

In the case of *cis*-2-butene-1,4-diol, which is structurally disposed toward ring closure, treatment with **1** gave 84% of 2,5-dihydrofuran. The DMSO dehydration method gave only polymeric material.²⁶ Dehydration over alumina gives good yields of 2,5-dihydrofuran²⁷ but requires refluxing at elevated temperatures for extensive periods.

Treatment of 1,5-pentanediol and diethylene glycol with **1** gave 39 and 40% yields of tetrahydropyran and dioxane. Dehydration of 1,5-pentanediol by heating in DMSO at 190° for 24 hr gave a 47% yield of tetrahydropyran.²⁴ The method of Franke,²⁸ as applied by

(27) M. Strohmeyer, U. S. Patent 3,165,536 (1965), *Chem. Abstr.*, 62, 11783e, 14633f(1965).

(28) A. Franke and A. Kroupa, *Monatsh. Chem.*, 69, 167 (1936).

Traynelis, *et al.*,²⁴ involving heating the diol in 50% H₂SO₄, gave 76% tetrahydropyran. Thus, synthetically useful yields of six-membered ring cyclic ethers are available *via* the treatment of the respective diol with **1** under mild conditions.

Oxepane formation does not occur by treatment of 1,6-hexanediol with **1**. Instead, acyclic ether formation occurs quantitatively.

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Photodehydrocyclizations in Stilbene-Like Compounds. IX.¹ 1,2-Phenyl Shifts in the Cyclization of 1-Phenylpentahelicenes

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Abstract: Photodehydrocyclization of 8'-phenyldi- β -naphthylethylene (XI) gives rise to two monocyclization products, *viz.*, 10-phenylnaphtho[1,2-*a*]anthracene (XII) and 1-phenylpentahelicene (10-phenyldibenzo[*c,g*]phenanthrene) (VIII), and to 42% benzocoronene (IX). It appeared that IX is formed *via* VIII. It is shown that the first step of this reaction is the photocyclization to XXXIII. On oxidation it forms a radical XXXVII which can undergo a 1,2-phenyl radical shift. After a second oxidation step 7-phenylbenzo[*ghi*]perylene (XL) is formed which undergoes a rapid photodehydrocyclization into the benzocoronene. The more general applicability of the reaction was shown by the photocyclization of some derivatives of XI into substituted benzocoronenes.

Photodehydrocyclizations belong to the best known photoreactions and have appeared to be of great value in the synthesis of many polynuclear aromatics (*e.g.*, helicenes). Since the discovery of the photoconversion of stilbene (I) into phenanthrene (dotted line in I) this type of reaction has extensively been investigated on many stilbene-like compounds, and good insight has been gained into the reactivity of these compounds in photocyclizations.²

Meanwhile a quite similar reaction has been found in compounds in which part of the olefinic moiety in stilbene has been incorporated into an aromatic system, *viz.*, in ortho diaryl aromatics like *o*-terphenyl³ (II), appropriate aryl substituted aromatics like 4-phenylphenanthrene⁴ (III) or fully condensed aromatics like pentahelicene⁵ (IV).

(1) Part VIII: see W. H. Laarhoven and M. H. de Jong, *Recl. Trav. Chim. Pays-Bas*, 92, 651 (1973).

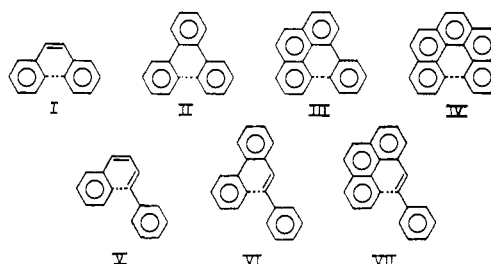
(2) For reviews, see (a) F. R. Stermitz in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, pp 247-282; (b) M. Scholz, F. Dietz, and M. Mühlstadt, *Z. Chem.*, 7, 329 (1967); (c) W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, 87, 687 (1968); (d) E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, *Chem. Soc.*, 23, 482 (1969); (e) F. B. Mallory and C. W. Mallory, *J. Amer. Chem. Soc.*, 94, 6041 (1972).

(3) (a) T. Sato, S. Shimada, and K. Hata, *Bull. Chem. Soc. Jap.*, 44, 2484 (1971), and ref cited therein; (b) R. J. Hayward, A. C. Hopkinson, and C. C. Leznoff, *Tetrahedron*, 28, 439 (1972).

(4) R. J. Hayward and C. C. Leznoff, *Tetrahedron*, 27, 2085 (1971).

(5) C. Goedicke and H. Stegemeier, *Ber. Bunsenges. Phys. Chem.*, 73, 782 (1969).

Furthermore, compounds in which one of the terminating aryl residues in I, II, or III has been replaced by an arylvinyl group (*e.g.*, styryl) as in 1,4-diphenylbutadiene⁶ (V), *o*-styrylbiphenyl⁷ (VI), and 4-styrylphenanthrene⁸ (VII) give also analogous cyclizations on irradiation.



With several ortho-substituted stilbene-like compounds it has been demonstrated that the presence of alkyl groups or halogen atoms at ring positions involved in the cyclization step does not prevent ring closure.^{9,10} Only in one case has migration of an ortho

(6) (a) G. J. Fonken, *Chem. Ind. (London)*, 1327 (1962); (b) C. C. Leznoff and R. J. Hayward, *Can. J. Chem.*, 48, 1842 (1970).

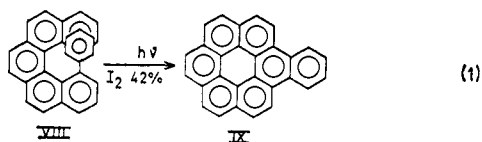
(7) W. H. Laarhoven and Th. J. H. M. Cuppen, *J. Chem. Soc., Perkin Trans. 1*, 2075 (1972).

(8) W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Tetrahedron*, 26, 1069 (1970).

