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Linear Conjugated Systems Bearing Aromatic Terminal Groups. XI. Syntheses and Electronic Spectra of α,ω-Diphenanthrylpolyenes

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The syntheses of α,ω-di(2-phenanthryl)-, di(3-phenanthryl)-, and di(9-phenanthryl)polyenes (I_n, I_n', and I_n'', $n=1$—6) by means of the Wittig reaction are described. Formylphenanthrenes (II, II′, II″), phenanthrylpropenals (III′, III″), phenanthrylpentadienals (IV, IV′, IV″) and muconaldehyde (VIII) were used as carbonyl components in the reaction. Phenanthrylmethyl-, phenanthrylpropenyl- and phenanthrylpentadienyltriphenylphosphonium bromides and 1,4-bis(triphenylphosphonium)-2-butene dibromide were converted into phosphoranes (V, V′, V″, VI, VI′, VII″, IX, IX′, IX″, VII) by a reaction with phenyllithium. The reaction of carbonyl components with phosphoranes with a proper combination yielded diphenanthrylpolyenes (I_n, I_n', I_n''). 2- and 3-Phenanthryl derivatives (I_n and I_n') exhibited electronic spectra with well-defined vibartional fine structure, whereas 9-phenanthryl derivative (I_n'') showed broad and structureless absorption curves. It was found that the plots of the longest-wavelength maxima ($\lambda_{\max}$) of I_n and I_n' against $n^{0.6}$ and $n^{0.8}$ give excellent straight lines which can be given by the empirical formulas:

$$I_n: \lambda_{\max} = 57.9n^{0.6} + 303 \text{ nm (in tetrahydrofuran)}$$

$$I_n': \lambda_{\max} = 30.3n^{0.8} + 348 \text{ nm (in tetrahydrofuran)}$$

A linear relationship between the square of wavelength of the longest-wavelength absorption maxima ($\lambda_{\max}$) and the number of ethylenic bond (n) [$\lambda^2_{\max} \propto n$, *i.e.*, $\lambda_{\max} \propto n^{0.5}$] has been recognized for the electronic spectra of several series of all-*trans*-polyenes.[1] However, the bathochromic shift of $\lambda_{\max}$ of α,ω-di(2-naphthyl)polyenes was found to be linearly proportional to $n^{0.7}$ suggesting a marked influence of the terminal groups on the electronic excitation of polyene chromophore.[2] Thus we considered it desirable to prepare other series of diarylpolyenes to get information on the role of terminal groups on the electronic spectral regularity. The present paper deals with the syntheses of α,ω-di(2-phenanthryl)-(I_n), α,ω-di(3-pehnanthryl)- (I_n'), and α,ω-di(9-phenanthryl)-polyenes (I_n''), and the spectral regularity of the former two series of polyenes (I_n and I_n').

Syntheses. The reaction sequence used in the syntheses of α,ω-diphenanthrylpolyenes (I_n, I_n', I_n'') is outlined in the Scheme. Phosphoranes were prepared by the reaction of phenyllithium with the corresponding triphenylphosphonium bromides. I_1, I_1', and I_1'' were obtained by the reaction of II, II′, and II″ with V, V′, and V″, respectively. III, III′, and III″ were prepared from II, II′, and II″ by a modified Arens and van Dorp method.[3] I_2 could be obtained from II and VI. The reaction of III′ and III″ with V′ and V″ afforded I_2' and I_2'', respectively. Treatment of IV and IV′ with V and V′ yielded I_3 and I_3'. I_3' was also prepared by the reaction of II′ with VII derived from 1,4-dibromo-2-butene.[4] The reaction of III″ with VI″ gave I_3''. The Wittig reaction of muconaldehyde (VIII) with V, V′, and V″ yielded I_4, I_4', and I_4'', respectively. IV, IV′, and IV″ were treated with IX, IX′, and IX″ to yield I_5, I_5', and I_5''. I_6, I_6', and I_6'' were obtained from VI, VI′, and VI″ and VIII.

1. $RCHO + RCH{=}PPh_3 \longrightarrow RCH{=}CHR$
   II, II′, II″ — V, V′, V″ — I_1, I_1', I_1''
2. $RCHO + RCH{=}CHCH{=}PPh_3 \longrightarrow R(CH{=}CH)_2R$
   II — VI — I_2
   $RCH{=}CHCHO + RCH{=}PPh_3 \longrightarrow R(CH{=}CH)_2R$
   III′, III″ — V′, V″ — I_2', I_2''
3. $R(CH{=}CH)_2CHO + RCH{=}PPh_3 \longrightarrow R(CH{=}CH)_3R$
   IV, IV′ — V, V′ — I_3, I_3'
   $RCHO + Ph_3P{=}CHCH{=}CHCH{=}PPh_3 \longrightarrow R(CH{=}CH)_3R$
   II′ — VII — I_3'
   $RCH{=}CHCHO + RCH{=}CHCH{=}PPh_3 \longrightarrow R(CH{=}CH)_3R$
   III″ — VI″ — I_3''
4. $2RCH{=}PPh_3 + OCH(CH{=}CH)_2CHO \longrightarrow R(CH{=}CH)_4R$
   V, V′, V″ — VIII — I_4, I_4', I_4''
5. $R(CH{=}CH)_2CHO + R(CH{=}CH)_2CH{=}PPh_3 \longrightarrow R(CH{=}CH)_5R$
   IV, IV′, IV″ — IX, IX′, IX″ — I_5, I_5', I_5''
6. $RCH{=}CHCH{=}PPh_3 + OCH(CH{=}CH)_2CHO \longrightarrow R(CH{=}CH)_6R$
   VI, VI′, VI″ — VIII — I_6, I_6', I_6''

Roman numerals with no prime, single prime and double prime denote the 2-phenanthryl, 3-phenanthryl and 9-phenanthryl isomers, respectively.

Scheme 1. Synthetic route of diphenanthrylpolyenes,

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* For Part X of this series, see Ref. 2.

