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Linear Conjugated Systems Bearing Aromatic Terminal Groups. X.[1] Syntheses and Electronic Spectra of α,ω-Di-1-naphthyl- and α,ω-Di-2-naphthylpolyenes

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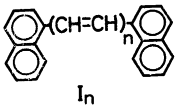
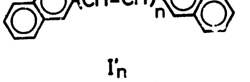
Syntheses of di-1-naphthyl- and di-2-naphthylpolyenes (I_n, $n=1$—4,6 and I_n', $n=1$—6) have been carried out by the Wittig reaction. Naphthaldehydes (III and III′), 3-naphthyl-2-propenals (V and V′), 5-naphthyl-2,4-pentadienals (VI and VI′) and muconic aldehyde were used as carbonyl components. Naphthylmethyltriphenylphosphonium halides (IV and IV′), 3-naphthyl-2-propenyltriphenylphosphonium bromides (XI and XI′) and 5-(2-naphthyl)-2,4-pentadienyltriphenylphosphonium bromide (XII′) were synthesized and converted into the corresponding phosphoranes by reaction with phenyllithium. The reaction of carbonyl moiety with phosphorane by a proper combination afforded dinaphthylpolyenes (I_n and I_n'). The electronic spectra of di-1-naphthylpolyenes (I_n) showed broad and structureless absorption curves. In contrast, the absorption curves of di-2-naphthylpolyenes (I_n') exhibited a distinct vibrational fine structure. It was found that the bathochromic shift of the longest-wavelength peak (λ_{max}) along with the increase of the number of double bond (n) can be expressed by the following empirical formula:

$$\lambda_{max}=45.4n^{0.7}+302 \text{ (nm in tetrahydrofuran)}$$

The electronic spectra of α,ω-di-1-anthrylpolyenes[1] suggest that the aromatic terminal groups exert an appreciable effect on the electronic excitation of polyene chromophore. However, the spectral regularity of dianthrylpolyenes could not be discussed in detail owing to the broad and structureless bands in the longest-wavelength region. Preparation of other di-



I_n
n=1~4, 6



I_n'
n=1~6

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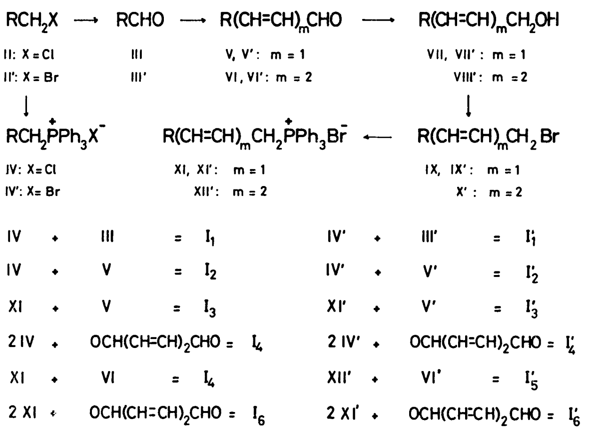
[1] Part IX of this series: Y. Takeuchi, S. Akiyama, and M. Nakagawa, This Bulletin, **45**, 3183 (1972).

arylpolyenes was desirable to get further information on the role of aromatic terminal groups in spectral regularity. This paper deals with the syntheses and electronic spectral properties of di-1-naphthyl- and di-2-naphthylpolyenes (I_n and I_n'), and the spectral regularity of the latter.

Syntheses. Syntheses of di-1-naphthyl- and di-2-naphthylpolyenes (I_n and I_n') have been carried out according to the reaction sequence outlined in the Scheme. 1-Chloromethyl-[2] and 2-bromomethylnaphthalenes were converted into the corresponding naphthylmethyltriphenylphosphonium halides (IV and IV′). 3-(1-Naphthyl)-2-propenal (V) was prepared by the Meyer-Schuster rearrangement of 1-naphthylethynylcarbinol.[3] 2-Naphthaldehyde (III′) prepared from 2-hydroxymethylnaphthalene was converted into 3-(2-naphthyl)-2-propenal (V′) by a modified J. F. Arens and van Dorp method,[4] since the Meyer-Schuster rearrangement of 2-naphthylethynylcarbinol gave less satisfactory results. Naphthyl-2-propen-1-ols (VII and VII′) obtained by the reduction of naphthyl-2-propenals (V and V′) by means of sodium borohydride were converted into unstable allylic bromides (IX and IX′). IX and IX′ afforded naphthylpropenyltriphenylphosphonium bromides (XI and XI′) on treatment with triphenylphosphine. The reaction of Grignard derivative of methoxybutenyne[5] with 1- or 2-naphthaldehyde (III or III′) followed by reduction with lithium aluminum hydride and treatment with acid yielded 5-(1-naphthyl)- or 5-(2-naphthyl)-2,4-pentadienal (VI or VI′). 5-(2-Naphthyl)-2,4-pentadien-1-ol (VIII′) was prepared by the reduction of 2-naphthylpentadienal (VI′) with sodium borohydride. 5-(2-Naphthyl)-pentadienyltriphenylphosphonium bromide (XII′) was obtained from 2-naphthylpentadienol (VIII) *via* bromide (X′).



