4 H), 7.78 (d, 1 H α), 7.87 (d, 1 H- α_3), 7.90 (d, 1 H α), 8.10 (d, 1 H- α_3), 8.38 (m, 1 H- α_3), 8.47–8.75 (m, 5 H).

Irradiation of 4,5-Diphenyltriphenylene (I). A solution of 114 mg of I and 152 mg of iodine in 3 l. of benzene was irradiated in a Rayonet reactor for 6.5 hr at 300 nm. After evaporation of most of the solvent the residue was separated by column chromatography on alumina and elution with pentane (500 ml) and benzene-pentane mixtures with increasing solvent ratio. Subsequently, the starting compound (5%) and the compounds IIIa, VI, and IV could be isolated.

1-Phenyldibenzo[*e,l*]pyrene (IIIa): yield 33%; mp 275–278°; *m/e* 378; uv_{max} (C₆H₆) 283 (log ϵ 4.78), 296 (4.72), 331 nm (4.27); nmr (CS₂, HMDS) δ 7.66 (t, 1 H), 7.92–8.10 (m, 5 H, C₆H₅), 8.04 (t, 1 H), 8.29 (q, 2 H), 8.40 (d, 1 H), 8.45 (d, 1 H- α_3), 8.58 (t, 1 H), 9.15 (m, 1 H- α_3), 9.20–9.43 (m, 5 H- α_3).

Benzo[*e*]naphtho[1,2,3,4-*ghi*]perylene (VI): yield 29%; mp 256–258° (xylene) (lit.¹⁰ 243–244°); *m/e* 376; uv_{max} (C₆H₆) [285 (log ϵ 4.57)], 295 (4.73), 306 (4.77), 312.5 (4.69), 328 (4.65), 357 (3.67), 374 (4.02), 394 (4.32), 416 nm (4.42); nmr (CS₂, TMS) δ 7.82–8.47 (m, 8 H), 8.86–9.36 (m, 8 H).

The same product could be obtained from tribenzo[*c,g,p*]chryse. For that purpose a solution of 400 mg of XVI in carbon disulfide was added to a mixture of 750 mg of aluminum chloride and 150 mg of sodium chloride. After evaporation of the solvent the mixture was heated for 30 min at 120° and then treated with water and diluted hydrochloric acid to destroy the excess of aluminum chloride. The residue was extracted with benzene and the extract dried over magnesium sulfate. The product was purified by passing over a column of alumina, elution with benzene, and sublimation at 240° (1 mm), followed by crystallization from xylene. The product

(19) W. Wislicenus and A. Fehrlé, *Chem. Ber.*, **48**, 1321 (1915).

(20) C. K. Bradsher and H. Rapoport, *J. Amer. Chem. Soc.*, **66**, 1281 (1944).

melted at 256–258° and showed the same spectroscopic data as given above.

Tribenzo[*e,ghi,k*]perylene (IV): yield 6%; mp 385°; identical in all properties with a sample, previously obtained from bis(9-phenanthryl)ethylene.⁶ IV was also obtained as the sole product by irradiation of IIIa in benzene with added iodine with a high-pressure mercury lamp.

1-(1-Phenyl-7-naphthyl)-4-phenylbut-1-en-3-yne. 7-Methyl-1-phenyl-naphthalene, prepared according to Bonnier and Rinaudo,²¹ was brominated with an equivalent amount of *N*-bromosuccinimide, and the resulting bromomethyl derivative without purification was converted into its triphenylphosphonium salt (mp 278–281°) by treatment with triphenylphosphine in boiling xylene. A Wittig synthesis with the salt and phenylpropargylaldehyde in methanol as solvent and with sodium methoxide as base delivered the desired diarylbutenyne. The pure *trans* isomer was isolated as described in similar, foregoing preparations: mp 133.5–135°; *m/e* 330; uv_{max} [220 (log ϵ 4.43)], 238.5 (4.43), [259 (4.38)], 282.5 (4.60), [287.5 (4.60)], 292 (4.61), 332.5 (4.61), [348 nm (4.49)]; nmr (CS₂, TMS) δ 6.25 and 6.92 (AB, J_{AB} = 16 Hz), 7.12–7.34 (m, 7 H), 7.35 (s, 5 H, C₆H₅), 7.47 (d, 1 H), 7.60–7.78 (m, 3 H _{α}).

4,5-Diphenylphenanthrene (II). A solution of the previous butenyne derivative in hexane was irradiated under similar conditions as used in the preparation of I: yield 65%; mp 169–171° (CH₃-OH); *m/e* 330 (100%, M⁺), 329 (88%, M⁺ - 1), 253 (98%, M⁺ - C₆H₅), 252 (100%); uv_{max} (CH₃OH) 230 (log ϵ 4.78), 282 (4.47), 292 (4.46), [310 (4.21)], 355 (2.82), 372 nm (2.72); nmr (CS₂, TMS) δ 6.46 (d, 4 H), 6.84 (t, 4 H), 6.91 (m, 2 H), 6.99 (d, 2 H), 7.39 (t, 2 H), 7.56 (s, 2 H), 7.63 (d, 2 H).