[1] L. N. Ferguson, *Chem. Revs.*, **43**, 408 (1948) and references cited therein; F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky. *J. Amer. Chem. Soc.*, **83**, 1675 (1961).

[2] A. Yasuhara, S. Akiyama, and M. Nakagawa, This Bulletin, **45**, 3638 (1972).

[3] O. Isler, M. Montavon, R. Rüegg, and P. Zeller, *Helv. Chim. Acta*, **39**, 259 (1956).

[4] S. W. Heitman, J. H. S. Weiland, and H. O. Huisman, *Koninkl. Ned. Akad. Wetenshap., Proc. Ser. B*, **64**, 165 (1961).

Table 1. Physical properties of diphenanthrylpolyenes

n	I_n			I_n'			I_n''		
	Color	Mp(°C)	δ (cm^{-1})	Color	Mp(°C)	δ (cm^{-1})	Color	Mp(°C)	δ (cm^{-1})
1	colorless	315—316	965	pale greenish yellow	288—289	980	pale greenish yellow	271—273	960
2	greenish yellow	296—297	983	greenish yellow	286	992	greenish yellow	270—272	975
3	yellow	287—288	993	yellow	295—296	1000	yellow	243—244	992
4	yellow	283	998 1000	yellow	284—285	1005	yellow	263	1000
5	orange yellow	300	965 1005	orange yellow	275—276	1008	orange yellow	233—236	1000
6	yellow	293—294		orange	286—287	1008	orange	231—232	1000

Table 2. Electronic spectral data of di(2-phenanthryl)polyenes (I_n)

n	λ_{max} (log ε) in nm in tetrahydrofuran							
1	277 (4.80)	285 (4.91)	298.5 (4.90)	337[a)]	348 (4.89)	360[a)]	375[a)]	
2	287 (4.67)	295 (4.65)	354 (4.88)	371 (5.01)	392 (4.89)			
3	285 (4.56)	296 (4.55)	312 (4.26)	371 (4.93)	390 (5.08)	414 (4.95)		
4	255 (4.60)	284 (4.47)	294 (4.53)	319 (4.24)	371[a)]	388 (4.99)	408 (5.15)	436 (5.06)
5	260 (4.90)	266 (4.84)	297 (4.46)	382[a)]	404 (5.05)	426 (5.18)	455 (5.10)	
6	270 (4.82)	292[a)]	350 (4.20)	417 (4.99)	441 (5.16)	471.5 (5.09)		

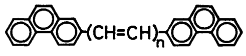
a) shoulder.

Table 3. Electronic spectral data of di(3-phenanthryl)polyenes (I_n')

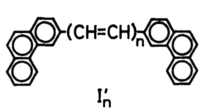
n	λ_{max} (log ε) in nm in tetrahydrofuran								
1	251.5 (4.81)	272.5 (4.68)	279[a)]	291[a)]	304.5 (4.23)	345[a)]	357 (4.75)	379 (4.62)	
2	253[a)]	280 (4.53)	299 (4.33)	313.5 (4.24)	360 (4.79)	378 (4.91)	399 (4.82)		
3	255[a)]	279 (4.40)	289 (4.41)	309 (4.24)	324 (4.27)	359[a)]	377 (4.87)	396 (5.02)	420 (4.91)
4	253 (4.89)	296 (4.32)	319 (4.18)	334 (4.30)	372[a)] (4.69)	391 (4.93)	414 (5.09)	440 (5.00)	
5	255 (4.89)	301 (4.28)	329 (4.26)	345 (4.42)	375 (4.66)	407 (4.92)	428 (5.07)	458 (5.00)	
6[b)]					356 (4.40)	421 (5.01)	443 (5.13)	474 (5.03)	

a) shoulder. b) measured in a glass cell.

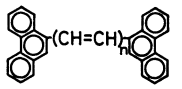
The color of the crystals, melting points and wave number of IR absorption due to C–H out-of-plane deformation (δ) of *trans*-double bond are summarized in Table 1. Regular increase in melting point with increase in the chain length in α,ω-diphenylpolyenes[5)] could not be observed in the series of diphenanthrylpolyenes (I_n, I_n', I_n'') as in di(1-anthryl)-[6)] and di(2-naphthyl)polyenes.[2)] The higher members of I_n were found to be scarcely soluble in usual organic solvents. Shift of δ to a higher wave number with the increase of n was observed in the three series of diphenanthrylpolyenes (I_n, I_n', I_n'') (Table 1). The same trend has been observed in the IR spectra of dianthryl-[6)] and dinaphthylpolyenes.[2)]



I_n



I_n'



I_n''

Electronic Spectra. Numerical data of the electronic spectra of I_n and I_n' are summarized in Tables 2 and 3. Absorption curves with well-developed fine structure were obtained for I_n and I_n', but broad and structureless ones for I_n'' (Figs. 1 and 2). The difference can be reasonably attributed to violation of coplanarity of the molecules of I_n'' caused by the steric interference between the hydrogen atoms at 1-, 1'-, 8-, and 8'-positions of the aromatic nuclei and β- and β'-positions of the ethylenic bonds. The same spectral behavior has been observed in other series of sterically hindered diarylpolyenes[2,5,7)] and explained in

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5) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928).

6) Y. Takeuchi, S. Akiyama, and M. Nakagawa, This Bulletin, **45**, 3183 (1972).

7) G. Wettermark, L. Tegner, and O. Mörtensson, *Arkiv. för Kemi*, **30**, 185 (1969).

