

# Photodehydrocyclizations in Stilbene-Like Compounds. X.<sup>1</sup> Rearrangements in the Photocyclization of 4,5-Diphenyltriphenylene and 4,5-Diphenylphenanthrene

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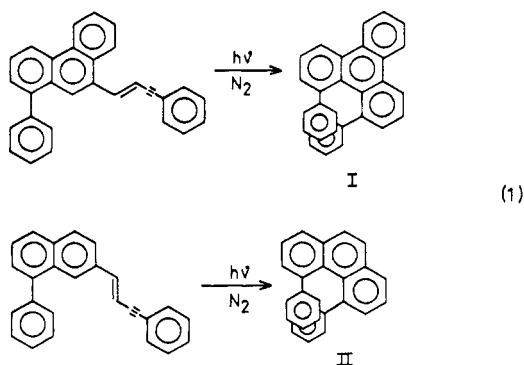
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**Abstract:** Photodehydrocyclizations of 4,5-diphenyltriphenylene (I) and 4,5-diphenylphenanthrene (II) are accompanied with a similar 1,2-phenyl shift as previously found in the photocyclization of 1-phenylpentahelicene. I gives 1-phenyldibenzo[*e,l*]pyrene (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 (XXIII) which undergoes the phenyl shift.

In the preceding paper<sup>1</sup> 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 diarylbutenyne *via* a novel photocyclization reaction<sup>2</sup> 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<sup>3a</sup> and 3,6-dihydroxy-4,5-bis(2-pyridyl)phenanthrene.<sup>3b</sup> X-Ray analysis of the 2,7-dibromo derivative of the latter compound<sup>4</sup> has revealed that the pyridyl residues are almost parallel and have a nonbonded intramolecular distance of 2.81 Å between C<sub>2</sub> of one pyridine and C<sub>2</sub>' of the other pyridine ring. The distortion of the phenanthrene moiety is evenly distributed

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<sup>+</sup> – C<sub>6</sub>H<sub>5</sub> 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 Murrell<sup>5</sup> 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 Al<sub>2</sub>O<sub>3</sub> 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 C<sub>30</sub>H<sub>18</sub> (*m/e* 378). A and C appeared to be isomers C<sub>30</sub>H<sub>16</sub> (*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,<sup>1</sup> 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

(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).

(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).

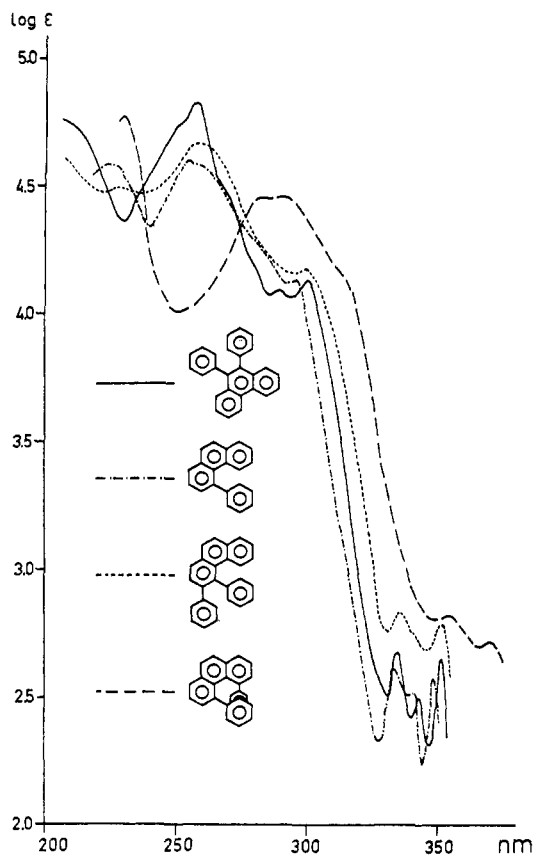
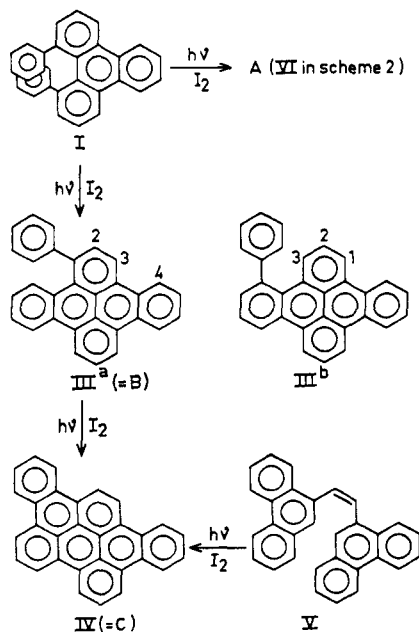