Scheme. Syntheses of dinaphthylpolyenes (I_n and I_n').
R means a 1- or 2-naphthyl group, and the prime on the Roman figure indicates that R is 2-naphthyl group.

The Wittig reaction between the aldehyde component (III, III′, V, V′, VI, and VI′) and the phosphorane moiety obtained from phosphonium halide (IV, IV′, XI, XI′, and XII′) according to the combination shown in the Scheme gave α,ω-dinaphthylpolyenes (I_{1-4}, I'_{1-3} and I'_5). The reaction of muconic aldehyde with phosphoranes derived from IV, IV′, XI, and XI′ afforded dinaphthyloctatetraenes (I_4 and I'_4) and dinaphthyldodecahexaenes (I_6 and I'_6), respectively. The 2-naphthyl series gave a lower yield than the 1-naphthyl series in the Wittig reaction (Table 1). Di-1-naphthylpolyenes (I_{1-4} and I_6) were found to be stable against heat and light and showed definite melting points. Di-2-naphthylpolyenes (I'_{1-6}) exhibited much higher melting points than those of 1-naphthyl analogues. Some of them decomposed on attempted melting point determination. Di-1-naphthylpolyenes (I_n) were found more soluble than di-2-naphthylpolyenes (I_n') in organic solvents. Decrease of solubility due to increase in the length of polyene chain was observed in both series. The color of crystals, melting points and the wave number of IR absorption in the region of C–H out-of-plane defor-

TABLE 1. PHYSICAL PROPERTIES AND YIELDS OF DINAPHTHYLPOLYENES (I_n and I_n')

n	Di-1-naphthylpolyenes (I_n)				Di-2-naphthylpolyenes (I_n')			
	Color of crystals	Mp(°C)	δ(cm^{-1})	Yield(%)	Color of crystals	Mp(°C)	δ(cm^{-1})	Yield(%)
1	pale yellow	160—162	$\underline{952}$[a], 970 975	34	pale yellow	258—259	956	74
2	pale yellow	173—173.5	978	71	pale yellow	271—273	$\underline{997}$, 967 953	32
3	yellow	217—219	1000	82	yellow	251—262 (decomp.)	$\underline{1002}$, 963	36
4	orange yellow	225	1005	*ca.* 100	yellow	266—267	$\underline{1005}$, 982	92
5	—		—	—	orange yellow	268—269 (decomp.)	1007, $\underline{984}$, 964	33
6	orange	240—242	1010	*ca.* 100	orange	265—273 (decomp.)	$\underline{1000}$, 963	35

a) The wave numbers of the strongest absorptions are underlined.

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[2] O. Grumitt and A. Buck, "Organic Syntheses," Coll. Vol. III, p. 195 (1955).

[3] I. Iwai and Y. Okajima, *Yakugaku Zasshi*, **79**, 1284 (1959).

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

[5] Cf., D. Marshall and M. C. Whiting, *J. Chem. Soc.*, **1956**, 4082.

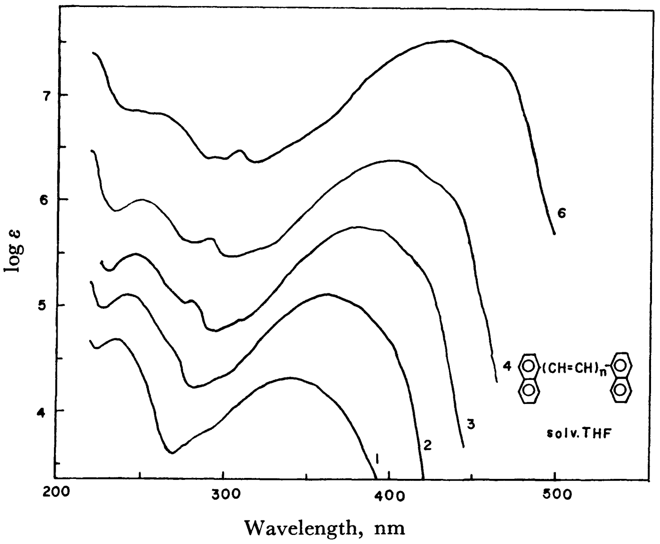

Fig. 1. Absorption curves of di-1-naphthylpolyenes (I_n). Each curve, except for the lowest one, has been displaced upward by a 0.5 log ε unit increment from one immediately below it. The curve of I_6 was displaced upward by a 1.0 log ε unit increment from that of I_4.

TABLE 2. ELECTRONIC SPECTRAL DATA OF I_n

n	λ_{max} (ε) in nm in tetrahydrofuran				
1	237 (47,100)	341 (20,300)			
2	242.3 (39,400)	270* (12,000)	362.5 (38,000)		
3	247.5 (30,700)	281.5 (11,400)	381 (52,900)		
4	252.5 (30,900)	280 (12,800)	292 (13,800)	406.5 (52,900)	
6	247.5 (18,500)	260 (20,700)	296.5 (10,100)	299 (11,200)	436.5 (107,700)

An asterisk indicates shoulder.

mation (δ) of *trans*-double bond are given in Table 1.