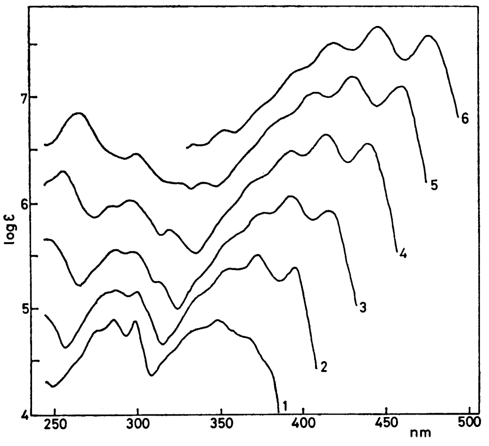

Fig. 1. Electronic spectra of di(2-phenanthryl)polyenes (I_n) in tetrahydrofuran. Each curve, except for the lowest one, has been displaced upward by a 0.5 log ε unit increment from one immediately below.

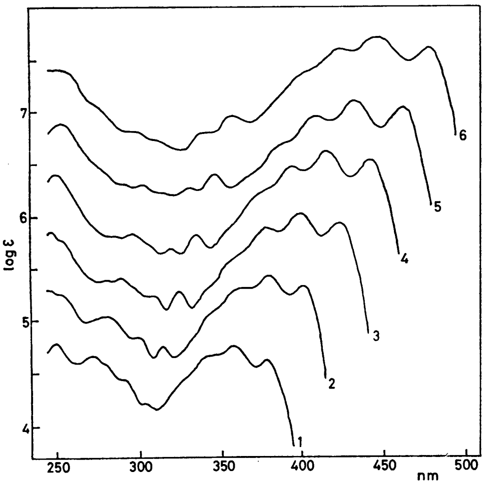

Fig. 2. Electronic spectra of di(3-phenanthryl)polyenes (I_n') in tetrahydrofuran. Each curve, except for the lowest one, has been displaced upward by a 0.5 log ε unit increment from one immediately below.

terms of nonplanarity of molecule.[7] The longest-wavelength absorption band consisting of three vibrational sub-bands seems to arise from an interaction of ^{1}La band of the terminal group with the absorption of polyene chromophore. The difference of wavelength $\Delta\lambda$ of the longest-wavelength sub-bands between a member of I_n or I_n' and the next higher member, I_{n+1} or I'_{n+1} decreases with the increase in the number of n. The same trend of bathochromic shift has been observed in various series of linear polyenes[1,2,5] in contrast with the increase of $\Delta\lambda$ in several series of diarylpoly-ynes.[8] This suggests the possibility that the mode of interaction of aromatic terminal groups with polyene chromophore differs from that with poly-yne chromophore.

Discussion on spectral regularity is limited to I_n and I_n', owing to difficulty of estimation of the exact location of longest-wavelength sub-band (λ_{I}) or next longest-wavelength sub-band (λ_{II}) of I_n'' because of the broad and structureless feature of their absorption curves. The longest-wavelength bands of I_n and I_n' are considered to shift linearly with the xth power of the number of ethylenic linkage (n).[2] It was revealed that the plots of λ_{I} and λ_{II} of I_n *versus* $n^{0.6}$ and those of I_n' *versus* $n^{0.8}$ give good straight lines (Figs. 3 and 4). The linear relationships can be well represented by the following empirical formulas:

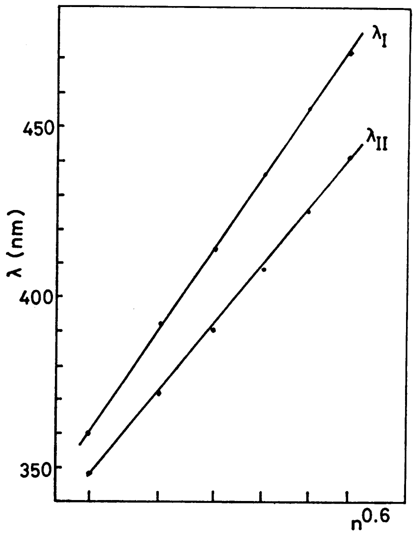

Fig. 3. Plot of $\lambda_{\max}$ *vs.* $n^{0.6}$ for di(2-phenanthryl)polyenes (I_n). λ_{I}: longest-wavelength maxima λ_{II}: second-longest-wavelength maxima

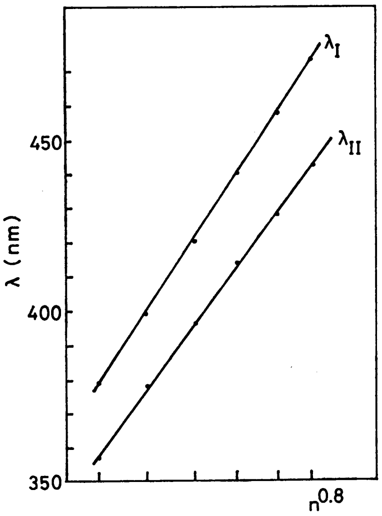

Fig. 4. Plots of $\lambda_{\max}$ *vs.* $n^{0.8}$ for di(3-phenanthryl)polyenes (I_n').
λ_{I}: longest-wavelength maxima
λ_{II}: second-longest-wavelength maxima

$$\lambda = An^x + B$$

$$I_n:\ \lambda_{\text{I}} = 57.9n^{0.6}+303\ \text{nm} \quad \text{(in tetrahydrofuran)}$$

$$\lambda_{\text{II}} = 48.6n^{0.6}+298\ \text{nm} \quad \text{(in tetrahydrofuran)}$$

$$I_n':\ \lambda_{\text{I}} = 30.3n^{0.8}+348\ \text{nm} \quad \text{(in tetrahydrofuran)}$$

$$\lambda_{\text{II}} = 27.1n^{0.8}+330.5\ \text{nm} \quad \text{(in tetrahydrofuran)}$$

The spectral regularity of acetylenic analogues of I_n and I_n', 2,2'-diphenanthrylpoly-ynes and 3,3'-diphenan-

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[8] M. Nakagawa, S. Akiyama, K. Nakasuji, and K. Nishimoto, *Tetrahedron*, **27**, 5401 (1971).

thrylpoly-ynes, could be expressed by $\lambda_I=13.9\ n^{1.3}+333$ and $\lambda_I=10.8\ n^{1.4}+347$, respectively.[9] The value of constant B was found to be similar in both series, but that of coefficient A to be much larger in the polyene series than in poly-yne analogues.