Figure 1. Uv spectra of some phenylphenanthrenes in methanol.

the melting point and uv spectrum of C with those of the irradiation product of bis(9-phenanthryl)ethylene (V) which is known<sup>6</sup> to be IV (see Scheme I).

Scheme I

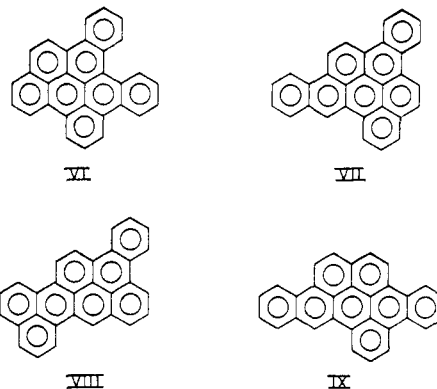


The ultimate formation of IV might also have occurred *via* 4-phenyldibenzo[*e,l*]pyrene (IIIb) which should arise if ring closure of I were accompanied with a 1,9-phenyl shift. The nmr spectrum of B points,

(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 ( $\delta$  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  $\delta$  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.<sup>7</sup> Its nmr spectrum showed only aromatic protons, present in two clearly separated multiplets of equal intensity at  $\delta$  7.82–8.47 and 8.86–9.36. The  $\delta$  value of the latter group of protons is found for  $\alpha_3$  protons<sup>8</sup> (e.g., in phenanthrene) or  $\alpha_4$  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.<sup>9</sup>



From a compound like VIII uv absorptions between 400 and 470 nm may be expected.<sup>7</sup> Therefore, this structure could also be rejected. Clar<sup>10</sup> 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 Bavin<sup>11</sup> 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.

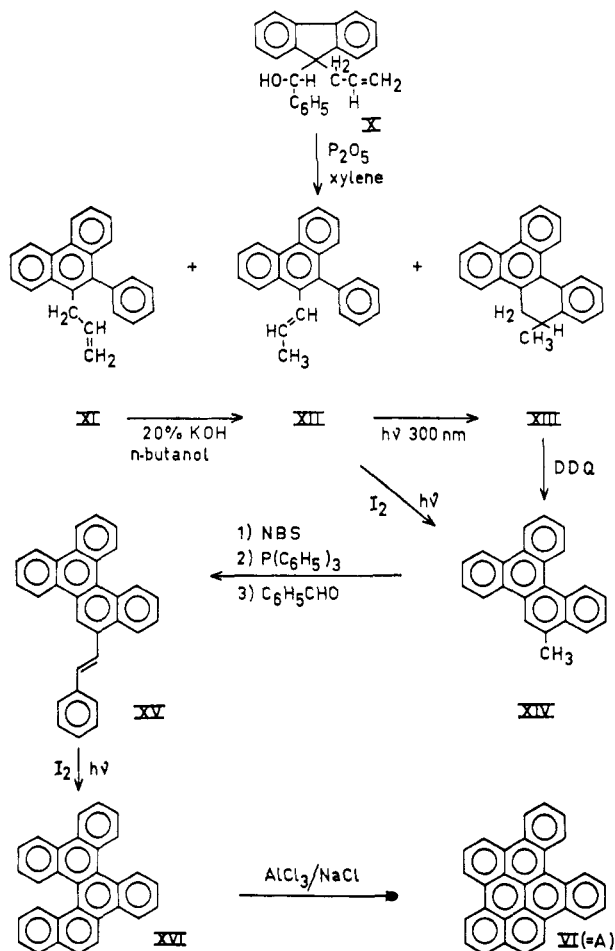
(8) The symbols  $H-\alpha_3$ ,  $H-\alpha_4$ ,  $H_7$ , etc., are used to differentiate the several aromatic protons to their specific positions as was done first by R. H. Martin, *Tetrahedron*, **20**, 897 (1964).

