BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2822—2827 (1973)

Linear Conjugated Systems Bearing Aromatic Terminal Groups. XII.[1] Syntheses and Electronic Spectra of α,ω-Di-2-pyrenyl- and α,ω-Di-2-fluorenylpolyenes

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(Received December 14, 1972)

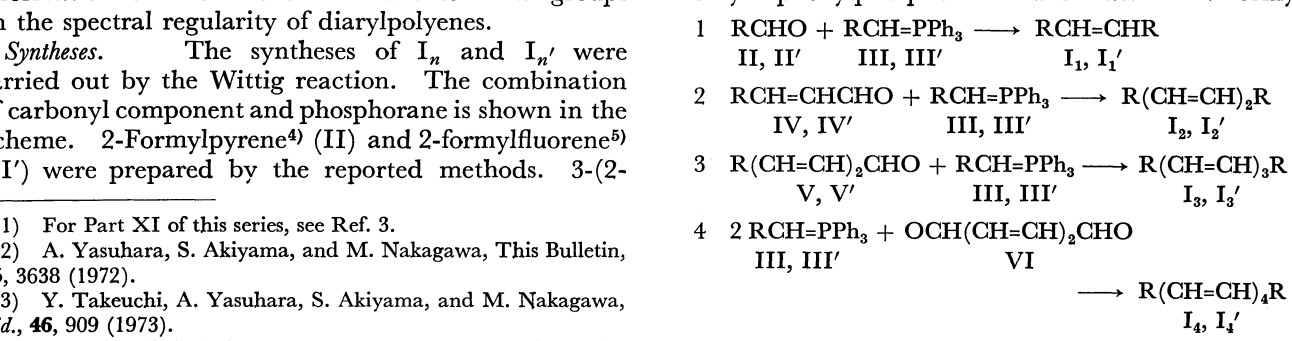
The syntheses of α,ω-di-2-pyrenyl- and α,ω-di-2-fluorenylpolyenes I_n and I_n' ($n=1$—6) by means of the Wittig reaction are described. Aldehydes II, II′, propenals IV, IV′, pentadienals V, V′ bearing 2-pyrenyl or 2-fluorenyl terminal group and muconaldehyde VI were used as carbonyl components. Phosphoranes III, III′, VII, VII′, VIII and VIII′ were prepared from methyl-, propenyl-, and pentadienyltriphenylphosphonium bromides substituted with 2-pyrenyl or 2-fluorenyl group by the reaction with phenyllithium. I_n and I_n' were obtained by the reaction of carbonyl components with phosphoranes by proper combination. It was found that the bathochromic shift of the longest-wavelength peaks of I_n and I_n' can be expressed by the following empirical equations:

$$I_n : \lambda = 44.6n^{0.7} + 314 \text{ (nm in tetrahydrofuran)}$$
$$I_n' : \lambda = 29.5n^{0.8} + 353 \text{ (nm in tetrahyhrofuran)}$$

The bathochromic shift of the longest-wavelength absorption maxima (λ) of some α,ω-diarylpolyenes [$Ar(CH=CH)_nAr$] can be expressed by the empirical formula $\lambda=An^x+B$.[2,3] The value of x changes with terminal group and the position of linking of polyene chain. This indicates a marked influence of terminal groups on the electronic excitation of polyene chromophore. The present paper deals with the syntheses and electronic spectral regularity of α,ω-di-2-pyrenyl- and α,ω-di-2-fluorenylpolyenes (I_n and I_n', $n=1$—6) which were carried out for the purpose of getting information on the role of aromatic terminal groups on the spectral regularity of diarylpolyenes.

Syntheses. The syntheses of I_n and I_n' were carried out by the Wittig reaction. The combination of carbonyl component and phosphorane is shown in the Scheme. 2-Formylpyrene[4] (II) and 2-formylfluorene[5] (II′) were prepared by the reported methods. 3-(2-Pyrenyl)-2-propenal (IV) was prepared by the reaction of lithium ethoxyacetylide with II followed by reduction with lithium aluminum hydride and anionotropic rearrangement under acidic conditions. 3-(2-Fluorenyl)-2-propenal (IV′) could be obtained by the Meyer-Schuster rearrangement of 1-(2-fluorenyl)-2-propyn-1-ol derived from II′. The reaction of Grignard derivative of methoxybutenyne with the aldehyde (II or II′) followed by reduction and acid treatment afforded 5-aryl-2,4-pentadienal (V or V′) in a reasonable yield.

Phosphorane (III) was prepared from 2-pyrenylmethyltriphenylphosphonium bromide.[6] 2-Formyl-



1) For Part XI of this series, see Ref. 3.

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

3) Y. Takeuchi, A. Yasuhara, S. Akiyama, and M. Nakagawa, *ibid.*, **46**, 909 (1973).

4) K. Nakasuji, S. Akiyama, and M. Nakagawa, *ibid.*, **45**, 875 (1972).