Experimental

All the melting points are not corrected. The electronic spectra were measured with a Hitachi EPS-3T spectrophotometer using a well-matched pair of 1 cm quartz cells. The IR spectra were obtained on a Hitachi EPI-2 spectrophotometer by KBr disk method. Pure and anhydrous solvents were used. Preparation of phosphoranes was carried out under nitrogen atmosphere using ethereal solution of phenyllithium as a base. The Wittig reaction was performed under shielding from light.

1,2-Diphenanthrylethylenes (I_1, I_1', and I_1''). *(a) 1,2-Di(2-phenanthryl)ethylene (I_1).* To a suspension of 2-phenanthrylmethyltriphenylphosphonium bromide[10] (0.64 g, 1.2 mmol) in benzene (20 ml) was added phenyllithium (0.175N, 6.8 ml). After stirring for 1 hr at room temperature, a solution of II[2] (0.21 g, 1.0 mmol) in benzene (10 ml) was added to the resulting orange red solution of phosphorane (V). The solvent was removed after the mixture had been stirred for 24 hr. The residue was digested with boiling benzene and the solution was passed through a short column of alumina. Pure I_1 was obtained as colorless crystals, mp 315—316°C, 0.109 g (28.7%) by concentration of the filtrate. Further concentration of the filtrate afforded the second crop of I_1, mp 309—312°C, 0.02 g (5.2%).

(b) 1,2-Di(3-phenanthryl)ethylene (I_1'). By a similar method to that used in the preparation of I_1, I_1' (mp 284—287°C, 0.258 g, 67.9%) was obtained from V′ [from the corresponding phosphonium bromide[10] (0.65 g, 1.2 mmol) and phenyllithium (0.69N, 1.7 ml)] and II′[9] (0.21 g, 1.0 mmol). Pure I_1', pale yellow needles, mp 288—289°C (from benzene).

(c) 1,2-Di(9-phenanthryl)ethylene (I_1''). The reaction of II′[9] (0.35 g, 1.5 mmol) with V″ [from 9-phenanthrylmethyltriphenylphosphonium bromide[10] (0.80 g, 1.5 mmol) and phenyllithium (0.09N, 16.6 ml)] afforded I_1'', mp 271—273°C (from toluene), $\lambda_{max}^{benzene}$ (log ε): 301 (4.27), 340 (4.30) nm.

Found: I_1, C, 94.58; H, 5.28%. I_1', C, 94.86; H, 5.38%. I_1'', C, 94.35; H, 5.28%. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30%.

3-Phenanthryl-2-propenals (III, III′, and III″). The preparation of 2-phenanthryl isomer (III) is described as a representative example, III′ and III″ being prepared by a similar procedure.

(a) 3-(2-Phenanthryl)-2-propenal (III). To a solution of lithium ethoxyacetylide prepared from 2-chlorovinyl ethyl ether (7.0 g, 0.066 mol) in tetrahydrofuran (20 ml) and lithium amide (from lithium 0.9 g, 0.13 g-atom) in liquid ammonia (130 ml) was added a solution of II[9] (4.0 g, 0.019 mol) in tetrahydrofuran (50 ml). After the mixture had been stirred for 48 hr at the boiling point of liquid ammonia, ammonium chloride (10 g) was added and the ammonia was allowed to evaporate. The residue was mixed with water and extracted with benzene. The extract, after being washed and dried, was concentrated to give crude ethoxyethynylcarbinol as a brown liquid. A solution of the crude carbinol in tetrahydrofuran (40 ml) was added to a suspension of lithium aluminum hydride (2.9 g, 0.078 mol) in the same solvent (50 ml). After being stirred for 2 hr at room temperature, the reaction mixture was treated with ethyl acetate (15 ml), water (10 ml), and 2N sulfuric acid (120 ml), successively. Crude III obtained as a brown liquid was dissolved in benzene-tetrahydrofuran and the solution was shaken with a saturated solution of sodium hydrogen sulfite to precipitate sulfite adduct of III. Decomposition of the adduct with 10% hydrochloric acid afforded pale yellow crystals, mp 118—123°C (1.19 g, 26.4%) which were recrystallized from benzene to give pure III, colorless cubes, mp 132—133°C.

(b) 3-(3-Phenanthryl)-2-propenal (III′). Crude III′ (0.87 g, 19.3%) obtained in crystalline state from II′[9] (4.0 g) was recrystallized from ethanol to afford pure III′, colorless plates, mp 114—115°C.

(c) 3-(9-Phenanthryl)-2-propenal (III″). Pale yellow needles (5.7 g, 37.2%) obtained from II′[9] (13.6 g) were recrystallized from benzene to yield pure III″, colorless needles, mp 158—159°C.

Found: III, C, 87.63; H, 5.23%. III′, C, 87.94; H, 5.06%. III″, C, 87.88; H, 5.70%. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21%.

3-Phenanthryl-2-propen-1-ols. Phenanthrylpropenols were obtained by the sodium borohydride reduction of III, III′, and III″. The preparation of 2-phenanthryl isomer is described as a typical example.

(a) 3-(2-Phenanthryl)-2-propen-1-ol. A suspension of sodium borohydride (1.20 g, 3.2 mmol) in methanol (20 ml) was added to a stirred solution of III (1.48 g, 6.4 mmol) in tetrahydrofuran (16 ml) and methanol (8 ml) at room temperature. After being stirred for 1.5 hr, dilute hydrochloric acid was added to the reaction mixture and extracted with benzene. The extract was washed, dried and treated with active charcoal at room temperature. Pale yellow crystals, mp 157—162°C, 1.31 g (87.9%) obtained by concentration of the extract were recrystallized from benzene to yield pure alcohol, pale yellow plates, mp 167—168°C.