(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.<sup>12</sup> 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 penta-helicene, XVI appeared to be stable on irradiation.<sup>13</sup> 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.

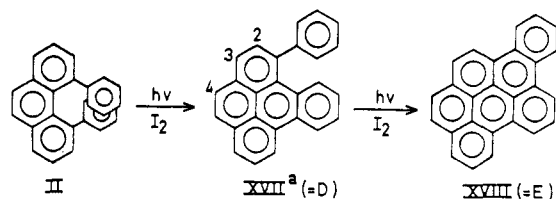
**Irradiation of 4,5-Diphenylphenanthrene (II).** In the hope to get insight into the nature of the new type of rearrangement occurring in the formation of VI from I, 4,5-diphenylphenanthrene (II) was irradiated under similar conditions as used in the irradiation experiments

(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 demonstrated<sup>6</sup> 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 penta-helicene derivatives. In a series of five penta-helicene compounds which do all photocyclize the range of  $\Sigma F^*$  is 0.899–0.984; e.g., for dibenzo[*c,g*]phenanthrene (XXI) and dibenzo[*f,j*]picene the  $\Sigma F^*$  values are 0.911 and 0.899. However, tribenzo[*c,g,p*]chrysene (XVI) is photo-stable ( $\Sigma F^* = 0.901$ ). This fact had to be explained by other reasons than these  $\Sigma F^*$  values.

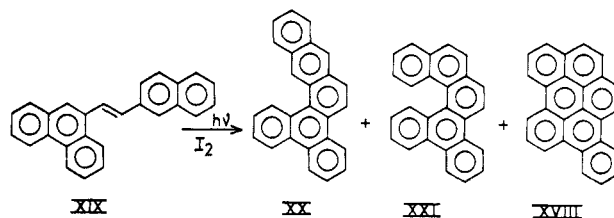
with I. Also in this case a rather complex reaction mixture was obtained when iodine was present. A similar irradiation in hexane without added iodine did not lead to substantial photoconversion. Even with longer reaction times, the starting compound could be recovered for the larger part. The reaction 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  $C_{26}H_{14}$  ( $m/e$  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*]pyrene (XVIIa) and dibenzo[*e,ghi*]perylene (XVIII), respectively (Scheme III). The uv spec-

Scheme III

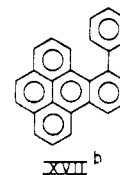


trum of E showed indeed absorptions characteristic for perylene derivatives. Furthermore, the compound appeared to be identical with that photoproduct from 1-( $\beta$ -naphthyl)-2-(9-phenanthryl)ethylene (XIX) which has the same molecular weight as E (Scheme IV). A

Scheme IV



structural formula XVII<sup>b</sup> for D, isomeric with XVII<sup>a</sup>, 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 XVII<sup>a</sup>. The other signals, two one-