5) R. Rieche, H. Gross, and E. Hoft, *Chem. Ber.*, **93**, 88 (1960).

6) S. Akiyama, K. Nakasuji, and M. Nakagawa, This Bulletin, **44**, 2231 (1971).

Table 1. Physical properties of di-2-pyrenyl- and di-2-fluorenylpolyenes (I_n and I_n')

	Di-2-pyrenylpolyene (I_n)			Di-2-fluorenylpolyene (I')		
n	Color of crystals	Mp (°C)	δ (cm^{-1})	Color of crystals	Mp (°C)	δ (cm^{-1})
1	greenish yellow	>360	951	colorless	304—305	967
2	pale yellow	354—355	974	yellow	301—302	990
3	yellow	329—330	980	yellow	296—297	1000
4	yellow	320	987	yellow	289—291	1005
5	orange	303	990	yellow	277	1005
6	orange	298—299		orange	298—300	1005

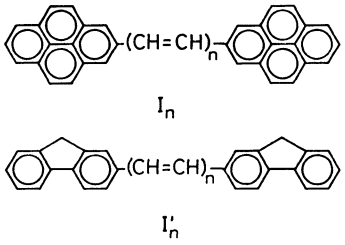
5 $R(CH=CH)_2CHO$ (V, V′) + $R(CH=CH)_2CH=PPh_3$ (VII, VII′) ⟶ $R(CH=CH)_5R$ (I_5, I_5')

6 $RCH=CHCH=PPh_3$ (VIII, VIII′) + $OCH(CH=CH)_2CHO$ (VI) ⟶ $R(CH=CH)_6R$ (I_6, I_6')

fluorene (II′) was reduced to 2-hydroxymethyl derivative by sodium borohydride, which was converted into 2-bromomethylfluorene by the usual method. 2-Fluorenylmethyltriphenylphosphonium bromide prepared by the reaction of triphenylphosphine with 2-bromomethylfluorene was treated with phenyllithium to give phosphorane (III′). Reduction of propenal (IV or IV′) with sodium borohydride afforded the corresponding propenol, which was converted into propenyl bromide and treated with triphenylphosphine to give triphenylphosphonium bromide. The reaction of phenyllithium with the phosphonium bromide gave phosphorane (VIII or VIII′). Similarly, 5-aryl-2,4-pentadienal (V or V′) was converted into phosphorane (VII or VII)′ *via* pentadienol and pentadienyl bromide.

1,2-Di(2-pyrenyl)- and 1,2-di(2-fluorenyl)ethylene (I_1 and I_1') were obtained by the reaction of aldehydes (II and II′) with phosphoranes (III and III′), respectively. The combination of propenal (IV or IV′) with phosphorane (III or III′) afforded 1,4-di(2-pyrenyl)- or 1,4-di(2-fluorenyl)-1,3-butadiene (I_2 or I_2'). 1,6-Di(2-pyrenyl)- and 1,6-di(2-fluorenyl)-1,3,5-hexatrienes (I_3 and I_3') were prepared by the reaction of pentadienals (V and V′) with phosphoranes (III and III′), respectively. The reaction of muconaldehyde (VI) with III or III′ afforded 1,8-di(2-pyrenyl)- or 1,8-di(2-fluorenyl)-1,3,5,7-octatetraene (I_5 or I_5'). The reaction of propenylidenephosphorane (VIII or VIII′) with muconaldehyde (VI) gave 1,12-di(2-pyrenyl)- or 1,12-di(2-fluorenyl)-1,3,5,7,9,11-dodecahexaene (I_6 or I_6').

The color of crystals, melting points and wave number of IR absorption in the region of C–H out-of-plane deformation (δ) of *trans*-double bond are summarized in Table 1. Regular increase in melting point with the increase of n reported for α,ω-diphenylpolyenes[7] could not be observed in the series of I_n and I_n'. The solubility of both series of polyenes



Scheme 1. Syntheses of di-2-pyrenyl- and di-2-fluorenylpolyenes (I_n and I'_n).

Table 2. Electronic spectral data of di-2-pyrenyl- and di-2-fluorenylpolyenes (I_n and I_n')[a]

	λ_{max} (log ε) in nm in tetrahydrofuran													
n	Di-2-pyrenylpolyenes (I_n)										Di-2-fluorenylpolyenes (I_n')			
1	251	310	324	341.5	359[b]	392[c]	415[c]				349[b]	363	382	
	(4.77)	(4.87)	(5.03)	(4.12)		(3.39)	(3.27)					(4.93)	(4.71)	
2	249[b]	258	268[b]	314[b]	333	344	365	385	399[b]	424[c]	364	380	404	
		(4.54)			(5.03)	(5.25)	(4.96)	(4.78)		(3.59)	(4.86)	(4.99)	(4.63)	
3	265	285	328	345	358	386	410	431[c]			262.5[b]	379.5	398.5	424
	(4.48)	(4.20)	(4.79)	(5.07)	(4.96)	(5.05)	(4.51)	(4.07)				(4.89)	(5.04)	(4.91)
4			326.5	345	351	386	401	431			275	394	432	461
											(4.21)	(4.95)	(5.10)	(5.00)
5			325	342	356	402	424	452			388[b]	409	432	461
												(5.00)	(5.16)	(5.09)
6	326	341	355	404	424	452	470[b]				295.5	423	446	476.5
											(4.37)	(5.06)	(5.20)	(5.13)

a) Owing to poor solubility, the spectra of I_{4-6} were measured with solutions of unknown concentration employing 10 cm glass cells. b) Shoulder. c) Absorption maxima of L_b species.