(b) 3-(3-Phenanthryl)-2-propen-1-ol. Crude alcohol (0.30 g) obtained from III′ (0.30 g) and sodium borohydride (0.30 g) were recrystallized from benzene to give 3-phenanthrylpropenol, colorless plates, mp 130.5—131.1°C.

(c) 3-(9-Phenanthryl)-2-propen-1-ol. Reduction of III″ (2.3 g) with sodium borohydride (2.3 g) yielded 9-phenanthrylpropenol (2.2 g, 96%) which was recrystallized from benzene to give pure material, colorless needles, mp 143—144°C.

Found: 2-isomer, C, 87.08; H, 6.03%. 3-isomer, C, 87.30; H, 5.99%. 9-isomer, C, 86.99; H, 5.96%. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02%.

3-Phenanthryl-2-propenyltriphenylphosphonium Bromides. The synthesis of 2-phenanthryl isomer is described as a representative example, the preparation of phenanthryl-2-propenyltriphenylphosphonium bromides being performed under similar reaction conditions.

(a) 3-(2-Phenanthryl)-2-propenyltriphenylphosphonium Bromide. To a solution of 3-(2-phenanthryl)-2-propen-1-ol (1.0 g, 4.3 mmol) in chloroform (50 ml) containing 4 drops of pyridine was added a solution of phosphorus tribromide (0.8 g, 3.0 mmol) in chloroform (10 ml) under cooling with an ice-salt bath, and the mixture was stirred for 30 min at the same temperature. After being stirred for 30 min at room temperature, the reaction mixture was poured onto ice-water. The organic layer, after being washed and dried, was treated with active charcoal at room temperature. Fine pale

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[9] S. Akiyama and M. Nakagawa, This Bulletin, **44**, 2237 (1971).

[10] S. Akiyama, K. Nakasuji, and M. Nakagawa, *ibid.*, **44**, 2231 (1971).

yellow crystals obtained by evaporation of the solvent were mixed with triphenylphosphine (1.3 g, 5.0 mmol) and benzene (30 ml) and the mixture was refluxed for 19 hr. The phosphonium bromide deposited as colorless plates, mp 235—241°C, 2.12 g (88.7%).

(b) 3-(3-Phenanthryl)-2-propenyltriphenylphosphonium Bromide. 3-Phenanthrylpropenol (0.217 g, 0.93 mmol) was converted into bromide with phosphorus tribromide (0.20 g, 0.73mmol). Treatment of the bromide with triphenylphosphine afforded phosphonium bromide, colorless crystals, mp 223—226°C, 0.309 g (59.4%).

(c) 3-(9-Phenanthryl)-2-propenyltriphenylphosphonium Bromide. The reaction of the bromide obtained from 9-phenanthryl-2-propenol (1.50 g, 6.4 mmol) and phosphorus tribromide (1.2 g, 4.4 mmol) with triphenylphosphine (1.9 g, 7.5 mmol) gave phosphonium bromide, colorless crystals, mp 144—146°C (from ethanol), 3.55 g (93.6%).

Found: C, 74.92; H, 5.11; Br, 14.55%. Calcd for $C_{35}H_{28}BrP$: C, 75.15; H, 5.01; Br, 14.30%.

5-Phenanthryl-2,4-pentadienals (IV, IV′, and IV″). As the three isomeric aldehydes were prepared by similar procedures, only IV is described in some detail.

(a) 5-(2-Phenanthryl)-2,4-pentadienal (IV). To a stirred solution of ethylmagnesium bromide in tetrahydrofuran [from ethyl bromide (4.4 g) and magnesium (0.70 g, 28 mg-atom)] was added a solution of 1-methoxy-1-buten-3-yne (3.2 g, 38.9 mmol) in tetrahydrofuran (12 ml). After being stirred for 30 min at 40°C and then for 30 min at room temperature, a solution of II[9] (4.0 g, 19.4 mmol) in the same solvent (20 ml) was added dropwise under cooling. After stirring for 12 hr at room temperature, ethanol (1.3 ml) and lithium aluminum hydride (1.1 g, 29 mmol) were added to the stirred mixture. After 2 hr, water (4 ml) and 4N sulfuric acid (100 ml) were added successively to the reaction mixture and stirring was continued for 2 hr. The reaction mixture was worked up in the usual way. Crude IV (3.89 g, 77.8%, mp 159—161°C) was recrystallized from ethanol to give pure IV, yellow needles, mp 161°C.

(b) 5-(3-Phenanthryl)-2,4-pentadienal (IV′). The reaction product obtained from the Grignard derivative of methoxybutenyne (5.0 g, 61 mmol) and II′[9] (6.2 g, 30 mmol) was reduced with lithium aluminum hydride (1.7 g, 35 mmol) and the reduction product was treated with 4N sulfuric acid. The aqueous layer was extracted with benzene. The combined organic layer was shaken with a saturated sodium hydrogen sulfite solution to precipitate sulfite adduct. Decomposition of the adduct with a dilute hydrochloric acid afforded yellow crystalline powder (5.7 g, 73.5%, mp 90—94°C) which was recrystallized from ethyl acetate to give pure IV′, yellow rods, mp 102°C.

(c) 5-(9-Phenanthryl)-2,4-pentadienal (IV″). Crude IV″, yellow crystalline powder, 2.50 g (32.3%), mp 170—173°C obtained from II″[9] (6.20 g, 0.030 mol), the Grignard derivative of methoxybutenyne (6.1 g, 0.074 mol) and lithium aluminum hydride (1.7 g, 0.035 mol) was rcerystallized from benzene to yield pure IV″, yellow rods, mp 177—178°C.

Found: IV, C, 88.03; H, 5.48%. IV′, C, 88.34; H, 5.47%. IV″, C, 88.16; H, 5.47%. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46%.

5-Phenanthryl-2,4-pentadien-1-ols. Reduction of IV, IV′, and IV″ in tetrahydrofuran-methanol with sodium borohydride followed by treatment of the products with a dilute hydrochloric acid afforded phenanthrylpentadienols.