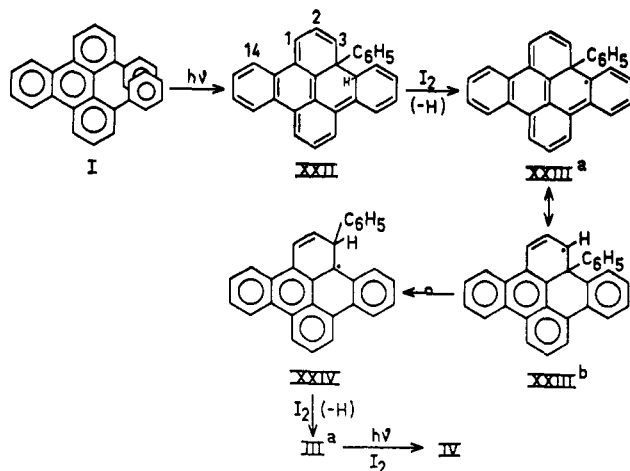
proton multiplets at 8.58 and 8.69 ( $H_8$  and  $H_9$ , respectively), an AB pattern between 7.75 and 8.02 with  $J_{AB} = 7.8$  Hz ( $H_2$  and  $H_3$ ), and a nearly collapsed AB pattern at 7.90 ( $H_4$  and  $H_5$ ) are consistent with this structure.

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.

## Discussion

In part IX of this series<sup>1</sup> it has been shown that photo-dehydrocyclizations in compounds with a phenyl substituent at a carbon atom involved in the ring closure are accompanied by a 1,2 shift of the phenyl group. It was argued that the rearrangement occurs in a radical formed by hydrogen abstraction from the primarily formed cyclization product. Applied to I the formation of the photoproducts IIIa and IV can be described as in Scheme V, and by leaving out the aromatic ring on the

Scheme V



left-hand side of all formulas a similar scheme arises for the conversion of II into XVIIa and XVIII.

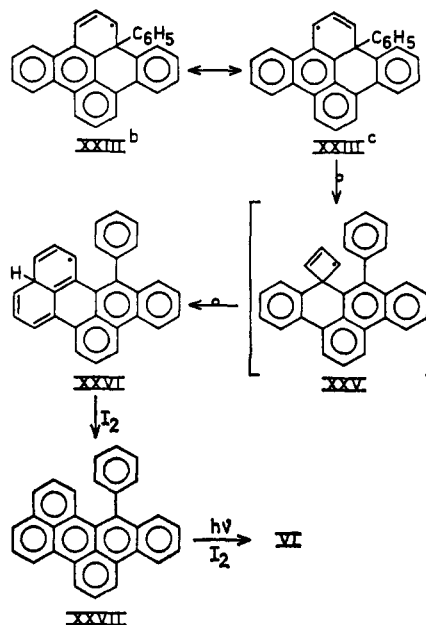
A possible explanation for the formation of the third photoproduct (VI) from I might be that in some way in XXII or XXIII the C<sub>3</sub>-C<sub>3a</sub> bond is broken and a C<sub>3</sub>-C<sub>14</sub> bond is formed. Such a rearrangement should more probably be in the radical XXIII than in XXII because, like IV, VI only arises on irradiation if iodine is present.<sup>14</sup> As a matter of fact, the suggestion given implies that the crowding at C<sub>3a</sub> in the radical XXIII may be relieved in two parallel ways: by removal of the phenyl group as presented in Scheme V, or by removal of C<sub>3</sub> as depicted in Scheme VI. Remarkably enough the yields of both IV and VI are about equal (30%).

The conversion of XXIII into XXVI in the latter scheme may be described as a sigmatropic shift of the allyl radical group. It leads to a radical which has a stability comparable with XXIV. Hydrogen abstraction by iodine should lead to 14-phenylbenzo[*e*]perylene (XXVII). The latter compound could not be detected in the irradiation mixture of I, but this is not uncommon for the first cyclization product from a compound which can undergo two subsequent cyclizations.<sup>1,15</sup>

The proposed reaction is a sigmatropic rearrangement in a radical. As far as we know no examples of this kind of reaction have been described before. The suggested scheme left undetermined whether the sigmatropic reaction is a true 1,5 shift or a sequence of subsequent shifts *via* intermediates like XXV.

It may be pointed out that this type of rearrangement should not lead to a polycyclic aromatic compound in the photocyclization of II; an intermediate radical

Scheme VI



comparable to XXVI cannot be formed in that case. The occurrence of a relatively large amount of tarry products and the presence of side products (F) probably containing an allylic residue in the reaction mixture obtained from II might indicate that also in that case an intermediate radical like XXIII does not only rearrange as given in Scheme V.