(9) (a) E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. C*, 1576 (1968); 163 (1970); (b) W. Carruthers and H. N. M.

substituent been reported; irradiation of 2,4,6-trimethylazobenzene gives 1,2,4-trimethylbenzo[*c*]cinnoline though in low yield (2%).¹⁰

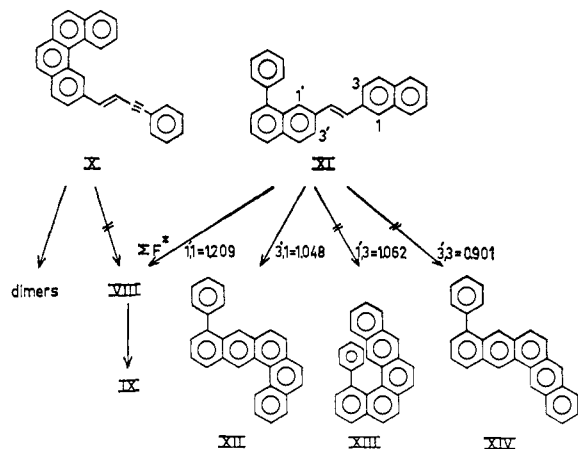
We found that the photocyclization of 1-phenylpentahelicene (10-phenyldibenzo[*c,g*]phenanthrene) (VIII) must be accompanied by migration of the phenyl group, apparently followed by a second cyclization step; benzo[*a*]coronene (IX) is the main product in this photoreaction and was obtained in 42% yield (eq 1).



Results

In investigations concerning the conformation of strongly overcrowded, polycyclic aromatics we attempted to synthesize 1-phenylpentahelicene (VIII) from 1-(2-benzo[*c*]phenanthryl)-4-phenylbut-1-en-3-yne (X) *via* the new, recently described enyne photocyclization.¹¹ However, even at concentrations as low as 10⁻⁵ mol/l. in benzene only a mixture of dimers was obtained. Therefore, we irradiated a benzenic solution of 8'-phenyldi- β -naphthylethylene (XI) because from ΣF^* values¹² it could be predicted that out of the four possible cyclization products (VIII, XII, XIII, and XIV, Scheme I) 1-phenylpentahelicene (VIII), 10-phenyl-

Scheme I



naphtho[1,2-*a*]anthracene (XII), and 1-phenylnaphtho[1,2-*a*]anthracene (XIII) should be formed in this way. Because of the steric hindrance in XIII the formation of this product was less probable.¹² Column chromatography (Al₂O₃) of the reaction mixture obtained after 4 hr of irradiation (360 nm) in the presence of 200 mol % of iodine yielded, however, three products. Two of them appeared to be monodehydrocyclization products (*m/e* 354). The one eluted first with hexane in 7% yield showed a broad, temperature-dependent absorption at high field in the nmr spectrum, fitting in with the expected 1-phenylpentahelicene (VIII); the second

Stewart, *J. Chem. Soc. C*, 556, 560 (1967); (c) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).

(10) G. M. Badger, R. J. Drewer, and G. E. Lewis, *Aust. J. Chem.*, **17**, 1037 (1964).

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

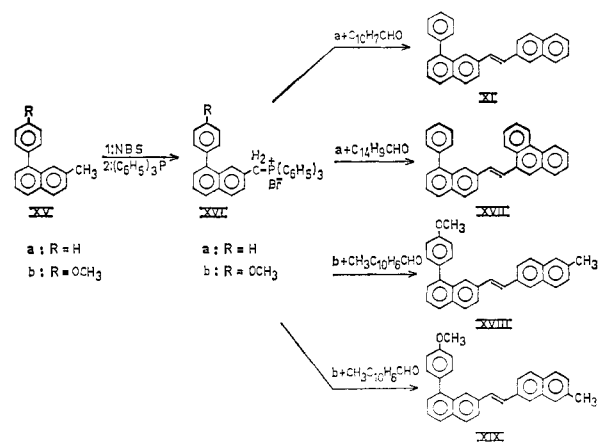
(12) W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Tetrahedron*, **26**, 4865 (1970).

one (10%) had two low-field singlets at δ 9.52 and 8.41 and a low-field multiplet at 9.18 in its nmr spectrum in CS₂. These data were anticipated for the anthracenic 9 and 10 protons and for the angular benzo[*c*]phenanthrene proton of XII, respectively, and excluded structures of the less probable cyclization products XIII and XIV.

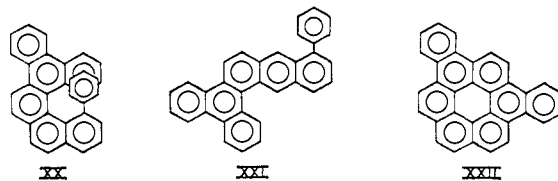
The third compound was isolated as the main product (42%). It had a parent peak at *m/e* 350 pointing to the loss of six hydrogen atoms during its formation, and peak matching confirmed that the molecular formula was C₂₈H₁₄. It could be shown that this product had arisen from VIII because irradiation of pure VIII in the presence of enough iodine yielded the same compound C₂₈H₁₄ as the only new product. (In an oxygen-free solution and without added iodine, VIII appeared to be photostable.) Uv and nmr data of the compound were quite similar to those given^{13,14} for benzocoronene (IX), but its melting point was slightly higher (310° instead of 293°). By an independent synthesis of IX from 2-phenylpentahelicene (XXVI, Scheme III), it could, however, conclusively be demonstrated that benzo[*a*]coronene was the main product in the photocyclization of VIII in the presence of an oxidant like iodine.

Several other appropriately substituted diarylethylenes (XVII, XVIII, and XIX) were then irradiated in order to establish if the remarkable rearrangement is of more general occurrence and to get insight into the mechanism of the reaction. The relevant compounds were synthesized by Wittig reactions in a similar way as applied in the preparation of XI (Scheme II).

Scheme II



Irradiation of XVII under similar conditions as used in the photocyclization of XI delivered likewise three products (XX, XXI, and XXII), corresponding to



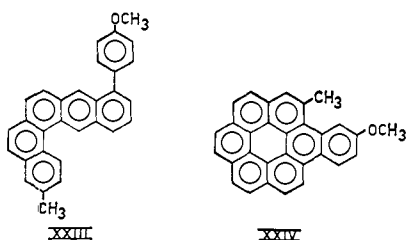
VIII, XII, and IX, in 2, 16, and 30% yields, respectively. With less iodine (50 mol %) the conversion was less

(13) E. Clar, "Polycyclic Hydrocarbons," Vol. II, Academic Press, London, 1964, p 86.

(14) E. Clar, U. Sanigök, and M. Zander, *Tetrahedron*, **24**, 2820 (1968).