(a) 5-(2-Phenanthryl)-2,4-pentadien-1-ol. IV (1.50 g, 5.8 mmol) in the mixed solvent (3: 1, 40 ml) and the hydride (0.45 g, 12 mmol) in methanol (10 ml) gave fairly pure 2-phenanthrylpentadienol, colorless crystals, mp 89—100°C, 1.45 g (96.2%) which were used directly in the following reaction.

(b) 5-(3-Phenanthryl)-2,4-pentadien-1-ol. Pale yellow crystalline powder, mp 143—149°C, 0.94 g (quantitative) obtained from IV′ (0.90 g, 3.5 mmol), the mixed solvent (2: 1, 12 ml) and the hydride (0.27 g, 6 mmol) in methanol (8 ml) was recrystallized from chloroform, yielding pure alcohol, yellow plates, mp 149—150°C.

(c) 5-(9-Phenanthryl)-2,4-pentadien-1-ol. IV″ (0.394 g, 1.5 mmol), the mixed solvent (2: 1, 30 ml) and the hydride (0.120 g, 3.2 mmol) in methanol (10 ml) gave colorless needles, mp 119—124°C, 0.399 g (quantitative) which were recrystallized from benzene–cyclohexane (1:1) to give pure material, colorless needles, mp 125°C.

Found: 3-isomer, C, 87.30; H, 6.07%. 9-isomer, C, 87.43; H, 6.18%. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19%.

5-Phenanthryl-2,4-pentadienyltriphenylphosphonium Bromides. The preparation of 9-phenanthryl isomer is described as a typical example.

(a) 5-(9-Phenanthryl)-2,4-pentadienyltriphenylphosphonium Bromide. To a solution of 5-(9-phenanthryl)-2,4-pentadien-1-ol (0.60 g, 2.3 mmol) in chloroform (30 ml) containing a drop of pyridine was added a solution of phosphorus tribromide (0.68 g, 2.5 mmol) in chloroform (10 ml) under cooling on an ice-salt bath. After being stirred for 1 hr at room temperature, the reaction mixture was poured onto ice–water. The organic layer, after being washed and dried, was evaporated and the residue was mixed with benzene (52 ml) and triphenylphosphine (0.76 g, 2.9 mmol). Phosphonium bromide, pale yellow crystals, mp *ca.* 117°C, 0.64 g (47.6%) crystallized out on standing the mixture overnight at room temperature. The filtrate was refluxed for 6 hr, giving a second crop of phosphonium bromide, mp 137—143°C, 0.567 g (42.1%). The combined crystals were recrystallized from ethanol to yield pure material, colorless cubes, mp 190—191.5°C.

Found: C, 74.48; H, 5.28; Br, 13.60%. Calcd for $C_{37}H_{30}BrP \cdot 1/2C_2H_5OH$: C, 75.00; H, 5.47; Br, 13.13%.

(b) 5-(2-Phenanthryl)-2,4-pentadienyltriphenylphosphonium Bromide. The reaction of triphenylphosphine (0.36 g, 1.4 mmol) with the bromide derived from 2-phenanthrylpentadienol (0.24 g, 0.92 mmol) and phosphorus tribromide (0.26 g, 0.97 mmol) afforded phosphonium bromide, light yellow crystals, mp 160—164°C, 0.27 g (50%). This was used without purification in the following reaction.

(c) 5-(3-Phenanthryl)-2,4-pentadienyltriphenylphosphonium Bromide. 3-Phenanthrylpentadienol (1.5 g, 5.77 mmol) was converted into the corresponding bromide by the reaction with phosphorus tribromide (1.8 g, 6.68 mmol). The bromide was refluxed with triphenylphosphine (2.3 g, 8.8 mmol) in benzene (40 ml) to give phosphonium bromide (1.27 g) which was used without purification in the subsequent reaction.

1,4-Diphenanthryl-1,3-butadienes (I_2, I_2', and I_2''). (a) 1,4-Di(2-phenanthryl)-1,3-butadiene (I_2). A suspension of 3-(2-phenanthryl)-2-propenyltriphenylphosphonium bromide (0.67 g, 1.2 mmol) in benzene (25 ml) was mixed with phenyllithium (0.73N, 1.6 ml) to give a dark red solution of phosphorane (VI). A solution of II[9] (0.21 g, 1.0 mmol) in benzene (11 ml) was added and the mixture was stirred for 24 hr at room temperature. The residue obtained by evaporating the solvent was extracted with hot benzene and the hot extract was passed through a short column of alumina. Concentration of the filtrate gave pure I_2, greenish yellow crystals, mp 296—297°C, 0.132 g. Further concentration of the filtrate afforded a slightly impure second crop of I_2, mp 288—297°C, 0.020 g (total yield 37.5%).

(b) 1,4-Di(3-phenanthryl)-1,3-butadiene (I_2'). To a yellow solution of V′ prepared from 3-phenanthrylmethyltriphenylphosphonium bromide (1.10 g, 2.07 mmol) in benzene (20 ml) and phenyllithium (0.31 N, 6.7 ml) was added a solution of III′ (0.322 g, 1.38 mmol) in the same solvent (15 ml), and the mixture was stirred for 28 hr at room temperature. The residue obtained by evaporating the solvent was extracted with hot benzene. I_2', mp 280—284°C, 0.174 g (31.1%) obtained by concentration of the extract was redissolved in hot benzene, and the hot solution was passed through a short column of alumina to give pure I_2', greenish yellow plates, mp 286°C.