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

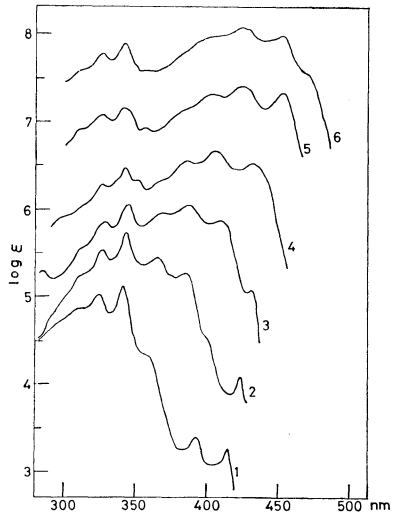


Fig. 1. Absorption curves of di-2-pyrenylpolyenes (I_n) in tetrahydrofuran. The spectra of I_{4-6} were measured with solutions of unknown concentration using 10 cm glass cells. Each curve, except for I_1, has been displaced upward by a 0.5 log ε unit increment from one immediately below it.

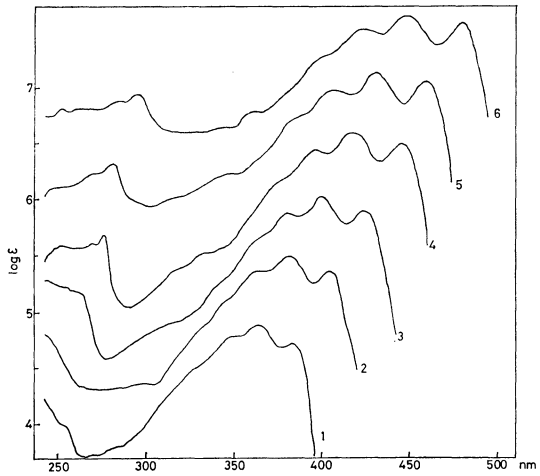


Fig. 2. Absorption curves of di-2-fluorenylpolyenes (I'_n) in tetrahydrofuran. Each curve, except for I_1', has been displaced upward by a 0.5 log ε unit increment from one immediately below it.

decreases markedly with the increase in n. Shift of δ to higher wave number along with the increase of n observed in other series of diarylpolyenes[2,3] was also found in the series of I_n and $I_{n'}$.

Electronic Spectra. Numerical data of the electronic spectra of I_n and $I_{n'}$ are summarized in Table 2. The absorption curves of both series of diarylpolyenes I_n and $I_{n'}$ exhibit well-defined vibrational fine structure (Figs. 1 and 2). The characteristic of electronic spectra of I_n and $I_{n'}$ is similar to that of other series of diarylpolyenes,[2,3] *i.e.*, the intense bands in the long-wavelength region, which seems to arise from an interaction of L_a band of the terminal group with the polyene chromophore, shift to longer wavelength with the increase in n. However, the increase in the length of polyene chain exerts a minor effect on the location of short wavelength bands. The weak absorption maxima at the longest-wavelength region observed in I_1, I_2, and I_3 can be attributed to the L_b band of pyrene nucleus. Discussion is given on the spectral regularity for the longest-wavelength sub-bands (λ) of the intense long-wavelength absorption band. It was found that the plots of λ of I_n and $I_{n'}$ *versus* $n^{0.7}$ and $n^{0.8}$, respectively, gave good straight lines (Figs. 3 and 4). The following empirical equations can well express the linear relationships:

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

$$I_n : \lambda = 44.6n^{0.7} + 314 \text{ (nm in tetrahydrofuran)}$$

$$I_n' : \lambda = 29.5n^{0.8} + 353 \text{ (nm in tetrahydrofuran)}$$

The linear relationship of acetylenic analogues of I_n and $I_{n'}$, 2,2'-dipyrenylpoly-ynes[4] and 2,2'-difluorenylpoly-ynes[8] can be expressed by $\lambda=12.6\ n^{1.4}+327$ (nm in toluene) and $\lambda=9.0\ n^{1.5}+350$ (nm in tetrahydrofuran). The value of A in polyene series were found to be much larger than those in poly-yne analogues. This indicates that the electronic interaction of aromatic terminal group with polyene chromophore differs from that with poly-yne system, since the value of A can be regarded as a measure of interaction between terminal group and unsaturated function.