Electronic Spectra. The absorption curves and numerical data of electronic spectra of both series of dinaphthylpolyenes (I_n and I_n') are shown in Figs. 1 and 2 and Tables 2 and 3. Di-1-naphthylpolyenes (I_n) show broad and structureless intense bands in the long-wavelength region indicating the presence of steric interference between hydrogen atoms of ethylenic bonds and those of *peri*- and *o*-positions of naphthalene nuclei. The intense absorption bands in the

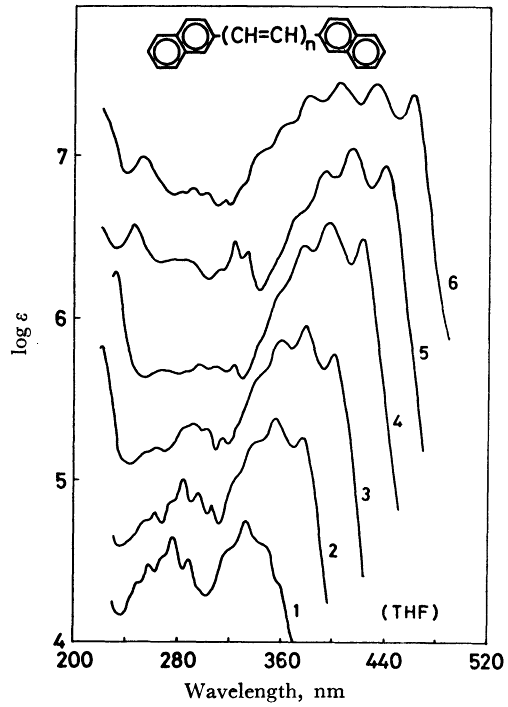

Fig. 2. Absorption curves of di-2-naphthylpolyenes (I_n'). Each curve, except for the lowest one, has been displaced upward by a 0.5 log ε unit increment from one immediately below it.

TABLE 3. ELECTRONIC SPECTRAL DATA OF I_n'

n	λ_{max} (ε) in nm in tetrahydrofuran									
1	249 (23,200)	257.5 (30,000)	267.7 (33,100)	276 (44,600)	287.5 (33,100)	297* (20,900)	320* (37,700)	333 (51,900)	347* (39,400)	357* (23,170)
2	240* (13,500)	253 (17,600)	261.7 (19,400)	275 (24,000)	284.5 (31,600)	295 (26,700)	305.8 (22,000)	342 (55,600)	356 (76,200)	377 (59,300)
3	222 (66,700)	256 (14,500)	262 (15,500)	265 (15,700)	284.5 (20,700)	291 (22,000)	301.5 (20,300)	315 (18,400)	343$^{a)}$ (43,500)	360 (69,900)
	379 (88,700)	401 (86,200)								
4	232 (62,700)	268 (15,000)	286 (14,700)	296.5 (16,600)	308.5 (16,600)	323.5 (16,500)	379 (86,100)	399 (123,000)	423 (104,000)	
5	245.5 (37,500)	273 (23,200)	283 (23,200)	292* (21,600)	312 (20,400)	324.5 (30,000)	333.5 (25,200)	373* (43,700)	393 (79,900)	415 (110,700)
	441 (88,000)									
6	251.5 (30,200)	265* (23,000)	280.5 (10,000)	290 (23,000)	301.5 (20,900)	314.5 (19,300)	340$^{a)}$ (35,300)	347 (36,900)	362* (46,900)	382 (71,700)
	404 (88,400)	433 (86,800)	462 (71,700)							

An asterisk indicates shoulder.

long-wavelength region in the electronic spectra of di-2-naphthylpolyenes (I_n') show a well-defined vibrational fine structure (Fig. 2). The long-wavelength band can be considered to arise from an interaction of ^1L_a band of naphthalene with polyene chromophore. The shoulder at longest-wavelength (357 nm) observed in the spectrum of di-2-naphthylethylene (I_1') seems to be related to the ^1L_b band of naphthalene nucleus. In the higher members (I'_{2-6}), the band related to ^1L_b seems to be submerged under intense ^1L_a bands. The spacings between the longest-wavelength sub-bands (λ_I) and the next longest-wavelength sub-bands (λ_{II}) are found to be 1400—1500 cm^{-1} except for di-2-naphthylethylene (I'_1) (Table 4).

Table 4. Spacing of vibrational fine structure of I'_n (cm^{-1})

n	1	2	3	4	5	6
	1210	1560	1450	1420	1420	1440

Regularity of the electronic spectra of di-1-naphthylpolyenes (I_n) could not be discussed owing to the broad and structureless features of the longest-wavelength bands. On the other hand, well-developed sub-peaks in the spectra of I_n' made it possible to determine the exact location of maxima at long-wavelength region. We consider the longest-wavelength bands of diarylpolyenes to shift linearly with the x-th power of the number of double bond (n), and the wavelength of maxima (λ_I and λ_{II}) might be expressed by the empirical formula

$$\lambda = A_n{}^x + B$$

just as in the case of diarylpoly-ynes. The plots of λ_I and λ_{II} *versus* $n^{0.7}$ gave good straight lines (Fig. 3).