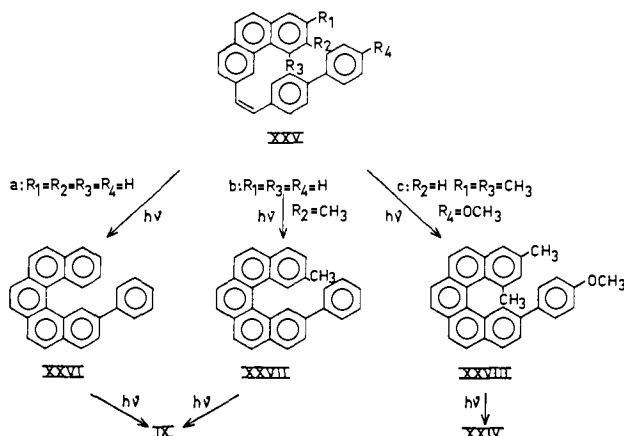
complete; an amount of XVII could be recovered and XX could not be isolated, but the ratio between XXI and XXII remained about 1 : 2.

The double-substituted derivative XVIII yielded only two products on irradiation in benzene with an excess of iodine. They appeared to be substitution products of XII and IX with structures as indicated in the formulas XXIII and XXIV, respectively; a 1-phenylpentahelicene



derivative could not be detected in the irradiation mixture of XVIII. The nmr spectrum of XXIV showed three clearly separated signals at low field in accordance with the presence of three angular phenanthrene-like protons. With the NOE technique it was not possible to determine if the only singlet among these low-field peaks belonged to a proton in the neighborhood of the methyl substituent, because none of the low-field signals increased on irradiation at the methyl frequency. The substitution pattern of XXIV could, however, unambiguously be established by an independent synthesis from XXVc as given in Scheme III.

Scheme III

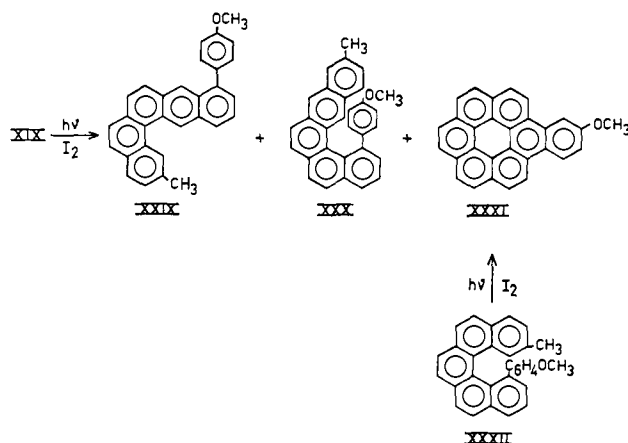


Finally, XIX yielded again three irradiation products, but none of them appeared to be comparable to VIII. The main products were the anthracene derivatives XXIX and XXX, comparable to XII and XIII in Scheme I. The structure of XXIX could easily be proven by uv and nmr spectroscopy. The nmr spectrum of the other product showed a temperature dependence comparable to that of VIII and XX which might point to a structure like XXXII. However, its uv spectrum did not show resemblance with those of VIII and XX, and its mass spectrum had a small $M - 1$ peak, which is quite unusual for compounds like XXXII. Moreover, the compound could not be converted into the benzocoronene derivative XXXI by irradiation but was easily oxidized as is commonly found with anthracenic derivatives.

The benzocoronene derivative XXXI, comparable to IX, appeared to be the third product (8%) in the irradiation mixture of XIX. It must have been formed

via XXXII as an intermediate, which itself could not be detected. The hope that the position of the methyl substituent in XIX and XXXII should have allowed the isolation of a second intermediate, involved in the formation of XXXI and indicative for the mode of rearrangement in this reaction, was not fulfilled (Scheme IV).

Scheme IV



Discussion

From our results it may be concluded that all four phenyl-substituted dinaphthylethylenes (XI, XVII, XVIII, and XIX) give two types of primary cyclization products on irradiation in the presence of iodine: an anthracenic compound (XII, XXI, XXIII, and XXIX, respectively) which in general could not be purified well because of rapid oxidation in air, and a pentahelicene derivative containing a 1-phenyl substituent (e.g., VIII and XX). According to ΣF^* values these products are the normal photodehydrocyclization products and will arise via a *trans*-dihydrophenanthrene-like intermediate as accepted in the photocyclization of stilbene.¹⁵

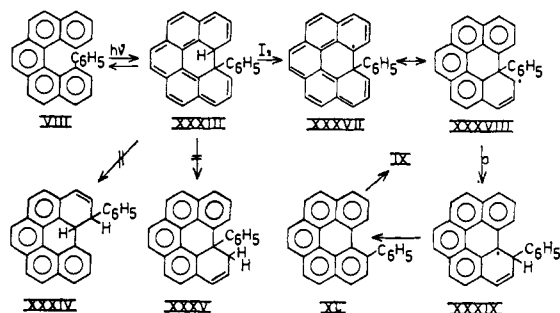
In all cases the 1-phenylpentahelicene derivative is further converted into a benzocoronene (IX, XXII, XXIV, and XXXI) which is usually the main product under the conditions used. As a matter of fact the 1-phenylpentahelicene derivative could not always be isolated. In this second photoreaction a rearrangement, a cyclization, and an oxidation are involved. So, it is very probable that it is a multistep reaction.

It may be assumed that the oxidation step takes place after the cyclization step as has been shown in the dehydrocyclization of stilbene by Fischer.¹⁶ Furthermore, it is very improbable that the rearrangement is the initial step. In that case a 2-phenylpentahelicene should have been formed as an intermediate (e.g., XXVI from VIII). However, in none of the reactions investigated could a 2-phenylpentahelicene be isolated, whereas it was shown that the photocyclization of XXVI leading to benzocoronene (IX) is not a very rapid reaction. Moreover, in none of the irradiation mixtures was the characteristic uv absorption of 2-phenylpentahelicene at 307 nm found; 1-phenylpentahelicene shows a minimum in its absorption curve at this wavelength. So, it may be assumed that the formation of IX from VIII starts with a cyclization leading to the intermediate

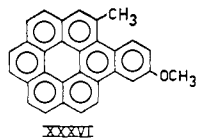
(15) (a) Th. J. H. M. Cuppen and W. H. Laarhoven, *J. Amer. Chem. Soc.*, **94**, 5914 (1972); (b) C. Goedicke and H. Stegemeier, *Chem. Phys. Lett.*, **17**, 492 (1972).