## Experimental Section

Spectrometric measurements were made with a Varian MAT SM2B mass spectrometer, a Cary 15 or a Beckman DK2A uv spectrophotometer, a Perkin-Elmer 257 ir apparatus, and a Varian HA-100 or XL100 nmr instrument. Melting points were measured on a Leitz melting point microscope and are uncorrected.

Irradiations were carried out in a cooled quartz tube surrounding a Philips HPK 125 mercury lamp, in a Rayonet reactor fitted with 300- or 360-nm lamps, or in quartz or Pyrex tubes of 1000 ml surrounded by four Sylvania blacklite F8T5 lamps. To reduce the formation of oxidation products during irradiation, the solutions were boiled previously and cooled in a stream of nitrogen.

Uv data between brackets concern inflections in the spectral curves. The symbols (d), (t), etc., used in the reproduction of nmr data do not always mean first-order doublets, triplets, etc., but concern sometimes clearly separated doublets or triplets of multiplets. In most cases the interpretation of nmr spectra has been done by decoupling and tickling and by comparison with spectra of known compounds.

**1-(4-Methyl-1-naphthyl)-4-phenylbut-1-en-3-yne.** 1-Bromo-methyl-4-methylnaphthalene, prepared by bromomethylation of 1-methylnaphthalene,<sup>16</sup> was converted into its triphenylphosphonium salt by treatment with triphenylphosphine in boiling xylene (mp 238–241°). To a solution of 9.94 g of the salt and 2.60 g of phenylpropargylaldehyde<sup>17,18</sup> in 100 ml of methanol 1.62 g of sodium methoxide was added in small portions. After 16 hr a *cis-trans* isomer mixture of the wanted product was filtered from the solution. Another batch was obtained by column chromatography of the filtrate on silica (over-all yield 80%). The isomers were obtained in pure form by column chromatography of the isomer mixture on Al<sub>2</sub>O<sub>3</sub> and crystallization from methanol. *Cis*: mp 106–107.5; *m/e* 268; *uv*<sub>max</sub> (CH<sub>3</sub>OH) 233 (log  $\epsilon$  4.54), 273 (4.23), 282.5 (4.30), 335 nm (4.21); nmr (CS<sub>2</sub>, TMS)  $\delta$  2.64 (s, 3 H, CH<sub>3</sub>), 5.99 and 7.28 (AB, ethylene, *J*<sub>AB</sub> = 11.8 Hz), 7.07–7.49 (m, 8 H), 7.89 (m, 1 H<sub>a</sub>), 7.95 (m, 1 H<sub>a</sub>), 8.11 (d, 1 H<sub>g</sub>). *Trans*: mp 115–116.5; *m/e* 268; *uv*<sub>max</sub> (CH<sub>3</sub>OH) 236 (log  $\epsilon$  4.55), [275 (4.25)], 282.5 (4.28),

(14) Irradiation of I (concn 10<sup>-2</sup>, iodine 5 × 10<sup>-3</sup> M) in the cavity of an esr instrument (Varian V4500) with a Philips SW500 high-pressure mercury lamp for 2 hr did not lead to a detectable amount of radicals. However, in the reaction mixture the presence of the photoproducts could be detected by uv spectroscopy.

(15) T. Sato and T. J. Morita, *Bull. Chem. Soc. Jap.*, **45**, 1548 (1972).

(16) G. Lock and R. Schneider, *Chem. Ber.*, **91**, 1770 (1958).

(17) B. W. Howk and J. C. Sauer, *J. Amer. Chem. Soc.*, **80**, 4607 (1958).

(18) C. F. H. Allen and C. O. Edens, Jr., "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1965, p 731.