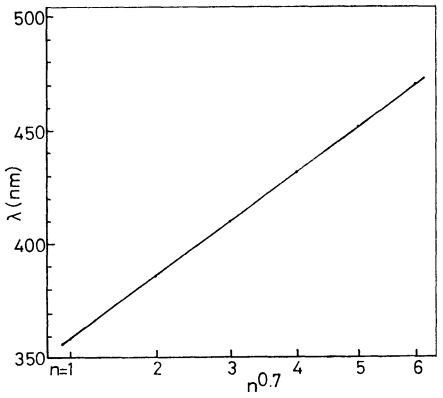


Fig. 3. Plot of λ *vs.* $n^{0.7}$ for di-2-pyrenylpolyenes (I_n).

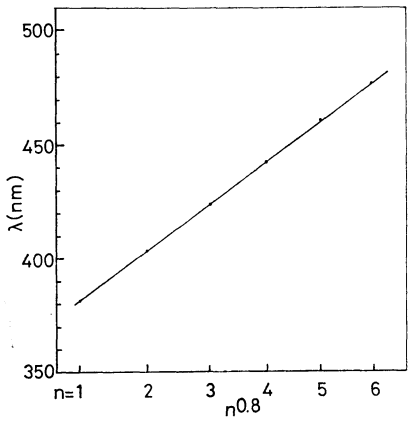


Fig. 4. Plot of λ *vs.* $n^{0.8}$ for di-2-fluorenylpolyenes (I_n').

Experimental

All melting points are not corrected. The electronic spectra were measured with a Hitachi EPS-3T spectrophotometer

8) K. Nakasuji, S. Akiyama, and M. Nakagawa, This Bulletin, **45**, 883 (1972).

using a well-matched pair of 1 cm quartz cells unless otherwise stated. IR spectra were obtained on a Hitachi EPI-2 spectrophotometer by the KBr-disk method. Preparation of phosphoranes was carried out under nitrogen atmosphere using an ethereal solution of phenyllithium as a base. The Wittig reaction was performed under shielding from light.

3-(2-Pyrenyl)-2-propenal (IV). 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, 0.8 g, 0.12 g-atom) in liquid ammonia (130 ml) was added a solution of II[4] (3.0 g, 0.013 mol) in tetrahydrofuran (40 ml). After being stirred overnight at the boiling point of ammonia, stirring was continued overnight at 0 °C allowing the ammonia to evaporate. Ammonium chloride (10 g) and water were added to the residue. The organic layer, after washing and drying, was concentrated to give a dark brown liquid which was dissolved in tetrahydrofuran (40 ml). Lithium aluminum hydride (2.2 g, 0.058 mol) in the same solvent (50 ml) was added to the solution and the mixture was stirred for 2 hr at room temperature. Ethyl acetate (10 ml) and 2 M sulfuric acid (100 ml) were added successively, and the mixture was stirred overnight at room temperature. The aqueous layer was extracted with benzene. The combined organic layer and extract, after being washed and dried, were concentrated under reduced pressure. Crystals, 0.26 g, mp 183—194 °C obtained by trituration of the residue with a small amount of ether–tetrahydrofuran were dissolved in benzene and passed through a short column of alumina. Crystals obtained from the filtrate were recrystallized from benzene to yield pure IV, mp 205—206 °C, IR: 1693 (C=O), 973, 963 (=C–H) cm^{-1}.

Found: C, 88.57; H, 4.72%. Calcd for $C_{19}H_{12}O$: C, 89.04; H, 4.72%.

5-(2-Pyrenyl)-2,4-pentadienal (V). A solution of II[4] (4.4 g, 19 mmol) in tetrahydrofuran (50 ml) was added to a solution of Grignard derivative of methoxybutenyne prepared by the reaction of the butenyne (3.2 g, 38.9 mmol) in tetrahydrofuran (12 ml) with ethylmagnesium bromide (from ethyl bromide, 4.3 g and magnesium, 0.70 g in the same solvent, 22 ml). After being stirred overnight at room temperature, ethanol (1.3 ml) and lithium aluminum hydride (1.1 g, 29 mmol) were added and stirred for 1.5 hr. Ethyl acetate (10 ml), water (10 ml) and 2 M sulfuric acid (100 ml) were successively added to the reaction mixture and stirred for 2 hr. The aqueous layer was extracted with tetrahydrofuran, and the extract was combined with the organic layer. Light brown crude crystals, mp 212—217 °C, 3.8 g (64.2%) obtained by evaporation of the combined organic layer, after being washed and dried, were dissolved in benzene and passed through a short column of alumina. Concentration of the filtrate afforded pure V, mp 219 °C, IR: 1673 (C=O), 990 (=C–H) cm^{-1}.