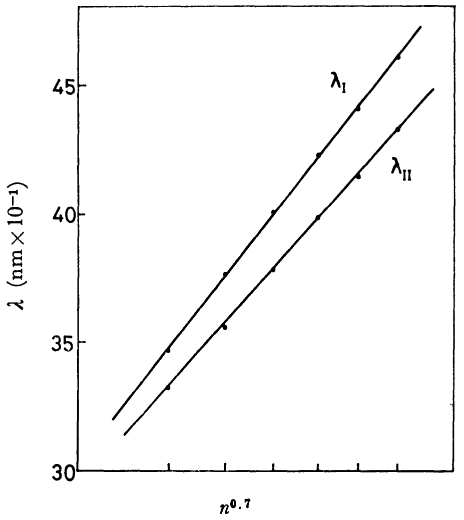

Fig. 3. Plot of λ_{max} *vs.* $n^{0.7}$ for di-2-naphthylpolyenes (I_n').
λ_I: longest-wavelength maxima
λ_{II}: second-longest-wavelength maxima

The linear relationships can be expressed by the following empirical formulas:

$\lambda_I = 45.4\, n^{0.7} + 302$ (nm in tetrahydrofuran)

$\lambda_{II} = 40.0\, n^{0.7} + 292$ (nm in tetrahydrofuran)

The calculated values show excellent agreement with the observed values (Table 5). The spectral regularity of 2,2′-dinaphthylpoly-ynes, acetylenic analogues of I_n', could be expressed by the empirical formula, $\lambda = 15.5\, n^{1.3} + 319$ (nm in tetrahydrofuran).[6,7] It should be noted that the B-values of both series are found to be nearly the same. However, the coefficient A of di-2-naphthylpolyenes (I_n') is much larger than that of 2,2′-dinaphthylpoly-yens.

Table 5. Observed and calculated λ_I and λ_{II} of I_n'

	n	1	2	3	4	4	6
λ_I	Calcd	347	377	401	423	441	462
	Obsd	347	375.5	400	422	442	461
	$\Delta\lambda$	0	1.5	1	1	−1	1
λ_{II}	Calcd	333	356	379	399	415	433
	Obsd	332	357	378	398	416	432
	$\Delta\lambda$	1	−1	1	1	−1	1

Experimental

All the melting points are uncorrected. The electronic spectra were measured with a Hitachi EPS-3T spectrophotometer at room temperature employing a well-matched pair of 1-cm quartz cells, otherwise stated. The IR spectra were obtained on a Hitachi EPI-2 infrared spectrophotometer by the KBr-disk method. Evaporation of solvent was performed under reduced pressure.

1-Naphthylmethyltriphenylphosphonium Chloride (IV). A solution of 1-chloromethylnaphthalene[2] (II, 12.3 g, 0.07 mol) and triphenylphosphine (20.2 g, 0.077 mol) in xylene (100 m*l*) was refluxed to yield a colorless precipitate. The precipitate was filtered and washed with benzene, yielding colorless crystalline powder (33.1 g, quantitative). The material was recrystallized from ethanol to afford IV as colorless plates, mp 292—301°C (decomp.).

Found: C, 79.62; H, 5.38; Cl, 8.15%. Calcd for $C_{29}H_{24}PCl$: C, 79.35; H, 5.51; Cl, 8.08%.

3-(1-Naphthyl)-2-propen-1-ol (VII). A solution of sodium borohydride (1.5 g, 0.04 mol) and 3-(1-naphthyl)-2-propenal (V, 4.0 g, 0.022 mol) prepared by the Meyer-Schuster rearrangement of 1-(1-naphthyl)-2-propyn-1-ol,[3] in 2-propanol (200 m*l*) was refluxed for 2 hr. The residue obtained by concentration of the reaction mixture was treated with dilute hydrochloric acid and extracted with ether. After washing and drying, the extract was evaporated to yield crude VII (3.08 g, 76.2%) as a brown liquid. The crude alcohol (VII) was subjected to the following reaction.

3-(1-Naphthyl)-2-propenyl Bromide (IX). To a solution of the crude alcohol (VII, 3.08 g, 0.017 mol) in chloroform (50 m*l*) containing 10 drops of pyridine was added a solution of phosphorus tribromide (2.16 g, 0.008 mol) in chloroform (20 m*l*) over a 30-min period. After stirring for 20 hr, cracked ice was added to the chilled reaction mixture and then the mixture was poured onto ice-water. The aqueous layer was extracted with chloroform. The extract was successively washed with water, a saturated sodium hydrogencarbonate solution and water, and dried. The residue obtained by evaporation of the extract was dissolved in carbon

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[6] K. Nakasuji, S. Akiyama, K. Akashi, and M. Nakagawa, This Bulletin, **43**, 3567 (1970).

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

tetrachloride and filtered. The crystals deposited on concentration of the filtrate were washed with the same solvent to afford IX as brownish yellow crystals, mp 56—59°C, 4.09 g (quantitative).