336 nm (4.49); nmr ( $\text{CS}_2$ , TMS)  $\delta$  2.65 (s, 3 H  $\text{CH}_3$ ), 6.28 and 7.66 (AB, ethylene,  $J_{AB}$  = 15.9 Hz), 7.11–7.53 (m, 9 H), 7.87 (m, 1  $\text{H}_\alpha$ ), 8.02 (m, 1  $\text{H}_\alpha$ ).

**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  $\text{Al}_2\text{O}_3$ . 9-Methyl-1-phenylphenanthrene was eluted with benzene/hexane (1:9) and crystallized from methanol: yield 54%; mp 96–98°;  $m/e$  268;  $uv_{\max}$  ( $\text{CH}_3\text{OH}$ ) [220 (log  $\epsilon$  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 ( $\text{CS}_2$ , TMS)  $\delta$  2.57 (s, 3 H  $\text{CH}_3$ ), 7.36 (s, 5 H,  $\text{C}_6\text{H}_5$ ), 7.26–7.62 (m, 5 H), 7.89 (m, 1  $\text{H}_\alpha$ ), 8.52 (m, 1  $\text{H}-\alpha_3$ ), 8.59 (m, 1  $\text{H}-\alpha_3$ ).

**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;  $uv_{\max}$  ( $\text{CH}_3\text{OH}$ ) 222.5 (log  $\epsilon$  4.64), [250 (4.50)], 260 (4.57), 286 (4.58), 341 nm (4.43); nmr ( $\text{CS}_2$ , TMS)  $\delta$  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,  $\text{C}_6\text{H}_5$ ), 7.88 (s, 1 H), 8.08 (m, 1  $\text{H}_\alpha$ ), 8.56 (m, 1  $\text{H}-\alpha_3$ ), 8.64 (m, 1  $\text{H}-\alpha_3$ ).

**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  $\text{Al}_2\text{O}_3$ , and I was eluted with  $\text{CCl}_4$ . The product was crystallized from methanol (yield 60%) and had mp 150–152°;  $m/e$  380 (100%,  $\text{M}^+$ ), 379 (29%,  $\text{M}^+ - 1$ ), 303 (53%,  $\text{M}^+ - \text{C}_6\text{H}_5$ ), 302 (78%), 190 (6%);  $uv_{\max}$  ( $\text{CH}_3\text{OH}$ ) [225 (log  $\epsilon$  4.56)], [260 (4.69)], 267 (4.76), 287 nm (4.60); nmr ( $\text{CS}_2$ , TMS)  $\delta$  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  $\text{H}-\alpha_3$ ), 8.43 (q, 2  $\text{H}-\alpha_3$ ).

**9-Allyl-10-phenylphenanthrene (XI).** Starting from 9-benzoylfluorene,<sup>19</sup> (9-allyl-9-fluorenyl)benzyl alcohol (X) was synthesized in an overall yield of 40% as described by Bavin:<sup>11</sup> mp 130–132° from hexane (lit.<sup>11</sup> 132–134°); nmr ( $\text{CS}_2$ , TMS)  $\delta$  1.90 (s, OH), 2.95 (d, 2 H,  $\text{CH}_2$ ), 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  $\text{P}_2\text{O}_5$  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;  $uv_{\max}$  ( $\text{CH}_3\text{OH}$ ) [222.5 (log  $\epsilon$  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 ( $\text{CS}_2$ , TMS)  $\delta$  3.48–3.64 (m,  $\text{CH}_2$ ), 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  $\text{H}_\alpha$ ), 8.45–8.61 (m, 2  $\text{H}-\alpha_3$ ); ir 1645  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$  stretch), 915 ( $\text{CH}_2$ ).

***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;  $uv_{\max}$  ( $\text{CH}_3\text{OH}$ ) 212 (log  $\epsilon$  4.52), [250 (4.65)], 257 (4.72), [270 (4.38)], 301 (4.09), [332 (3.14)], 351 nm (2.69); nmr ( $\text{CS}_2$ , TMS)  $\delta$  1.72 (d, 3

H,  $\text{CH}_3$ ), 5.56–6.31 (AB, 2 H, ethylene,  $J_{AB}$  = 16 Hz), 7.09–7.62 (m, 10 H), 8.17 (m, 1  $\text{H}_\alpha$ ), 8.55 (m, 2  $\text{H}-\alpha_3$ ); ir 970  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$  trans).