(16) T. Knittel-Wisnonsky, G. Fischer, and E. Fischer, *Tetrahedron Lett.*, 2853 (1972).

XXXIII. Surprisingly, on irradiation of VIII in a thoroughly degassed solution (eight freezing–thawing cycles at 10^{-5} mm), no coloration, indicative for the formation of XXXIII, nor any change in the uv spectrum can be observed, as is found on irradiation of stilbene and many stilbene-like compounds under such conditions. However, a solution of unsubstituted pentahelicene also does not show any coloration on irradiation in the absence of an oxidant,¹⁷ whereas dehydrocyclization into benzo[ghi]perylene occurs very rapidly if an oxidant is present.



There are no indications to suppose that the initial cyclization step is followed by a rearrangement due to a sigmatropic shift of either the phenyl group or a hydrogen atom, because in the irradiation experiments with degassed solutions products like XXXIV or XXXV could equally not be detected. A strong argument against such a supposition is that on irradiation of XVIII an intermediate corresponding to XXXIV should not lead to the benzocoronene derivative XXIV that was found but to the isomer XXXVI and that no simple way can



be suggested for the formation of benzocoronene from XXXV. So it is probable that the cyclization step is followed by an oxidation step leading to the radical XXXVII. Up to this stage the reaction pathway is quite similar to that accepted in the photodehydrocyclizations of stilbene-like compounds.

We suppose that the radical which is better represented by the more aromatic structure XXXVIII undergoes a 1,2-phenyl shift, leading to a third intermediate XXXIX. Several of such 1,2-phenyl shifts are known, in which the unpaired electron always becomes located at a tertiary carbon atom.¹⁸ In this stage (XXXIX) the oxidation can be completed by giving rise to the phenylbenzoperylene XL, from which benzocoronene can arise *via* a normal dehydrocyclization. Also this final cyclization must be a very fast reaction, apparently even when a methyl substituent is present at C_{15} in

(17) E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. C*, 163 (1970).

(18) (a) S. Winstein and F. H. Seubold, Jr., *J. Amer. Chem. Soc.*, **69**, 2916 (1947); (b) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 538 (1952); (c) J. W. Wilt and H. Philip, *J. Org. Chem.*, **24**, 441 (1959); *ibid.*, **25**, 891 (1960); (d) H. Pines and C. N. Pillai, *J. Amer. Chem. Soc.*, **82**, 2921 (1960); (e) H. Pines and C. T. Goetschel, *ibid.*, **87**, 4207 (1965); (f) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965); (g) G. W. Griffin, J. Corell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, **87**, 1410 (1965); (h) J. J. Brophy and G. W. Griffin, *Tetrahedron Lett.*, 493 (1970); (i) B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Amer. Chem. Soc.*, **93**, 2327 (1971); (j) H. E. Zimmerman and D. J. Sam, *ibid.*, **88**, 4905 (1966).

XL; following the photocyclization of 2-phenylpentahelicene (XXVI) into IX by uv, which will occur *via* the same intermediate (XL), we found five sharp isosbestic points indicating that the concentration of this intermediate during the reaction remains very low.

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 HA100 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 350-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. The symbols H_α , $H-\alpha_3$, $H-\alpha_4$, H_γ , etc., are used to differentiate the several aromatic protons to their specific positions as was first done by Martin.¹⁹ In most cases the interpretation of nmr spectra has been done by decoupling and tickling and by comparison with spectra of known compounds.

7-Methyl-1-phenylnaphthalene (XVa) was synthesized according to Bonnier and Rinaudo.²⁰ It was monobrominated with *N*-bromosuccinimide and without purification of the bromide converted into the triphenylphosphonium salt (XVIa), mp 278–281°, using boiling xylene as solvent.

7-Methyl-1-(*p*-methoxyphenyl)naphthalene (XVb). The product of the Grignard reaction of *p*-methoxyphenylmagnesium bromide and 7-methyltetralone was dehydrated with formic acid. The resulting 7-methyl-1-(*p*-methoxyphenyl)-3,4-dihydronaphthalene was dehydrogenated with 2,3-dichloro-5,6-dicyanoquinone in refluxing benzene during 2 days. Purification by column chromatography on silica gel with carbon tetrachloride as eluent gave XVb (mp 51–53°) (*m/e* 248) in 60% yield.

The triphenylphosphonium derivative (XVIb), mp 243–245°, was obtained *via* the bromomethyl derivative (mp 90–98°) as described for XVa.

8'-Phenyldi- β -naphthylethylene (XI) was obtained in 80% yield from a Wittig reaction between XVIa and β -naphthaldehyde using sodium methoxide as base and DMF as solvent; in methanol the yield is much lower (16%). The mixture of isomers was separated by column chromatography on silica with a benzene/hexane mixture as eluent. *Cis*: mp 95–105°; *m/e* 356; nmr (CS_2 , TMS) δ 6.67 (s, 2 H, ethylene), 6.76–7.82 (m, 18 H). *Trans*: mp 158–159° (from $CH_3OH/CH_3COOC_2H_5$); *m/e* 356; uv_{max} (C_2H_5OH) [215 (log ϵ 4.62)], [250 (4.44)], [258 (4.53)], [270 (4.66)], 276 (4.71), [285 (4.59)], [296 (4.49)], [323 (4.53)], 335 (4.62), [345 nm (4.54)]; nmr (CS_2 , TMS) δ 7.15 (s, 2 H, ethylene), 7.22–7.47 (m, 4 H), 7.40 (s, 5 H phenyl), 7.57–7.83 (m, 9 H).

1-(1-Phenyl-7-naphthyl)-2-(9-phenanthryl)ethylene (XVII) was obtained in a similar way as the foregoing compound in 76% yield from XVIa and phenanthraldehyde. *Trans*: mp 154–156°; *m/e* 406; uv_{max} (CH_3OH) 224 (log ϵ 4.65), [227 (4.65)], 251 (4.69), [263 (4.67)], 268 (4.68), [295 (4.37)], 339 nm (4.45); nmr (CS_2 , TMS) δ 7.25 and 7.09 (part of the AB pattern of the ethylene protons, $J_{AB} = 16$ Hz), 7.26–7.91 (H, 13 H), 7.41 (s, 5 H, phenyl), 8.13 (m, 1 H_α), 8.50 (m, 1 $H-\alpha_3$), 8.58 (m, 1 $H-\alpha_4$).