Irradiation of 4,5-diphenylphenanthrene (II) was done under similar conditions as used in the irradiation of I. After concentration of the solution the reaction mixture was separated by column chromatography over alumina. With pentane/benzene (9:1) 12% of the starting compound was eluted as the first fraction. In one experiment a second fraction could be eluted with pentane/benzene (6:1). However, this fraction appeared not to be homogeneous. Its nmr spectrum showed peaks at δ 6.34 and 6.43 (allylic protons?) and a narrow intense multiplet at 6.78 but also signals of 1-phenylbenzo[*e*]pyrene (XVIIa). Elution with pentane/benzene (3:1) yielded 40% of XVIIa in pure form as a third fraction. Finally, dibenzo[*e,ghi*]perylene (XVIII) was eluted in 6% yield with pentane/benzene (1:3). The physical constants of the products isolated follow.

1-Phenylbenzo[*e*]pyrene (XVIIa): mp 189–192° (CH₃OH); *m/e* 328; uv_{max} (CH₃OH) [222 (log ϵ 4.66)], 247 (4.41), 269 (4.49), 280 (4.49), [288 (4.45)], [328 (4.27)], 336.5 nm (4.35); nmr (CS₂, TMS) δ 7.00 (t, 1 H), 7.27–7.42 (m, 5 H, C₆H₅), 7.40 (t, 1 H), 7.81 (d, 1 H), 7.88 (t, 1 H), 7.90 (s, 2 H), 7.75 and 8.02 (AB, J_{AB} = 7.8 Hz), 8.04 (d, 1 H), 8.58 (m, 1 H- α_3), 8.69 (m, 1 H- α_3).

Dibenzo[*e,ghi*]perylene (XVIII): mp 301–303° from benzene

(21) J. M. Bonnier and J. Rinaudo, *Bull. Soc. Chim. Fr.*, **37**, 146 (1970).

(22) Reference 9, p 63. The difference in melting point is most probably due to the differences in melting point determination. Clar used an evacuated tube; we used a melting point microscope.

(lit.²² 288°); *m/e* 326; uv_{max} (C₆H₆) 284.5 (log ϵ 4.54), 296.5 (4.72), 309 (4.84), 328 (3.87), 343 (4.14), 357.5 (4.38), 376 (4.51), 392 (3.39), 404 nm (3.17). The same product was obtained in 85% yield by irradiation of a solution of XVIIa in benzene with a high-pressure lamp and in the presence of iodine. The isolation of XVIII from a reaction mixture obtained by irradiation of XIX is described below.

1-(β -Naphthyl)-2-(9-phenanthryl)ethylene (XIX). Bromination of 9-methylphenanthrene, obtained according to Russel and Weiner²³ with *N*-bromosuccinimide in carbon tetrachloride, gave the 9-bromomethylphenanthrene²⁴ (mp 114–116°) which was converted into its triphenylphosphonium salt (mp 286–291°). The Wittig synthesis from the salt and β -naphthaldehyde with sodium methoxide in DMF yielded a mixture of *cis*- and *trans*-XIX (37%). The mixture was treated with iodine in carbon tetrachloride, to isomerize the *cis* compound, and then passed over a column of silica gel. *trans*-XIX was eluted with benzene/pentane (1:9) and crystallized from CH₂Cl₂/methanol: mp 149–151°; *m/e* 330; uv_{max} (CH₂Cl₂) 260 (log ϵ 4.67), 338 nm (4.47); nmr (CS₂, TMS) δ 7.15–7.93 (m, 15 H), 8.06–8.22 (m, 1 H _{α}), 8.43–8.63 (m, 2 H- α_3).

Irradiation of 1-(β -Naphthyl)-2-(9-phenanthryl)ethylene (XIX). XIX (600 mg) and an equivalent amount of iodine were dissolved in 3 l. of benzene, and the solution was irradiated for 4 hr at 360 nm. The reaction mixture was separated by chromatography on alumina in the usual way. Elution with benzene/hexane mixtures with increasing solvent ratio gave three compounds.

Dibenzo[*c,g*]chrysene (XXI) eluted with benzene/hexane (1:8): yield 26%; mp 177–179° (ethanol); *m/e* 328; uv_{max} (CH₃OH) 227 (log ϵ 4.67), 251.5 (4.63), 260 (4.58), 279 (4.57), 298 (4.57), 308.5 (4.61), [328 (4.29)], [345 (3.76)], 372 (3.05), 393 nm (2.66); nmr (CS₂, TMS) δ 7.05 (t, 2 H), 7.31 (t, 1 H), 7.38 (t, 1 H), 7.53 (q, 2 H), 7.67 (s, 2 H), 7.73 (d, 2 H), 8.20 (d, 1 H), 8.22–8.44 (m, 4 H), 8.47 (q, 1 H).

Dibenzo[*b,g*]chrysene (XX) eluted with benzene/hexane (1:3): yield 28%; mp 213–215° (CH₂Cl₂/CH₃OH); *m/e* 328; uv_{max} (C₆H₆) 289.5 (log ϵ 4.67), 301 (4.83), 313.5 (4.95), 347.5 (3.69), 364 (3.85), 384 (4.00), 406 nm (3.91); nmr (CS₂, TMS) δ 7.43 (q, 2 H), 7.60 (q, 4 H), 7.87–8.05 (m, 3 H _{α}), 8.35 (s, 1 H- γ), 8.39 (d, 1 H- α_3), 8.46–8.70 (m, 3 H- α_3), 8.88–9.01 (m, 1 H- α_4), 9.31 (s, 1 H- γ_2).

Dibenzo[*e,ghi*]perylene (XVIII) eluted with benzene in 12% yield. Physical properties are equal to those of the sample obtained from II (see above).

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(23) G. A. Russel and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).

(24) P. Lambert and R. H. Martin, *Bull. Soc. Chim. Belg.*, **61**, 124, 129 (1952).