Found: C, 89.17; H, 4.92%. Calcd for $C_{21}H_{14}O$: C, 88.86; H, 5.22%.

3-(2-Pyrenyl)-2-propen-1-ol. To a stirred solution of IV (0.434 g, 1.7 mmol) in a mixture of tetrahydrofuran (50 ml) and methanol (5 ml) was added a solution of sodium borohydride (0.5 g, 13 mmol) in methanol (10 ml). After being stirred for 1 hr at room temperature, dilute hydrochloric acid was added to the reaction mixture, the organic solvent being removed under reduced pressure. The residue was extracted with benzene. The extract, after being washed and dried, was concentrated to give pale yellow crystals, mp 111—118 °C, 0.30 g (quantitative), which were recrystallized from benzene to yield pure propenol, colorless plates, mp 130.5—131.1 °C, IR: 3300—3200 (O–H), 1105 (C–O), 993, 974, 965 (=C–H· cm^{-1},

Found: C, 87.30; H, 5.99%. Calcd for $C_{19}H_{14}O$: C, 87.15; H, 6.02%.

5-(2-Pyrenyl)-2,4-pentadien-1-ol. A solution of sodium borohydride (1.0 g, 27 mmol) in methanol (40 ml) was added to a stirred solution of V (1.5 g, 5.6 mmol) in tetrahydrofuran (100 ml). After being stirred for 2 hr at room temperature, dilute hydrochloric acid and water were successively added to the reaction mixture. Yellow plates deposited, 1.05 g (69.5%), were recrystallized from benzene to give pure pentadienol, yellow plates, mp 175—176 °C, IR: 3300 (O–H), 987 (=C–H) cm^{-1}.

Found: C, 88.47; H, 5.67%. Calcd for $C_{21}H_{16}O$: C, 88.20; H, 5.92%.

3-(2-Pyrenyl)-2-propenyltriphenylphosphonium Bromide. A solution of phosphorus tribromide (0.85 g, 3.0 mmol) in chloroform (15 ml) was added, under cooling on an ice-salt bath, to a solution of 3-(2-pyrenyl)2-propen-1-ol (0.43 g, 1.66 mmol) in the same solvent containing 5 drops of pyridine. After being stirred for further 1 hr at room temperature, the reaction mixture was poured onto ice-water. The organic layer was successively washed with water, dilute hydrochloric acid, and water, and dried. Pale yellow crystals obtained by evaporating the solvent were mixed with triphenylphosphine (0.65 g, 2.4 mmol) in benzene (20 ml) and the mixture was refluxed overnight to give phosphonium bromide, colorless crystals, mp 240—252 °C, 0.338 g (34.9%).

5-(2-Pyrenyl)-2,4-pentadienyltriphenylphosphonium Bromide. Crude bromide obtained as greenish yellow crystals by the reaction of pyrenylpentadienol (0.80 g, 2.94 mmol) with phosphorus tribromide (1.8 g, 6.75 mmol) by the above procedure were mixed with triphenylphosphine (1.3 g, 5.0 mmol) in benzene (50 ml) and the mixture was refluxed for 15 hr to give phosphonium bromide, pale yellow crystals, mp 239—244 °C, 1.4 g (79.8%).

1,2-Di(2-pyrenyl)ethylene (I_1). To a suspension of 2-pyrenylmethyltriphenylphosphonium bromide[6] (0.67 g, 1.2 mmol) in benzene (20 ml) was added phenyllithium (0.88N, 1.4 ml). After being stirred for 20 min at room temperature, a solution of II[4] (0.23 g, 1.0 mmol) in benzene (20 ml) was added to the resulting orange red solution of III, and the mixture was stirred for 24 hr at room temperature. The solvent was removed under reduced pressure and the residue was extracted with hot benzene. Pale greenish yellow needles, mp>360 °C, 0.110 g (25.7%) obtained by cooling the extract were dissolved in hot benzene and passed through a short column of alumina to give pure I_1, greenish yellow plates, mp>360 °C, IR: 1598, 1440, 951, 865, 833, 807, 700 cm^{-1}.

Found: C, 95.39; H, 4.72%. Calcd for $C_{34}H_{20}$: C, 95.30; H, 4.70%.

1,4-Di(2-pyrenyl)-1,3-butadiene (I_2). A solution of 3-(2-pyrenyl)-2-propenal (0.26 g, 1.0 mmol) in benzene (45 ml) was added to a solution of III prepared from 2-pyrenylmethyltriphenylphosphonium bromide[6] (0.67 g, 1.2 mmol) in benzene (20 ml) and phenyllithium (0.73N, 1.6 ml). After the mixture had been stirred for 24 hr at room temperature, the solvent was removed under reduced pressure, and the residue was extracted with hot toluene. Yellow needles, mp 339—340 °C, 0.024 g (5.3%) obtained by concentrating the extract were dissolved in hot toluene, and the hot solution was percolated through a short column of alumina. Pure I_2, pale yellow needles, mp 354—355 °C, IR: 1600, 1440, 974, 870, 835, 818, 700 cm^{-1} was obtained from the filtrate.