**9,10-Dihydro-10-methylbenzo[*g*]chrysene (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 oil<sup>11</sup> in nearly quantitative yield:  $m/e$  294;  $uv_{\max}$  ( $\text{CH}_3\text{OH}$ ) 258, [267], [276], 306, 317, and 331 nm; nmr ( $\text{CS}_2$ , TMS)  $\delta$  1.25 (d, 3 H,  $\text{CH}_3$ ), 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*]chrysene (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.<sup>11</sup> 115–116°, and lit.<sup>20</sup> 150–151°);  $m/e$  292;  $uv_{\max}$  ( $\text{CH}_3\text{OH}$ ) 210.5 (log  $\epsilon$  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 ( $\text{CS}_2$ , TMS)  $\delta$  2.82 (s, 3 H,  $\text{CH}_3$ ), 7.40–7.65 (m, 6 H), 8.01 (m, 1  $\text{H}_\alpha$ ), 8.27 (s, 1  $\text{H}-\alpha_3$ ), 8.40–8.60 (m, 3  $\text{H}-\alpha_3$ ), 8.67 (m, 1  $\text{H}-\alpha_3$ ), 8.77 (m, 1  $\text{H}-\alpha_3$ ).

**10-Styrylbenzo[*g*]chrysene (XV).** The above product XIV was treated with *N*-bromosuccinimide in carbon tetrachloride giving 82% of the 10-bromomethylbenzo[*g*]chrysene (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  $\epsilon$  4.72), 272 (4.71), 291 (4.70), 360 nm (4.42); nmr ( $\text{CS}_2$ , TMS)  $\delta$  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  $\text{H}_\alpha$ ), 8.42–8.62 (m, 4  $\text{H}-\alpha_3$ ), 8.66 (m, 1  $\text{H}-\alpha_3$ ), 8.78 (m, 1  $\text{H}-\alpha_3$ ).

**Tribenzo[*c,g,p*]chrysene (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;  $uv_{\max}$  ( $\text{CH}_3\text{OH}$ ) [215 (log  $\epsilon$  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 ( $\text{CS}_2$ , TMS)  $\delta$  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  $\text{H}_\alpha$ ), 7.87 (d, 1  $\text{H}-\alpha_3$ ), 7.90 (d, 1  $\text{H}_\alpha$ ), 8.10 (d, 1  $\text{H}-\alpha_3$ ), 8.38 (m, 1  $\text{H}-\alpha_3$ ), 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;  $uv_{\max}$  ( $\text{C}_6\text{H}_6$ ) 283 (log  $\epsilon$  4.78), 296 (4.72), 331 nm (4.27); nmr ( $\text{CS}_2$ , HMDS)  $\delta$  7.66 (t, 1 H), 7.92–8.10 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 8.04 (t, 1 H), 8.29 (q, 2 H), 8.40 (d, 1 H), 8.45 (d, 1  $\text{H}-\alpha_3$ ), 8.58 (t, 1 H), 9.15 (m, 1  $\text{H}-\alpha_3$ ), 9.20–9.43 (m, 5  $\text{H}-\alpha_3$ ).

**Benzo[*e*]naphtho[1,2,3,4-*ghi*]perylene (VI):** yield 29%; mp 256–258° (xylene) (lit.<sup>10</sup> 243–244°);  $m/e$  376;  $uv_{\max}$  ( $\text{C}_6\text{H}_6$ ) [285 (log  $\epsilon$  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 ( $\text{CS}_2$ , TMS)  $\delta$  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*]chrysene. 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

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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.<sup>6</sup> 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-phenylnaphthalene, prepared according to Bonnier and Rinaudo,<sup>21</sup> 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;  $u_{\nu_{\max}}$  [220 (log  $\epsilon$  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 (CS<sub>2</sub>, TMS)  $\delta$  6.25 and 6.92 (AB,  $J_{AB}$  = 16 Hz), 7.12–7.34 (m, 7 H), 7.35 (s, 5 H, C<sub>6</sub>H<sub>5</sub>), 7.47 (d, 1 H), 7.60–7.78 (m, 3 H <sub>$\alpha$</sub> ).