3-(1-Naphthyl)-2-propenyltriphenylphosphonium Bromide (XI). A solution of bromide (IX, 4.09 g, 0.021 mol) and triphenylphosphine (5.56 g, 0.021 mol) in toluene (70 m*l*) was refluxed for 17 hr. Pale yellow solid deposited was collected by filtration and washed with toluene. The crude material 8.21 g, 98.1%) was recrystallized twice from ethanol to give pure phosphonium bromide (XI), mp 238—240°C,

Found: C, 73.28; H, 5.25; Br, 15.29%. Calcd for $C_{31}H_{26}PBr$: C, 73.09; H, 5.14; Br, 15.68%.

5-(1-Naphthyl)-2,4-pentadienal (VI). To a stirred solution of 4-methoxy-3-buten-1-yne (1.58 g, 0.019 mol) in tetrahydrofuran (10 m*l*) maintained at 38—40°C was added over a 30-min period a solution of ethylmagnesium bromide in the same solvent (20 m*l*) [prepared from ethyl bromide, 2.8 g (0.026 mol) and magnesium, 0.31 g (0.013 g-atom)] under nitrogen atmosphere. After stirring for further 30 min at room temperature, the mixture was chilled in an ice-salt bath and a solution of 1-naphthaldehyde (III, 1.0 g, 0.0064 mol) in tetrahydrofuran (20 m*l*) was added over a 25-min period. Stirring was continued overnight. A saturated solution of ammonium chloride (50 m*l*) was added to the reaction mixture under cooling with an ice-salt bath. The aqueous layer was extracted with ether. The combined organic layer was dried and evaporated to give a red liquid. Crude 1-(1-naphthyl)-5-methoxy-4-penten-2-yn-1-ol thus obtained was dissolved in ether (20 m*l*). The ethereal solution was added over a 40-min period to a stirred solution of lithium aluminum hydride (0.72 g, 0.019 mol) in ether (20 m*l*) under cooling in an ice-salt bath. After further stirring for 6.5 hr at room temperature, a mixture of ethyl acetate (5 m*l*) and ether (6 m*l*) and then ethyl acetate (3.5 m*l*), water (3 m*l*) and 4 N sulfuric acid (27 m*l*) were added successively to the ice-cooled reaction mixture. After being stirred overnight at room temperature, the aqueous layer was extracted with ether. The combined ethereal solution was washed successively with a solution of sodium hydrogencarbonate and water, and dried. Crude 1-naphthylpentadienal (VI, 1.108 g) was obtained as brownish liquid on evaporation of the solvent. This material was subjected to chromatography on silica gel and used in the subsequent reaction.

2-Hydroxymethylnaphthalene. To a refluxing solution of lithium aluminum hydride (6.50 g, 0.171 mol) in ether (200 m*l*) was added a solution of methyl 2-naphthoate (32.8 g, 0.171 mol) in ether (200 m*l*) and tetrahydrofuran (50 m*l*) over a period of 30 min. After the mixture had been stirred for 3 hr under reflux, methanol (60 m*l*) was added under cooling in an ice-bath and stirring was continued overnight. A saturated solution of ammonium chloride containing hydrochloric acid was added to the reaction mixture. The aqueous layer was extracted with ether. The combined organic layer was washed successively with aqueous sodium carbonate solution and water, and dried. Colorless crystals (27.1 g, 97.1%) obtained by evaporating the solvent were recrystalized from ethanol to give pure 2-hydroxymethylnaphthalene, mp 80—82°C (lit,[8] mp 80—80.5°C).

2-Naphthaldehyde (III′). A solution of 2-hydroxymethylnaphthalene (15.8 g, 0.10 mol) in pyridine (40 m*l*) was added to an ice-cooled suspension of chromium trioxide-pyridine complex in pyridine [prepared from chromium trioxide, (31.5 g, 0.30 mol) and pyridine (350 m*l*)] and kept at the same temperature for 1 hr. The reaction mixture was then allowed to stand at room temperature for 2 hr, and poured onto water and extracted with ether (1.5 *l*). The extract was washed successively with 10% hydrochloric acid, water, 10% aqueous sodium carbonate solution and water, and dried. Colorless crystals (14.8 g, 94.9%) obtained by evaporation of the solvent were recrystallized from carbon tetrachloride and then from ethanol, yielding pure III′, mp 60—61°C (lit,[9] 59—60°C).

2-Bromomethylnaphthalene (II′). To an ice-cooled and stirred solution of 2-hydroxymethylnaphthalene (5.0 g, 0.032 mol) in chloroform (70 m*l*) containing 1 m*l* of pyridine was added dropwise a solution of phosphorus tribromide (9.6 g, 0.035 mol) in chloroform (15 m*l*). After stirring for 1 hr at room temperature, crushed ice was added to the reaction mixture under ice-cooling and the mixture was then poured onto ice-water. The aqueous layer was extracted with chloroform. The combined chloroform layer was washed successively with sodium hydrogencarbonate solution and water, and dried. Evaporation of the solvent afforded colorless crystals, 6.1 g (87.1%) which were recrystallized from ethanol to give pure II′, mp 53—55°C (lit, 48°C[10], 53—56°C[11]).