1-[1-(*p*-Methoxyphenyl)-7-naphthyl]-2-(6-methyl-2-naphthyl)ethylene (XVIII). 2-Bromomethyl-6-methylnaphthalene²¹ was converted into 6-methyl-2-naphthaldehyde (mp 123–124°) by a Sommelet reaction. A Wittig reaction of the aldehyde with XVIb under similar conditions as described in the synthesis of XI gave a mixture of *cis*- and *trans*-XVIII (85% yield) from which the *trans* isomer was separated by column chromatography. *Trans*: mp 136–142°; *m/e* 400; nmr (CS_2 , TMS) δ 2.44 (s, 3 H, CH_3), 3.80 (s, 3 H, OCH_3), 6.97 and 6.88 (part of an AB pattern, 2 $H_{AB} = 8.5$ Hz), 7.11–7.75 (m, 16 H), 7.80 (s, 1 H_α).

(19) R. H. Martin, *Tetrahedron*, **20**, 897 (1964).

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

(21) N. P. Buu-Hoi and J. Lecocq, *J. Chem. Soc.*, 830 (1946).

1-[1-(*p*-Methoxyphenyl)-7-naphthyl]-2-(7-methyl-2-naphthyl)ethylene (XIX) was prepared in 60% yield in a similar way as XVIII starting from 2-bromomethyl-7-methylnaphthalene.²¹ The intermediate, 7-methyl-2-naphthaldehyde, had mp 113–115°. Trans (contaminated with some cis isomer): mp 136–140°; *m/e* 400; nmr (CS₂, TMS) δ 2.39 (s, 3 H, CH₃), 3.74 (s, 3 H, OCH₃), 6.6–7.8 (m, 18 H).

Irradiations of the dinaphthylethylene derivatives XI and XVII–XIX were done in a degassed benzene solution with 50–300 mol % of iodine as oxidant and Sylvania 360-nm lamps as the light source. After completion of the reaction the solvent was evaporated and the residue chromatographed on a column of Al₂O₃. Eluted fractions were purified by crystallization.

Photoproducts obtained from XI follow.

1-Phenylpentahelicene (VIII): yield 7%; mp 174–178°; *m/e* 354; uv_{max} (CH₃OH) [245 (log ϵ 4.40)], [260 (4.13)], [315 (3.84)], 327 (3.90), 346 (3.98), 358 nm (3.97); nmr (CS₂, TMS) δ 8.05 (d, 2 H), 7.55–6.80 (multiplet of several doublets), 6.60–6.20 (broad asymmetric signal, 6 H); on lowering of temperature the latter signal sharpens and a multiplet arises at higher field; at –32° a sharp signal is present at 6.51 accompanied by complex multiplets at both sides.

10-Phenylanthro[1,2-*a*]anthracene (XII): yield 10%; *m/e* 354; uv_{max} (CH₂Cl₂) 303, 315, 342, 359, and 383 nm; nmr (CS₂, TMS) δ 7.33–7.80 (m, 13 H), 7.85 (d, 1 H α_2), 8.07 (d, 1 H α_1), 8.41 (s, 1 H γ_1); 9.18 (m, 1 H α_4), 9.52 (s, 1 H γ_4).

Benzo[*a*]coronene (IX): yield 42%; mp 309.5–311°, measured with a melting point microscope (lit.¹³ 292–294° in an evacuated tube); *m/e* 350; uv_{max} (C₆H₆) [295 (log ϵ 4.56)], 306 (4.85), 318 (5.11), 341 (4.25), 357 (4.26), 374 (4.20), 406 (2.83), 414 (2.76), 431 nm (2.42); nmr (HMPA, HMDS) 5.50–5.65 (m, 2 H), 6.43 (s, 4 H), 6.48 (s, 2 H), 6.57 (d, 2 H), 7.05–7.25 (m, 2 H), 7.41 (d, 2 H). The same product was obtained on irradiation of a solution of XXVa or XXVb with added iodine.

Irradiation of XVII gave three products.

12-Phenylidibenzo[*c,g*]chrysene (XX): yield 2%; mp 88–91°; *m/e* 404; uv_{max} (CH₃OH) 225 (log ϵ 4.52), 252 (4.67), [285 (4.34)], [295 (4.22)], [311 (4.05)], 349 (4.08), 366 nm (4.00); nmr (CS₂, TMS) δ 8.3–6.7 (m), 6.3–5.9 (unresolved broad signal, at 0° resolved into several multiplets ranging from 6.4 to 5.5; the temperature dependence points to free rotation of the phenyl group at higher temperatures).

12-Phenylidibenzo[*b,g*]chrysene (XXI): yield 16%; mp 205–211°; *m/e* 404; uv_{max} (CH₃OH) 226 (log ϵ 4.59), [245 (4.59)], [253 (4.66)], [263 (4.72)], 268.5 (4.77), 287.5 (4.71), 299 (4.85), 312 (4.92), [350 (3.70)], 366 (3.84), 385 (3.96), 407 nm (3.88); nmr (CS₂, TMS) δ 7.32–7.76 (m, 11 H), 7.83 (d, 1 H α_2), 7.99 (d, 1 H α_1), 8.34 (d, 1 H α_3), 8.45 (s, 1 H γ_1), 8.55 (q, 1 H α_3), 8.65 (q, 2 H α_3), 9.01 (m, 1 H α_4), 9.39 (s, 1 H γ_4).

Dibenzo[*a,g*]coronene (XXII): yield 30%; mp 343–345° (lit.²² 327–328° in an evacuated tube); *m/e* 400; uv_{max} (C₆H₆) 291 (log ϵ 4.62); [300 (4.59)], 310.5 (4.89), 325 (5.15), 344 (4.52), 357 (4.37), 375 (4.36), 407 (2.85), 415 (2.77), 431 nm (2.40); nmr (HMPA, HMDS) δ 5.41–5.78 (m, 4 H), 6.54 (d, 2 H), 6.36 (s, 2 H), 6.94–7.17 (m, 4 H), 7.37 (d, 2 H), 7.39 (s, 2 H).

The irradiation of XVIII gave only two products.

3-Methyl-10-(*p*-methoxyphenyl)naphtho[1,2-*a*]anthracene (XXIII): yield 15%; mp 207–210°; *m/e* 398; nmr (CDCl₃, TMS) δ 2.61 (s, 3 H, CH₃), 3.91 (s, 3 H, OCH₃), 7.02–7.85 (m, 12 H), 8.11 (m, 1 H α_2), 8.51 (s, 1 H γ_1), 9.19 (d, 1 H α_4), 9.63 (s, 1 H γ_4).