(c) 1,4-Di(9-phenanthryl)-1,3-butadiene (I_2''). To a solution of V″ prepared from 9-phenanthrylmethyltriphenylphosphonium bromide (0.80 g, 1.5 mmol) and phenyllithium (0.15 N, 10.0 ml) was added a solution of III″ (0.350 g, 1.5 mmol) in benzene (18 ml). Greenish yellow crystalline powder obtained after stirring the mixture for 6 hr at room temperature was triturated with a small amount of benzene, and the powder was extracted with hot toluene. Greenish yellow needles, mp 269—171°C, 0.557 g (25.8%) deposited on cooling the extract were dissolved in hot toluene and the hot solution was percolated through a thin layer of alumina to give pure I_2'', greenish yellow needles, mp 270—272°C, $\lambda_{\max}^{\text{benzene}}$ (log ε): 367 (4.56) nm.

Found: I_2, C, 94.67; H, 5.63%. I_2', C, 94.54; H, 5.62%. I_2'', C, 94.33; H, 5.46%. Calcd for $C_{32}H_{22}$: C, 94.54; H, 5.46%.

1,6-Diphenanthryl-1,3,5-hexatrienes (I_3, I_3', and I_3''). (a) 1,6-Di(2-phenanthryl)-1,3,5-hexatriene (I_3). To a solution of V prepared from 2-phenanthrylmethyltriphenylphosphonium bromide (0.80 g, 1.5 mmol) in benzene (25 ml) and phenyllithium (0.38 N, 4.0 ml) was added a solution of IV (0.322 g, 1.25 mmol) in the same solvent (25 ml). After the mixture had been stirred for 24 hr at room temperature, the product was extracted with hot benzene and the hot extract was passed through a short column of alumina. Concentration of the filtrate afforded I_3, yellow plates, mp 287—288°C. Further concentration of the filtrate yielded a sceond crop of I_3, mp 276—279°C, total 0.386 g (71.5%).

(b) 1,6-Di(3-phenanthryl)-1,3,5-hexatriene (I_3'). From 3-Phenanthrylmethyltriphenylphosphonium Bromide. A solution of IV′ (0.26 g, 1.0 mmol) in benzene (12 ml) was added to a solution of V′ in the same solvent (20 ml) prepared from 3-phenanthrylmethyltriphenylphosphonium bromide (0.64 g, 1.2 mmol) and phenyllithium (0.69 N, 1.7 ml). After being stirred for 72 hr at room temperature, the product was extracted with hot toluene. Fine yellow crystals, mp 295—296°C, 0.15 g (34.9%) obtained by concentrating the extract were dissolved in hot toluene and passed through a short column of alumina to yield I_3', yellow plates, mp 295—296°C.

From 3-Formylphenanthrene (II′) and Bis-phosphorane (VII). To an ice-cooled solution of 1,4-bis(triphenylphosphonium)-2-butene dibromide[4] (0.75 g, 1.0 mmol) in ethanol (26 ml) were added simultaneously over a 12 min period a solution of lithium methoxide (from lithium, 0.14 g, 0.02 g-atom and methanol, 28 ml) and a solution of II′ (0.45 g, 2.2 mmol) in ethanol (42 ml) and the mixture was stirred for 4 hr at 0°C. Fine yellow crystals, mp 285—291°C, 0.068 g (15.8%) deposited after stirring overnight at room temperature were washed with ethanol and recrystallized from benzene to yield pure I_3', yellow plates, mp 294.5°C.

(c) 1,6-Di(9-phenanthryl)-1,3,5-hexatriene (I_3''). To a solution of VI″ in benzene (15 ml) prepared from 3-(9-phenanthryl)-2-propenyltriphenylphosphonium bromide (0.840 g, 1.5 mmol) and phenyllithium (0.17 N, 17.6 ml) was added a solution of III″ (0.348 g, 1.5 mmol) in the same solvent (20 ml). After being stirred overnight at room temperature, the product was washed with a small amount of benzene and extracted with hot toluene. The hot extract was percolated through a thin layer of alumina and the filtrate was concentrated to yield pure I_3'', yellow needles, mp 243—244°C, $\lambda_{\max}^{\text{benzene}}$ (log ε): 384 (4.67) nm.

Found: I_3, C, 94.15; H, 5.57%. I_3' (from IV′), C, 94.15; H, 5.57%. I_3' (from II′), C, 94.04; H, 5.59%. I_3'', C, 94.30; H, 5.55%. Calcd for $C_{34}H_{24}$: C, 94.41; H, 5.60%.

1,8-Diphenanthryl-1,3,5,7-octatetraenes (I_4, I_4', and I_4''). (a) 1,8-Di(2-phenanthryl)-1,3,5,7-octatetraene (I_4). To a solution of V in benzene (20 ml) obtained from 2-phenanthrylmethyltriphenylphosphonium bromide (0.64 g, 1.2 mmol) and phenyllithium (0.18 N, 6.8 ml) was added a solution of VIII (0.055 g, 0.50 mmol) in benzene (7 ml). After the mixture had been stirred overnight at room temperature, the product was digested with boiling benzene. Concentration of the extract afforded yellow crystals (0.0935 g). The mother liquor was passed through a short column of alumina and the filtrate was concentrated to yield a second crop of yellow crystals (0.013 g). The combined crude crystals (mp 280—281°C) dissolved in hot benzene were percolated through a short column of alumina to give pure I_4, yellow plates, mp 283°C.

(b) 1,8-Di(3-phenanthryl)-1,3,5,7-octatetraene (I_4'). A mixture of VIII (0.056 g, 0.5 mmol) and V′ derived from 3-phenanthrylmethyltriphenylphosphonium bromide (0.64 g, 1.2 mmol) and phenyllithium (0.69 N, 1.7 ml) was stirred for 24 hr at room temperature. The product dissolved in hot toluene was passed through a short column of alumina. Fine yellow crystals, mp 279—285°C, 0.0935 g (20.4%) obtained from the filtrate were dissolved in hot toluene and percolated through a thin layer of alumina to yield pure I_4', yellow plates, mp 284—285°C.