2-Naphthylmethyltriphenylphosphonium Bromide (IV′). A solution of triphenylphosphine (6.71 g, 0.0256 mol) in benzene (100 m*l*) was added to a solution of 2-bromomethylnaphthalene (II′, 5.60 g, 0.0253 mol) in benzene (100 m*l*). After the mixture had been stirred under reflux for 4.5 hr, the solid deposited was collected and washed with benzene, yielding colorless crystals, 11.4 g (93.4%). Recrystallization of the crystals from ethanol yielded pure IV′, mp 251—252°C lit,[12] mp 248—251°C (decomp.)).

3-(2-Naphthyl)-2-propenal (V′). *(a) By the Meyer-Schuster Rearrangement*: To an ice-cooled and stirred solution of ethynylmagnesium bromide in tetrahydrofuran (70 m*l*) [prepared from ethyl bromide, 7.0 g (0.064 mol), magnesium, 1.2 g (0.05 g-atom) and excess acetylene][13] was added a solution of 2-naphthaldehyde (III′, 5.0 g, 0.032 mol) in the same solvent (10 m*l*). The mixture was stirred overnight under cooling in an ice-bath. The reaction mixture was poured onto a saturated solution of ammonium chloride (150 m*l*). The aqueous layer was extracted with ether (200 m*l*). The combined organic layer was dried and evaporated. The residue was dissolved in benzene and passed through a short column of alumina (10 g). 1-(2-Naphthyl)-2-propyn-1-ol was obtained as pale yellow crystals (6.1 g) on concentration of the filtrate. The crude carbinol was dissolved in a mixture of dioxane (150 m*l*), water (25 m*l*) and concentrated sulfuric acid (3 m*l*) and the mixture was refluxed for 30 hr. The mixture was then poured onto water (280 m*l*) and extracted with benzene (300 m*l*). The extract was washed successively with 10% aqueous solution of sodium hydrogencarbonate (50 m*l*) and water (100 m*l*) and dried. Brown crystals obtained by evaporation of the solvent were dissolved in ether-benzene and the solution was stirred with a saturated solution of sodium hydrogensulfite for 3 hr to give sulfite adduct of V′. The adduct deposited was collected and decomposed with a dilute sodium hydroxide solu-

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8) E. Bamberger and O. Boekmann, *Ber.*, **20**, 1115 (1887).

9) E. B. Hershberg and J. Cason, "Organic Syntheses," Coll. Vol. III, p. 627 (1955).

10) P. Mamalis, J. Green, and D. McHale, *J. Chem. Soc.*, **1960**, 229.

11) O. A. Pintado, *Rec. Fac. Cienc. Quim. Univ. Nacl. La Plata*, **29**, 53 (1955—56), *Chem. Abstr.*, **53**, 264^a (1959).

12) J. P. Geert and R. H. Martin, *Bull. Soc. Chim. Belges*, **69**, 563 (1960).

13) E. R. H. Jones, L. Skatteböl, and M. C. Whiting, *J. Chem. Soc.*, **1956**, 4765.

tion. 2-Naphthylpropenal (V′) liberated was taken up in benzene. After washing and drying, the benzene solution was evaporated. The residue redissolved in benzene (50 m*l*) was passed through a thin layer of alumina (4 g). Evaporation of the filtrate gave pure V′ as pale yellow crystals, mp 119—122°C, 1.26 g (21.6%).

(b) By the Modified Arens and van Dorp Method: To a stirred solution of lithium amide [from lithium (2.1 g, 0.303 g-atom)] in liquid ammonia (160 m*l*) was added over a 20-min period a solution of 2-chlorovinyl ethyl ether (16.52 g, 0.16 mol) in tetrahydrofuran (15 m*l*) under cooling in a dry ice-ethanol bath, and the mixture was stirred for further 1.5 hr at −60°C. To a solution of lithium ethoxyacetylide thus prepared was added a solution of 2-naphthaldehyde (III′, 5.95 g, 0.038 mol) in tetrahydrofuran (50 m*l*) over a period of 30 min. After the mixture had been stirred overnight at −40—30°C, ammonium chloride (18 g) was added to the mixture under cooling in a dry ice-ethanol bath. Stirring was continued for 15 min at −60°C. Ammonia was then allowed to evaporate. The residue was mixed with a saturated ammonium chloride solution (200 m*l*) and the organic layer was separated. The aqueous layer was extracted with ether (500 m*l*). The combined organic layer was dried and evaporated to yield a red liquid. A benzene solution of the red liquid was passed through a short column of alumina (5 g). The reddish liquid obtained by evaporation of the filtrate was dissolved in ether (30 m*l*). The ethereal solution was added to an ice-cooled solution of lithium aluminum hydride (2.01 g, 0.053 mol) in ether (70 m*l*) and stirring was continued overnight at room temperature. Ethyl acetate (10 m*l*) and 6 N sulfuric acid (100 m*l*) were then added dropwise in the ice-cooled reaction mixture and stirring was continued for 7 hr at room temperature. The organic layer was separated and the aqueous layer was extracted with ether and then with benzene. After washing and drying, the combined organic layer gave orange yellow crystals on evaporation of the solvent. The filtrate obtained by percolation of a benzene solution of the crude crystals through a column of alumina (15 g) was concentrated to yield 2-naphthylpropenal (V′, 4.5 g, 64.8%) which was recrystallized from ethanol to yield pure V′, pale yellow crystals, mp 122—124°C (lit, mp 118—119°C[14]; mp 125°C[15]).