4-Methoxy-2-methylbenzo[*a*]coronene (XXIV). The crude product, 25%, was purified by sublimation at 260° (0.5 mm), followed by repeated crystallizations from hexane/dichloromethane: mp 202–203.5°; *m/e* 394; uv_{max} (C₆H₆) [314 (log ϵ 4.87)], 324.5 (5.09), 346 (4.30), 364 (4.28), 380.5 (4.16), 415 (3.27), 440 nm (3.46); nmr (CS₂, TMS) δ 3.39 (s, 3 H, CH₃), 3.97 (s, 3 H, OCH₃), 7.33 (d, 1 H), 8.25–8.50 (m, 8 H), 8.39 (s, 1 H), 8.89 (d, 1 H), 9.05 (d, 1 H). *Anal.* Calcd for C₃₀H₂₀O: C, 91.34; H, 4.60. Found: C, 90.1; H, 4.6. The same product was obtained by irradiation of a solution of XXVc as will be described below.

The irradiation of XIX gave again three products.

2-Methyl-10-(*p*-methoxyphenyl)naphtho[1,2-*a*]anthracene (XXIX): yield 25%; *m/e* 398; nmr (CS₂, TMS) δ 2.59 (s, 3 H, CH₃), 3.73 (s, 3 H, OCH₃), 7.1–7.8 (m, 12 H), 7.92 (d, 1 H α_2), 8.37 (s, 1 H γ_1), 8.93 (s, 1 H α_4), 9.46 (s, 1 H γ_4).

11-Methyl-1-(*p*-methoxyphenyl)naphtho[1,2-*a*]anthracene (XXX): yield 25%; *m/e* 398; uv_{max} (hexane) 231, 272, 316, [344 nm]; nmr (CS₂, TMS) δ 2.20 (s, 3 H, CH₃), 3.45 (s, 3 H, OCH₃), 6.94–7.84 (m,

12 H), 5.77–6.13 (broad asymmetric signal, 4 H); on lowering of temperature the signal sharpens; at –52° two AB patterns arise at 6.37 and 6.07 (J_{AB} = 8.5 Hz) and at 5.58 and 5.47 (J_{AB} = 8.5 Hz).

4-Methoxybenzo[*a*]coronene (XXXI): yield 8%; mp 222–225° (xylene); *m/e* 380; uv_{max} (C₆H₆) 321 (log ϵ 5.07), 334 (4.56), 343.5 (4.40), 361 (4.35), 375.5 (4.22), 409.5, (3.12), 434 nm (326); nmr (CDCl₃) δ 4.10 (s, 3 H, OCH₃), 7.53 (d, 1 H), 8.40–8.65 (m, 9 H), 9.03 (d, 1 H), 9.14 (d, 1 H), 9.21 (d, 1 H).

The compounds XXVa–c were synthesized as follows.

1-(*p*-Biphenyl)-2-(3-phenanthryl)ethylene (XXVa) was synthesized by a Wittig reaction from the triphenylphosphonium salt of 3-bromomethylphenanthrene¹² and 4-biphenylaldehyde with sodium methoxide in DMF (65% yield). Cis: mp 142–144° (CCl₄); *m/e* 356; uv_{max} (CH₃OH) 252.5 (log ϵ 4.73), [267 (4.50)], 319.5 nm (4.35); nmr (CS₂, TMS) δ 6.67 and 6.79 (AB, 2 H, ethylene), 7.16–7.78 (m, 16 H), 8.24 (m, 1 H α_2), 8.47 (s, 1 H α_3). Trans: mp 224–226°; *m/e* 356; uv_{max} (CH₃OH) 244 (log ϵ 4.49), 254 (4.49), [280 (4.39)], 287 (4.41), [335 (4.69)], 345 (4.73), [367 nm (4.46)]; nmr (CS₂, TMS) δ 7.27 (s, 2 H, ethylene), 7.21–7.84 (m, 16 H), 8.58 (s, 1 H α_3), 8.60 (m, 1 H α_3).

1-(*p*-Biphenyl)-2-(6-methyl-3-phenanthryl)ethylene (XXVb), 3,6-Dimethylphenanthrene²³ (mp 143–145°) was obtained by photo-dehydrocyclization of 4,4'-dimethylstilbene, and the product was treated with 1 equiv of *N*-bromosuccinimide in CCl₄. The mixture of the mono and dibromo substitution products was refluxed with triphenylphosphine in xylene for 8 hr. A Wittig reaction of the crude phosphonium salt and 4-biphenylaldehyde with sodium ethoxide in ethanol gave a rather complex reaction mixture. The wanted *cis*- and *trans*-XXVb were isolated by column chromatography on silica with benzene/hexane (1:2) as eluent, followed by crystallization from ethanol (30% yield). Cis: mp 130–132° (C₂H₅OH); *m/e* 370; uv_{max} (CH₃OH) [250 (log ϵ 4.72)], 254 (4.74), [270 (4.51)], 322 nm (4.33); nmr (CS₂, TMS) δ 2.42 (s, 3 H, CH₃), 6.67 and 6.77 (AB, 2 H, ethylene, J_{AB} = 12 Hz), 7.15–7.66 (m, 15 H), 8.00 (s, 1 H α_3), 8.46 (s, 1 H α_3). Trans: mp 209–212° (CH₂Cl₂); *m/e* 370; uv_{max} (CH₃OH) 227 (log ϵ 4.42), 245 (4.52), 255 (4.52), [285 (4.45)], 289 (4.46), [335 (4.59)], 348.5 (4.76), [355 (4.70)], 373.5 nm (4.47); nmr (CS₂, TMS), δ 2.62 (s, 3 H, CH₃), 7.20–7.74 (m, 17 H), 8.40 (s, 1 H α_3), 8.57 (s, 1 H α_3).