(c) 1,8-Di(9-phenanthryl)-1,3,5,7-octatetraene (I_4''). To a solution of V″ in benzene (15 ml) prepared from 9-phenanthrylmethyltriphenylphosphonium bromide (0.800 g, 1.5 mmol) and phenyllithium (0.14 N, 10.7 ml) was added a solution of VIII (0.056 g, 0.5 mmol) in benzene (6 ml). After being stirred for 6 hr at room temperature, crystalline powder deposited was washed with benzene and digested with hot toluene. Concentration of the extract afforded yellow needles, mp 255—257°C, 0.107 g (46.7%). A second crop of yellow needles, mp 236—241°C, 0.065 g (28.3%) was obtained from the filtrate on concentration. A hot toluene solution of the first crop was percolated through a short column of alumina to give pure I_4'', yellow needles, mp 263°C, $\lambda_{\max}^{\text{benzene}}$ (log ε): 296 (4.52), 403 (4.83) nm.

Found: I_4, C, 94.00; H, 5.69%. I_4', C, 94.33; H, 5.68%. I_4'', C, 94.40; H, 5.67%. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72%.

1,10-Diphenanthryl-1,3,5,7,9-decapentaenes (I_5, I_5', and I_5''). (a) 1,10-Di(2-phenanthryl)-1,3,5,7,9-decapentaenes (I_5). A solution of IV (0.136 g, 0.53 mmol) in benzene (18 ml) was added to a benzene solution (20 ml) of IX prepared from 5-(2-phenanthryl)-2,4-pentadienyltriphenylphosphonium bromide (0.34 g, 0.59 mmol) and phenyllithium (0.97 N, 0.6 ml) and the mixture was stirred for 27 hr at room temperature. Yellow solid obtained by evaporation of the solvent was digested with hot toluene. Concentration of the extract afforded yellow plates, mp 284—288°C, 0.086 g (33.7%) which were redissolved in hot toluene and passed through a short column of alumina to give pure I_5, orange yellow plates, mp 300°C.

(b) 1,10-Di(3-phenanthryl)-1,3,5,7,9-decapentaene (I_5'). To a solution of IX′ in benzene (20 ml) prepared from 5-(3-

phenanthryl)-2,4-pentadienyltriphenylphosphonium bromide (0.70 g, 1.2 mmol) and phenyllithium (0.098N, 9.6 ml) was added a solution of IV′ (0.26 g, 1.0 mmol) in benzene (15 ml). After being stirred for 49 hr at room temperature, the reaction product was extracted with hot toluene. Concentration of the extract yielded I_5', orange yellow plates, mp 275—276°C, 10 mg.

(c) 1,10-Di(9-phenanthryl)-1,3,5,7,9-decapentaene (I_5''). A solution of IV″ (0.214 g, 0.83 mmol) in benzene (20 ml) was added to a solution of IX″ in the same solvent (30 ml) obtained from 5-(9-phenanthryl)-2,4-pentadienyltriphenylphosphonium bromide (0.480 g, 0.83 mmol) and phenyllithium (0.16N, 5.2 ml). After being stirred for 19 hr at room temperature, crystalline solid deposited was washed with benzene and extracted with hot toluene. The hot extract was percolated through a short column of alumina. Orange yellow needles, mp 233—236°C, 0.070 g (17.4%) obtained on concentration of the filtrate were redissolved in hot toluene and again passed through a thin layer of alumina to yield pure I_5'', yellow needles, mp 248—249°C, $\lambda_{\max}^{\text{benzene}}$ (log ε): 305 (4.43), 420 (4.81) nm.

Found: I_5, C, 93.55; H, 5.83%. I_5', C, 93.71; H, 5.82%. I_5'', C, 93.86; H, 5.90%. Calcd for $C_{38}H_{28}$: C, 94.18; H, 5.82%.

1,12-Diphenanthryl-1,3,5,9,11-dodecahexaenes (I_6, I_6', and I_6''). *(a) 1,12-Di(2-phenanthryl)-1,3,5,7,9,11-dodecahexaene (I_6).* A solution of VIII (0.052 g, 0.5 mmol) in benzene (10 ml) was added to a solution of VI in the same solvent (25 ml) prepared from 3-(2-phenanthryl)-2-propenyltriphenylphosphonium bromide (0.714 g, 1.3 mmol) and phenyllithium (0.84N, 1.5 ml) and the mixture was stirred for 21 hr at room temperature. The reaction product was extracted with hot toluene. Orange crystals obtained by concentrating the extract were dissolved in hot toluene and percolated through a thin layer of alumina to give pure I_6, orange crystals, mp 293—294°C.

(b) 1,12-Di(3-phenanthryl)-1,3,5,7,9,11-dodecahexaene (I_6'). By a similar procedure to that for I_6, 3-(3-Phenanthryl)-2-propenyltriphenylphosphonium bromide (0.309 g, 0.56 mmol), phenyllithium (0.19N, 2.9 ml) and VIII (0.030 g, 0.28 mmol) afforded I_6', orange rods, mp 286—287°C (from toluene), 11.5 mg (8.2%).

(c) 1,12-Di(9-phenanthryl)-1,3,5,7,9,11-dodecahexaene (I_6''). A solution of VI″ in benzene (15 ml) prepared from 3-(9-phenanthryl)-2-propenyltriphenylphosphonium bromide (0.670 g, 1.2 mmol) and phenyllithium (0.135N, 8.9 ml) was mixed with a solution of VIII (0.044 g, 0.4 mmol) in benzene (7 ml). After being stirred overnight at room temperature, the reaction product was extracted with hot toluene. Orange crystals, mp 217—220°C, 0.117 g (57.4%) obtained by concentrating the extract were redissolved in hot toluene. Percolation of the hot solution through a short column of alumina afforded pure I_6'', orange needles, mp 231—232°C, $\lambda_{\max}^{\text{benzene}}$ (log ε): 314 (4.35), 434 (5.17) nm.

Found: I_6, C, 93.97; H, 5.88%. I_6', C, 93.89; H, 5.94%. I_6'', C, 93.93; H, 5.97%. Calcd for $C_{40}H_{30}$: C, 94.08; H, 5.92%.