3-(2-Naphthyl)-2-propen-1-ol (VII′). To a solution of 2-naphthylpropenal (V′, 1.91 g, 0.0105 mol) in tetrahydrofuran (50 m*l*) was added sodium borohydride (0.48 g, 0.0127 mol) and the mixture was refluxed for 1 hr under stirring. The reaction mixture was concentrated, treated with dilute hydrochloric acid and extracted with benzene. After washing and drying, the extract was evaporated to yield yellow crystals, 1.83 g (94.8%) which were recrystallized from carbon tetrachloride, thus affording pure VII′, mp 103—105°C.

Found: C, 84.43; H, 6.44%. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57%.

3-(2-Naphthyl)-2-propenyl Bromide (IX′). To an ice-cooled solution of 2-naphthylpropenol (VII′, 0.96 g, 0.0052 mol) in chloroform (30 m*l*) containing pyridine (1 m*l*) was added dropwise a solution of phosphorus tribromide (1.42 g, 0.0052 mol) in chloroform (10 m*l*). The mixture was stirred for 1 hr at 10°C. Cracked ice was then added to the reaction mixture under ice-cooling. After most of the organic solvent has been removed, the mixture was poured onto water and extracted with benzene. The extract, after washing and drying, was concentrated to afford IX′ as colorless crystals, 0.9 g (70%). This material was used without further purification in the following reaction.

3-(2-Naphthyl)-2-propenyltriphenylphosphonium Bromide (XI′). A solution of 2-naphthylpropenyl bromide (IX′, 0.9 g, 0.0036 mol) and triphenylphosphine (0.91 g, 0.0037 mol) in benzene (50 m*l*) was stirred for 48 hr at room temperature. Colorless crystals deposited (1.478 g, 80.0%) were recrystallized from aqueous ethanol to give colorless plates, mp 235—236°C. An analytical specimen was prepared on drying the crystals at 130°C for 6 hr *in vacuo*.

Found: C, 73.50; H, 5.31; Br, 15.54%. Calcd for $C_{31}H_{26}BrP$: C, 73.09; H, 5.14; Br, 15.69%.

5-(2-Naphthyl)-2,4-pentadienal (VI′). To a solution of ethylmagnesium bromide (0.04 mol) in tetrahydrofuran (40 m*l*) was added a solution of 4-methoxy-3-buten-1-yne (4.45 g, 0.054 mol) in the same solvent (30 m*l*) under nitrogen atmosphere at 40°C. After the evolution of ethane subsided, 2-naphthaldehyde (III′, 5.0 g, 0.032 mol) in tetrahydrofuran (30 m*l*) was added dropwise to the ice-cooled reaction mixture. After stirring overnight, the reaction mixture was poured onto an ice-cooled saturated solution of ammonium chloride (150 m*l*). The aqueous layer was extracted with ether. The extract was combined with the organic layer and dried. The residue obtained by evaporation of the solvent was dissolved in benzene and passed through a short column of alumina. Evaporation of the filtrate gave a reddish liquid which was dissolved in ether (50 m*l*). The ethereal solution was added dropwise to an ice-cooled and stirred solution of lithium aluminum hydride (1.53 g, 0.0404 mol) in ether (100 m*l*) and the mixture was stirred for 2 hr at 18°C. To this were added ethyl acetate (20 m*l*, 0.20 mol) and, after 30 min, 9 N sulfuric acid (90 m*l*). After being stirred overnight, the aqueous layer was extracted with benzene. The combined organic layer was worked up according to the usual manner and evaporated to give yellowish brown crystals, 3.64 g (54.6%). The crystals were recrystallized from carbon tetrachloride to yield pure 2-naphthylpentadienal (VI′), mp 135—137°C.

Found: C, 86.11; H, 5.78%. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81%.

5-(2-Naphthyl)-2,4-pentadien-1-ol (VIII′). To a suspension of finely powdered sodium borohydride (0.36 g, 0.0096 mol) in a mixture of tetrahydrofuran (90 m*l*) and ethanol (10 m*l*) was added a solution of 2-naphthylpentadienal (VI′, 2.0 g, 0.0096 mol) in tetrahydrofuran (30 m*l*). After the mixture had been refluxed for 1 hr, stirring was continued for 1 hr at room temperature. The reaction mixture was concentrated to one-third its original volume and mixed with dilute hydrochloric acid. The aqueous layer was extracted with benzene. After washing and drying, the combined organic layer was evaporated to give VIII′ as yellow crystals, 1.98 g (98.1%). Slightly crude VIII′ was used in the following reaction without further purification.

5-(2-Naphthyl)-2,4-pentadienyl Bromide (X′). To an ice-cooled and stirred mixture of 2-naphthylpentadienol (VIII′, 1.98 g, 0.0094 mol), tetrahydrofuran (40 m*l*) and pyridine (2 m*l*) was added dropwise a solution of phosphorus tribromide (2.55 g, 0.0094 mol) in tetrahydrofuran (10 m*l*). After stirring for 1.5 hr at room temperature, cracked ice was added to the reaction mixture under ice-cooling. The aqueous layer obtained by evaporation of the organic solvent was extracted with benzene. After the usual washing and drying, the extract was concentrated to afford X′ as yellow crystals, 1.57 g (61.0%). This material was subjected directly to the following reaction.