4'-Methoxy-4-biphenylaldehyde. Treatment of 4'-methoxy-4-methylbiphenyl²⁴ (mp 109°) with an equivalent amount of *N*-bromosuccinimide in carbon tetrachloride gave 4'-methoxy-4-bromomethylbiphenyl, mp 116–117° (CCl₄), in 75% yield. This product (5.84 g) was added to a solution of 0.468 g of sodium in 60 ml of absolute ethanol and 2 g of 2-nitropropane, and the mixture was stirred for 4 hr at room temperature. After evaporation of the ethanol 100 ml of ether and 100 ml of water were added, the layers were separated, and the ether layer was washed with two 50-ml portions of 10% sodium hydroxide solution and then with water. After drying over magnesium sulfate the solvent was removed and the residue purified by column chromatography and crystallization from methanol: yield 68%; mp 104–106°; nmr (CCl₄, TMS) δ 3.82 (3 H, OCH₃), 6.89 and 7.46 (AB, 4 H, J_{AB} = 8.9 Hz), 7.60 and 7.80 (AB, 4 H, J_{AB} = 8.4 Hz), 9.93 (s, 1 H, CHO). *Anal.* Calcd for C₁₄H₁₂O₂: C, 79.23; H, 5.70. Found: C, 79.7; H, 5.7.

3,5-Dimethyl-4'-carboxymethylstilbene. Sodium methoxide (2.95 g) was added to a mixture of 12.60 g of 3,5-dimethylbenzyltriphenylphosphonium bromide (mp 317–321°) and 4.49 g of 4-carboxymethylbenzaldehyde²⁵ in 100 ml of methanol. After 14 hr the crystalline *trans*-3,5-dimethyl-4'-carboxymethylstilbene could be separated by filtration. On pouring the filtrate through a silica column the *cis* isomer was eluted with benzene/hexane (30:70), over-all yield 51%. Cis: oil; *m/e* 266; uv_{max} (CH₃OH) 238 (log ϵ 4.21), 297 nm (4.05); nmr (CS₂, TMS) δ 2.13 (s, 6 H, 2CH₃), 3.72 (s, 3 H, OCH₃), 6.43 and 6.53 (AB, 2 H, ethylene, J_{AB} = 12.4 Hz), 6.72 (s, 3 H), 7.18 and 7.73 (AB, 4 H, J_{AB} = 8.3 Hz). Trans: mp 105–107°; uv_{max} (CH₃OH) 232.5 (log ϵ 4.11), 235 (4.10), [248 (3.86)], 324 nm (4.59); nmr (CS₂, TMS) δ 2.17 (s, 6 H, 2CH₃), 3.78 (s, 3 H, OCH₃), 6.79 (s, 1 H), 6.97 (s, 2 H, ethylene), 6.99 (s, 2 H), 7.39 and 7.85 (AB, 4 H, J_{AB} = 8.5 Hz). *Anal.* Calcd for C₁₈H₁₈O₂: C, 81.17; H, 6.81. Found: C, 81.0; H, 6.8.

2,4-Dimethyl-6-carboxymethylphenanthrene. The *trans* isomer

(23) O. Kruber and A. Raethel, *Chem. Ber.*, 87, 1472 (1954).

(24) H. N. Khastagir and B. K. Bhattacharyya, *J. Indian Chem. Soc.*, 26, 296 (1949).

(25) H. B. Hass and M. L. Bender, *J. Amer. Chem. Soc.*, 71, 1767 (1949).

(22) Reference 13, p 88.

(1.7 g) of the foregoing product and 0.3 g of iodine were dissolved in 5 l. of benzene, and the solution was irradiated for 16 hr with a high-pressure mercury lamp. The solvent was evaporated, the residue chromatographed on silica, and the wanted product eluted with benzene/hexane (3:2). It was crystallized from methanol: yield 68%; mp 105–107°; uv_{\max} (CH₃OH) 213 (log ϵ 4.23), 231 (4.49), [240 (4.55)], 251 (4.70), 255.5 (4.69), [277 (4.10)], 309 (4.13), 317 (4.16), [340 (3.37)], 359 nm (2.70); nmr (CS₂, TMS) δ 2.43 (s, 3 H, CH₃), 3.02 (s, 3 H, CH₃), 3.86 (s, 3 H, OCH₃), 7.20 (s, 1 H), 7.37 (s, 1 H), 7.52 (s, 2 H), 7.70 and 7.99 (AB, 2 H, J_{AB} = 8.3 Hz), 9.44 (s, 1 H- α_3). *Anal.* Calcd for C₁₈H₁₆O₂: C, 81.79; H, 6.10. Found: C, 81.6; H, 6.0.

2,4-Dimethyl-6-hydroxymethylphenanthrene. Reduction of the previous compound with lithium aluminium hydride in ether gave the alcohol in nearly quantitative yield. The product crystallized from methanol in colorless needles with mp 145.5–147.5°: m/e 236; uv_{\max} (CH₃OH) 227 (log ϵ 4.29), 254 (4.92), 279 (4.07), 289.5 (4.04), 301.5 (4.13), 320 (2.57), 336 (2.66), 345 (2.45), 352 nm (2.59); nmr (CDCl₃, TMS) δ 1.81 (s, OH), 2.52 (s, 3 H, CH₃), 3.11 (s, 3 H, CH₃), 4.91 (s, 2 H, CH₂), 7.32 (s, 1 H), 7.54 (s, 1 H), 7.66 (s, 2 H), 7.54 and 7.86 (AB, 2 H, J_{AB} = 8.3 Hz), 8.85 (s, 1 H- α_3).

2,4-Dimethyl-6-bromomethylphenanthrene. Treatment of the above alcohol with a saturated solution of hydrogen bromide in benzene yielded the bromide (88%, mp 100–102° from CCl₄), which was converted into its triphenylphosphonium bromide with an equivalent amount of triphenylphosphine in refluxing benzene.