Found: C, 94.62; H, 4.76%. Calcd for $C_{36}H_{22}$: C, 95.12; H, 4.88%.

1,6-Di(2-pyrenyl)-1,3,5-hexatriene (I_3). To a solution of III prepared from phosphonium bromide[6] (0.61 g, 1.1 mmol)

in benzene (20 ml) and phenyllithium (0.89N, 1.2 ml) was added a solution of 5-(2-pyrenyl)-2,4-pentadienal (0.24 g, 0.9 mmol) in benzene (70 ml) and the mixture was stirred for 26 hr at room temperature. Crystalline residue obtained by evaporating the solvent was extracted with hot benzene. Yellow fine needles, mp 308—315 °C, 0.035 g (8.1%), obtained on cooling the extract, were dissolved in hot toluene and passed through a short column of alumina to give pure I_3, yellow plates, mp 329—330 °C, IR: 1597, 1440, 980, 875, 870, 833, 804, 700 cm^{-1}.

Found: C, 95.18; H, 5.07%. Calcd for $C_{38}H_{24}$: C, 94.97; H, 5.03%.

1,8-Di(2-pyrenyl)-1,3,5,7-octatetraene (I_4). 2-Pyrenylmethyltriphenylphosphonium bromide[6] (0.67 g, 1.2 mmol) in benzene (20 ml) was treated with phenyllithium (0.88N, 1.4 ml) to give a solution of III. A solution of muconaldehyde (VI, 0.055 g, 0.5 mmol) in benzene (10 ml) was added to the solution of III and the mixture was stirred for 24 hr at room temperature. The solvent was removed under reduced pressure and the residue was digested with hot toluene. Fine orange yellow needles, mp 269—276 °C, 0.109 g (21.5%) obtained by concentrating the extract were dissolved in hot toluene. Percolation of the hot solution through a thin layer of alumina afforded pure I_4, mp 320 °C, IR: 1595, 1440, 992, 878, 853, 833, 810, 700 cm^{-1}.

Found: C, 93.89; H, 5.23%. Calcd for $C_{40}H_{26}$: C, 94.83; H, 5.17%.

1,10-Di(2-pyrenyl)-1,3,5,7,9-decapentaene (I_5). To a dark red solution of VII prepared from 5-(2-pyrenyl)-2,4-pentadienyltriphenylphosphonium bromide (0.283 g, 0.47 mmol) in benzene (25 ml) and phenyllithium (0.73N, 0.7 ml) was added a solution of 5-(2-pyrenyl)-2,4-pentadienal (0.11 g, 0.40 mmol) in the same solvent (65 ml). After being stirred for 24 hr at room temperature, the solvent was removed under reduced pressure. The residue dissolved in hot toluene was passed through a short column of alumina. Concentration of the filtrate afforded pure I_5, orange needles, mp 303 °C, IR: 1595, 1440, 990, 880, 860, 835, 700 cm^{-1}.

Found: C, 94.49; H, 5.37%. Calcd for $C_{42}H_{28}$: C, 94.70; H, 5.30%.

1,12-Di(2-pyrenyl)-1,3,5,7,9,11-dodecahexaene (I_6). A solution of muconaldehyde (VI, 0.0265 g, 0.25 mmol) in benzene (7 ml) was added to a solution of VIII prepared from 3-(2-pyrenyl)-2-propenyltriphenylphosphonium bromide (0.338 g, 0.58 mmol) in benzene (20 ml) and phenyllithium (0.84N, 0.7 ml). After the mixture had been stirred for 22 hr, the solvent was removed under reduced pressure. The residue dissolved in hot toluene was passed through a thin layer of alumina. Concentration of the filtrate yielded pure I_6, orange needles, mp 298—299 °C, 3 mg.

Found: C, 94.06; H, 5.31%. Calcd or $C_{44}H_{30}$: C, 94.59; H, 5.41%.

3-(2-Fluorenyl)-2-propenal (IV'). A mixture of concentrated sulfuric acid (2.4 ml), water (20 ml), dioxane (118 ml) and 1-(2-fluorenyl)-2-propyn-1-ol[8] (5.9 g, 26.8 mmol) was refluxed for 48 hr. Water was added to the reaction mixture and the aqueous layer was extracted with benzene. The combined organic layer, after being washed and dried, was concentrated to give a dark brown liquid. The liquid was triturated with a small amount of ethyl acetate containing a trace of ether to cause crystallization (yellow crystals, mp 97—107 °C, 3.05 g). The filtrate, after being evaporated, was dissolved in benzene and shaken with a saturated sodium hydrogen sulfite solution for 48 hr. Decomposition of sulfite adduct with a dilute sodium hydroxide afforded an additional amount of yellow crystals, mp 100—105 °C, 0.805 g. The combined crystals (3.85 g, 65.2%) were recrystallized from benzene to yield pure IV', mp 114 °C, colorless crystals, IR: 1675 (C=O), 970 (=C–H) cm^{-1}.