**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° (CH<sub>3</sub>OH); *m/e* 330 (100%, M<sup>+</sup>), 329 (88%, M<sup>+</sup> – 1), 253 (98%, M<sup>+</sup> – C<sub>6</sub>H<sub>5</sub>), 252 (100%);  $u_{\nu_{\max}}$  (CH<sub>3</sub>OH) 230 (log  $\epsilon$  4.78), 282 (4.47), 292 (4.46), [310 (4.21)], 355 (2.82), 372 nm (2.72); nmr (CS<sub>2</sub>, TMS)  $\delta$  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  $\delta$  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° (CH<sub>3</sub>OH); *m/e* 328;  $u_{\nu_{\max}}$  (CH<sub>3</sub>OH) [222 (log  $\epsilon$  4.66)], 247 (4.41), 269 (4.49), 280 (4.49), [288 (4.45)], [328 (4.27)], 336.5 nm (4.35); nmr (CS<sub>2</sub>, TMS)  $\delta$  7.00 (t, 1 H), 7.27–7.42 (m, 5 H, C<sub>6</sub>H<sub>5</sub>), 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- $\alpha_3$ ), 8.69 (m, 1 H- $\alpha_5$ ).

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

(lit.<sup>22</sup> 288°); *m/e* 326;  $u_{\nu_{\max}}$  (C<sub>6</sub>H<sub>6</sub>) 284.5 (log  $\epsilon$  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-( $\beta$ -Naphthyl)-2-(9-phenanthryl)ethylene (XIX).** Bromination of 9-methylphenanthrene, obtained according to Russel and Weiner<sup>23</sup> with *N*-bromosuccinimide in carbon tetrachloride, gave the 9-bromomethylphenanthrene<sup>24</sup> (mp 114–116°) which was converted into its triphenylphosphonium salt (mp 286–291°). The Wittig synthesis from the salt and  $\beta$ -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 CH<sub>2</sub>Cl<sub>2</sub>/methanol: mp 149–151°; *m/e* 330;  $u_{\nu_{\max}}$  (CH<sub>2</sub>Cl<sub>2</sub>) 260 (log  $\epsilon$  4.67), 338 nm (4.47); nmr (CS<sub>2</sub>, TMS)  $\delta$  7.15–7.93 (m, 15 H), 8.06–8.22 (m, 1 H <sub>$\alpha$</sub> ), 8.43–8.63 (m, 2 H- $\alpha_3$ ).

**Irradiation of 1-( $\beta$ -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;  $u_{\nu_{\max}}$  (CH<sub>3</sub>OH) 227 (log  $\epsilon$  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 (CS<sub>2</sub>, TMS)  $\delta$  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° (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH); *m/e* 328;  $u_{\nu_{\max}}$  (C<sub>6</sub>H<sub>6</sub>) 289.5 (log  $\epsilon$  4.67), 301 (4.83), 313.5 (4.95), 347.5 (3.69), 364 (3.85), 384 (4.00), 406 nm (3.91); nmr (CS<sub>2</sub>, TMS)  $\delta$  7.43 (q, 2 H), 7.60 (q, 4 H), 7.87–8.05 (m, 3 H <sub>$\alpha$</sub> ), 8.35 (s, 1 H <sub>$\gamma$</sub> ), 8.39 (d, 1 H- $\alpha_3$ ), 8.46–8.70 (m, 3 H- $\alpha_3$ ), 8.88–9.01 (m, 1 H- $\alpha_4$ ), 9.31 (s, 1 H- $\gamma_2$ ).

**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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