1-[4-(*p*'-Methoxybiphenyl)]-2-(2,4-dimethyl-6-phenanthryl)ethylene (XXVc) was obtained in 70% yield by a Wittig reaction with 2.83 g of the above phosphonium salt and 1.12 g of 4'-methoxy-4-biphenylaldehyde in 150 ml of DMF with sodium ethoxide as base; in methanol the yield is much lower. The reaction mixture was subjected to column chromatography on silica. With hexane first some 2,4,6-trimethylphenanthrene was eluted. *cis*-XXVc was eluted with benzene/hexane (1:2) and the trans isomer with benzene/hexane (2:1) as eluent. *Cis*: mp 139–141° (CH₃OH/CH₂Cl₂); uv_{\max} (CH₃OH) 255 (log ϵ 4.73), [272 (4.52)], 331 nm (4.47); nmr (CS₂, TMS) δ 2.42 (s, 3 H, CH₃), 2.57 (s, 3 H, CH₃), 3.71 (s, 3 H, OCH₃), 6.57 and 6.67 (AB, 2 H, ethylene J_{AB} = 12 Hz), 6.75 and 7.30 (AB, 4 H, J_{AB} = 8.8 Hz), 7.05 (s, 1 H), 7.24 (s, 4 H), 7.28 and 7.60 (AB, 2 H, J_{AB} = 8.3 Hz), 7.42 (s, 1 H), 7.45 (s, 2 H), 8.66 (s, 1 H- α_3). *Anal.* Calcd for C₃₁H₂₆O: C, 89.82; H, 6.32. Found: C, 89.6; H, 6.3. *Trans*: mp 239–242° (CH₃OH/CH₂Cl₂); uv_{\max} (CH₂Cl₂) 246 (log ϵ 4.57), [255 (4.50)], [260 (4.42)], 283 (4.42), 293 (4.43), 358 (4.74), [375 nm (4.58)]; nmr (AsCl₃, TMS) δ 2.54 (s, 3 H, CH₃), 3.21 (s, 3 H, CH₃), 3.87 (s, 3 H, OCH₃), 6.98 and 7.06 (part of an AB pattern, ethylene, J_{AB} = 8.6 Hz), 7.26–7.76 (m, 13 H), 7.89 (s, 2 H), 8.93 (s, 1 H- α_3). *Anal.* Calcd for C₃₁H₂₆O: C, 89.82; H, 6.32. Found: C, 89.4; H, 6.2.

2,4,6-Trimethylphenanthrene: mp 84° (methanol); m/e 220; uv_{\max} (CH₃OH) 213 (log ϵ 4.34), 227 (4.26), [248 (4.24)], 254 (4.91), 278.5 (4.07), 289 (4.01), 300.5 (4.11), 320 (2.76), 336 (2.79), 352 nm (2.80); nmr (CS₂, TMS) δ 2.31 (s, 3 H, CH₃), 2.43 (s, 3 H, CH₃), 2.87 (s, 3 H, CH₃), 7.01 (s, 1 H), 7.24 (s, 1 H), 7.28 and 7.41 (AB, 2 H, J_{AB} = 8.8 Hz), 7.14 and 7.52 (AB, 2 H, J_{AB} = 8.0 Hz), 8.39 (s, 1 H- α_3).

9-Phenyldibenzo[*c,g*]phenanthrene (XXVI). A solution of XXVa in deaerated benzene was irradiated for 7.5 hr with a threefold

excess of iodine. After evaporation of most of the solvent the residue was chromatographed on Al₂O₃. XXVI was obtained in 54% yield by elution with a benzene/hexane mixture. By raising the benzene/hexane ratio in the eluent, 29% benzocoronene (IX) was obtained as a second product. XXVI had mp 187–189° (CH₃OH): m/e 354; uv_{\max} (CH₃OH) 221 (log ϵ 4.65), 235 (4.77), [245 (4.61)], 273 (4.64), [278 (4.60)], 307 (4.40), [330 nm (4.22)]; nmr (CS₂, TMS) δ 7.09–7.33 (m, 6 H), 7.43 (t, 1 H), 7.61 and 7.84 (AB, 2 H, J_{AB} = 8.2 Hz), 7.70–7.78 (m, 6 H), 7.85 (m, 1 H), 8.55 (m, 1 H- α_3), 8.59 (s, 1 H- α_3). Irradiation of XXVI in benzene with added iodine yielded again benzocoronene (29%), whereas 55% of XXVI could be recovered. 7-Phenylbenzo[*ghi*]perylene could not be isolated or detected in the irradiation mixture.

9-Methyl-12-phenyldibenzo[*c,g*]phenanthrene (XXVII) was obtained in 66% yield in a similar way as XXVI by irradiation of XXVb for 3.5 hr. In this case only a few per cent IX could be isolated as a second product. XXVII had mp 128–130° (CH₃OH): m/e 368; uv_{\max} (CH₃OH) [220 (log ϵ 4.64)], 224 (4.67), 238 (4.81), [247 (4.62)], 275 (4.65), 308 (4.39), [315 (4.36)], [335 (4.29)], 380 nm (2.38); nmr (CS₂, TMS) δ 2.25 (s, 3 H, CH₃), 7.13–7.40 (m, 6 H), 7.61–7.88 (m, 8 H), 7.91 (d, 1 H), 8.36 (s, 1 H- α_3), 8.69 (s, 1 H- α_3). Irradiation of XXVII for 5 hr yielded again benzocoronene (IX) (23%) leaving 66% of the starting compound. 7-Methyl-8-phenylbenzo[*ghi*]perylene was not found in the reaction mixture.

8,10-Dimethyl-12-(*p*-methoxyphenyl)dibenzo[*c,g*]phenanthrene (XXVIII). A solution of 150 mg of XXVc and an equivalent amount of iodine in 1 l. of dry deaerated benzene was irradiated for 9 hr under nitrogen. After evaporation of the solvent the residue was chromatographed on silica gel to remove polymeric products, and the crude product was again chromatographed on alumina. XXVIII could be eluted in 52% yield with benzene/hexane (1:2); 4-methoxy-2-methylbenzo[*a*]coronene (XXIV) was isolated in 11% yield by elution with benzene/hexane (3:2). XXVIII had mp 218–220° (CH₃OH): uv_{\max} (CH₃OH) 231 (log ϵ 4.71), 255 (4.52), 281 (4.63), 289.5 (4.63), [310 (4.39)], [333 (4.16)], [355 (3.87)], [400 nm (2.35)]; nmr (CS₂, TMS) δ 1.58 (s, 3 H, CH₃), 2.59 (s, 3 H, CH₃), 3.68 (s, 3 H, OCH₃), 6.63 and 7.07 (AB, 4 H, J_{AB} = 8.9 Hz), 6.99 (s, 1 H), 7.52 and 7.78 (AB, 2 H, J_{AB} = 8.3 Hz), 7.51–7.77 (m, 7 H), 7.99 (s, 1 H- α_3). *Anal.* Calcd for C₃₁H₂₆O: C, 90.26; H, 5.86. Found: C, 89.6; H, 5.8. Irradiation of XXVIII in a similar way for 8 hr gave a reaction mixture containing 60% of the starting compound and 37% of XXIV but no 6-methyl-8-(*p*-methoxyphenyl)benzo[*ghi*]perylene.

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