Found: C, 86.91; H, 5.42%. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49%.

5-(2-Fluorenyl)-2,4-pentadienal (V'). Methoxybutenyne (3.2 g, 38.9 mmol) in tetrahydrofuran (12 ml) was converted into the Grignard derivative by the reaction with ethylmagnesium bromide in the same solvent (22 ml) (from ethyl bromide, 4.4 g and magnesium, 0.70 g, 28 mg-atom). A solution of II'[5] (3.7 g, 19 mmol) in the same solvent (12 ml) was added to the Grignard reagent and the mixture was stirred for 15 hr at room temperature. Ethanol (1.3 ml) and lithium aluminum hydride (1.1 g, 29 mmol) were added to the reaction mixture. After being stirred for 1 hr at room temperature, water (6 ml) and 2 M sulfuric acid (100 ml) were successively added under ice-cooling, and worked up by the usual way to yield crude V', orange yellow crystals, mp 137—143 °C, 2.4 g (51.3%) which were recrystallized from ethyl acetate, yielding pure V', yellow plates, mp 158—159 °C, IR: 1665 (C=O), 995 (=C–H) cm^{-1}.

Found: C, 87.55; H, 5.76%. Calcd for $C_{18}H_{14}O$: C, 87.88; H, 5.73%.

3-(2-Fluorenyl)-2-propen-1-ol. Treatment of 3-(2-fluorenyl)-2-propenal (0.110 g, 0.5 mmol) with sodium borohydride according to a procedure similar to that for 2-pyrenyl analogue afforded fluorenylpropenol, colorless crystals, mp 133—143 °C, 1.02 g (92.5%), which were recrystallized from benzene to yield pure material, colorless plates, mp 155—156 °C, IR: 3300—3200 (O–H), 1010 (C–O), 995, 968 (=C–H) cm^{-1}.

Found: C, 86.10; H, 6.28%. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35%.

5-(2-Fluorenyl)-2,4-pentadien-1-ol. According to a similar procedure to that for 2-pyrenyl analogue, 5-(2-fluorenyl)-2,4-pentadienal (1.0 g) was reduced with sodium borohydride, yielding fine yellow crystals, mp 106—113 °C, 0.90 g (78.8%).

3-(2-Fluorenyl)-2-propenyltriphenylphosphonium Bromide. Fluorenylpropenol (1.40 g, 6.3 mmol) in chloroform (50 ml) containing 4 drops of pyridine was treated with phosphorus tribromide (1.2 g, 4.4 mmol) in chloroform (20 ml). The reaction of crude bromide in boiling benzene (25 ml) with triphenylphosphine (1.9 g, 7.3 mmol) afforded fine pale yellow crystals, 1.26 g which were recrystallized from ethanol–benzene to give pure phosphonium bromide, colorless crystals, mp 158—159 °C.

Found: C, 76.67; H, 5.42; Br, 12.66%. Calcd for $C_{34}H_{28}BrP \cdot C_6H_6$: C, 76.79; H, 5.48; Br, 12.77%.

5-(2-Fluorenyl)-2,4-pentadienyltriphenylphosphonium Bromide. Fluorenylpentadienol (0.75 g, 3.0 mmol) was converted into bromide by the reaction of phosphorus tribromide (0.41 g, 1.5 mmol) according to a procedure similar to that for pyrenyl analogue. Crude bromide, fine yellow crystals, was mixed with a solution of triphenylphosphine (0.95 g, 3.6 mmol) in benzene (40 ml) and the mixture was refluxed for 9.5 hr. The reaction mixture was allowed to stand overnight at room temperature to yield phosphonium bromide, fine colorless crystals, mp 243—257 °C, 0.24 g (18.0%).

1,2-Di(2-fluorenyl)ethylene (I_1'). To a suspension of 2-fluorenylmethyltriphenylphosphonium bromide[8] (0.78 g, 1.2 mmol) in benzece (25 ml) was added phenyllithium (0.73N, 1.8 ml) and the mixture was stirred for 30 min at room temperature. To the resulting solution of III' was added II'[9] (0.19 g, 1.0 mmol) in benzene (10 ml). After being stirred for 26 hr at room temperature, the solvent was removed under reduced pressure. Crude crystals, colorless plates, mp 268—300 °C, 0.102 g (29.6%) obtained by extraction of the residue with hot benzene followed by concentration were

dissolved in hot benzene and passed through a short column of alumina. Pure I_1', colorless plates, mp 304—305 °C, IR: 1454, 1428, 1395, 967, 870, 767, 732 cm^{-1} was obtained from the filtrate.

Found: C, 94.34; H, 5.66%. Calcd for $C_{28}H_{20}$: C, 94.45; H, 5.59%.

1,4-Di(2-fluorenyl)-1,3-butadiene (I_2'). To a benzene solution of III′ prepared from 2-fluorenylmethyltriphenylphosphonium bromide (0.73 g, 1.5 mmol) and phenyllithium (0.48N, 3.1 ml) was added a solution of IV′ (0.22 g, 1.0 mmol) in the same solvent (15 ml). After the mixture had been stirred for 40 hr at room temperature, the solvent was removed under reduced pressure and the residue was extracted with hot benzene. Yellow crystals, mp 297—300 °C, 0.124 g (32.4%) obtained by concentrating the extract were dissolved in benzene and percolated through a thin layer of alumina to give pure I_2', yellow plates, mp 301—302 °C, IR: 1453, 1418, 1395, 990, 878, 763, 730 cm^{-1}.

Found: C, 94.41; H, 5.75%. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%.

Concentration of mother liquor of the first crop of crystals afforded the second crop of I_2', yellow plates, mp 267—277 °C, 0.147 g (36%).

1,6-Di(2-fluorenyl)-1,3,5-hexatriene (I_3'). A solution of V′ (0.36 g, 1.5 mmol) in benzene (26 ml) was added to a solution of III′ prepared from phosphonium bromide (0.935 g, 1.8 mmol) and phenyllithium (0.47N, 3.8 ml) and the mixture was stirred for 46 hr. The residue obtained by removing the solvent under reduced pressure was extracted with hot benzene and toluene. The extract was concentrated to give yellow fine crystals, mp 272—286 °C, 0.519 g (84.5%) which were dissolved in hot toluene and percolated through a short column of alumina to give pure I_3', yellow plates, mp 296—297 °C, IR: 1452, 1425, 1395, 1000, 880, 764, 730 cm^{-1}.

Found: C, 93.74; H, 5.93%. Calcd for $C_{32}H_{24}$: C, 94.08; H, 5.92%.

1,8-Di(2-fluorenyl)-1,3,5,7-octatetraene (I_4'). A solution of III′ was prepared from phosphonium bromide (0.625 g, 1.2 mmol) in benzene (20 ml) and phenyllithium (0.50N, 2.4 ml). A solution of VI (0.055 g, 0.5 mmol) in the same solvent (15 ml) was added to the solution of III′. After being stirred for 26 hr at room temperature, the solvent was removed under reduced pressure. Yellow fine crystals, mp 279—287 °C, 0.205 g (94.3%) obtained by extracting the residue with hot toluene followed by concentration were dissolved in hot toluene and passed through a short column of alumina, yielding pure I_4', yellow needles, mp 289—291 °C, IR: 1450, 1395, 1005, 880, 830, 760 cm^{-1}.

Found: C, 93.72; H, 6.03%. Calcd for $C_{34}H_{26}$: C, 93.97; H, 6.03%.

1,10-Di(2-fluorenyl)-1,3,5,7,9-decapentaene (I_5'). A solution of V′ (0.0985 g, 0.40 mmol) in benzene (10 ml) was mixed with a solution of VII′ in the same solvent (15 ml) prepared from 5-(2-fluorenyl)-2,4-pentadienyltriphenylphosphonium bromide (0.240 g, 0.54 mmol) and phenyllithium (0.58N, 0.9 ml). After the mixture had been stirred for 28 hr at room temperature, the solvent was removed under reduced pressure and the residue was extracted with hot toluene. Yellow fine crystals, mp 268—276 °C, 0.0684 g (37.2%) obtained by concentrating the extract were dissolved in hot toluene. Percolation of the hot solution through a thin layer of alumina afforded pure I_5', fine yellow needles, mp 277 °C, IR: 1453, 1395, 1005, 882, 836, 817, 760 cm^{-1}.

Found: C, 93.52; H, 6.03%. Calcd for $C_{36}H_{28}$: C, 93.87; H, 6.13%.

1,12-Di(2-fluorenyl)-1,3,5,7,9,11-dodecahexaene (I_6'). To a solution of VIII′ prepared from 3-(2-fluorenyl)-2-propenyltriphenylphosphonium bromide (0.656 g, 1.2 mmol) in benzene (20 ml) and phenyllithium (1.04N, 1.1 ml) was added a solution of VI (0.055 g, 0.5 mmol) in the same solvent (7 ml) and the mixture was stirred for 20 hr at room temperature. Orange powder obtained by evaporating the solvent under reduced pressure was digested with hot toluene. Concentration of the extract afforded orange fine crystals, mp 267—279 °C, 0.104 g (21.4%) which were dissolved in hot toluene and passed through a short column of alumina. Pure I_6', fine orange crystals, mp 298—300 °C, IR: 1452, 1395, 1005, 882, 760 cm^{-1} was obtained from the filtrate.

Found: C, 93.26; H, 6.20%. Calcd for $C_{38}H_{30}$: C, 93.79; H, 6.21%.