5-(2-Naphthyl)-2,4-pentadienyltriphenylphosphonium Bromide (XII′). A solution of X′ (1.57 g, 0.00575 mol) and triphenylphosphine (2.10 g, 0.00802 mol) in benzene (60 m*l*)

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[14] S. Israelashvili, Y. Gottlieb, M. Imber, and A. Habas, *J. Org. Chem.*, **16**, 1519 (1951).

[15] C. Jutz, *Chem. Ber.*, **91**, 1867 (1958).

was refluxed to yield colorless crystalline precipitate. The precipitate was filtered and washed with benzene to give yellow fine crystals, 2.255 g (73.3%). The crystals were recrystallized three times from ethanol, yielding pure phosphonium bromide (XII′), mp 217.7—219.1°C (decomp.).

Found: C, 73.51; H, 5.30; Br, 15.15%. Calcd for $C_{33}H_{28}PBr$: C, 74.02; H, 5.27; Br, 14.92%.

1,2-Di(1-naphthyl)ethylene (I_1). To a stirred suspension of 1-naphthylmethyltriphenylphosphonium chloride (IV, 8.8 g, 0.020 mol) in benzene (65 m*l*) was added an ethereal solution of phenyllithium (0.98 N, 20.5 m*l*, 0.020 mol) under nitrogem atmosphere. After the resulting deep red solution had been stirred for 30 min, a solution of 1-naphthaldehyde (III, 3.4 g, 0.020 mol) in benzene (10 m*l*) was added and the mixture was stirred for 111 hr at room temperature. Yellowish red precipitate deposited was collected and washed with benzene. Ethanol was added to a hot solution of the precipitate in benzene to give a pale yellow precipitate (1.5 g, 34%). The material was recrystallized three times from ethanol and dissolved in benzene. The benzene solution was passed through a short column of alumina (10 g). The crystals obtained on concentrating the filtrate were recrystallized from cyclohexane to give pure I_1 as pale yellow crystals, mp 160—162°C (lit,[16] 161°C).

Found: C, 94.55; H, 5.79%. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75%.

1,4-Di(1-naphthyl)-1,3-butadiene (I_2). To a stirred solution of 1-naphthylmethylidenetriphenylphsophorane prepared from 1-naphthylmethyltriphenylphsophonium chloride (IV, 1.38 g, 0.0032 mol) in benzene (20 m*l*) and an ethereal solution of phenyllithium (5 m*l*, 0.0032 mol) was added under nitrogen atmosphere a solution of 3-(1-naphthyl)propenal (V, 0.568 g, 0.0031 mol) in benzene (10 m*l*). Stirring was continued for 20 hr to cause deposition of a yellow precipitate. The precipitate was washed with toluene and digested with the same solvent. The extract was concentrated to yield bright yellow needles, 0.678 g (71.1%). A benzene solution of the crystals was treated with active charcoal and the filtrate was passed through a thin layer of alumina. The crystals obtained from the filtrate were recrystallized three times from acetic acid to afford pure I_2 as yellow crystals, mp 173—173.5°C (lit,[14] mp 170°C).

Found: C, 94.37; H, 5.98%. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

1,6-Di(1-naphthyl)-1,3,5-hexatriene (I_3). A solution of 3-(1-naphthyl)-2-propen-1-ylidenetriphenylphosphorane was prepared by the reaction of phosphonium bromide (XI, 3.08 g, 0.006 mol) in benzene (40 m*l*) with an ethereal solution of phenyllithium (7.72 m*l*, 0.006 mol) under nitrogen atmosphere. After the resulting deep red solution had been stirred for 30 min, a solution of 3-(1-naphthyl)propenal (V, 1.0 g, 0.0055 mol) in benzene (20 m*l*) was added over a 20-min period under cooling. Stirring was continued for 15 hr. The yellow precipitate formed was digested with hot toluene. Concentration of the extract gave yellow crystals, 1.503 g (82.4%) which were dissolved in benzene and passed twice through a thin layer of alumina. The crystals obtained from the filtrate were recrystallized three times from benzene to afford pure I_3, mp 217—219°C.

Found: C, 93.93; H, 6.33%. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06%.

1,8-Di(1-naphthyl)-1,3,5,7-octatetraene (I_4). *(a) From 1-Naphthylmethyltriphenylphosphonium Chloride and Muconaldehyde.* A mixture of 1-naphthylmethyltriphenylphosphonium chloride (IV, 1.317 g, 0.003 mol) in benzene (40 m*l*) and an ethereal solution of phenyllithium (5.8 m*l*, 0.003 mol) was stirred for 40 min under nitrogen atmosphere. To the resulting deep red solution of phosphorane was added rapidly a solution of muconaldehyde (0.110 g, 0.001 mol) in benzene (10 m*l*). After stirring overnight a crystalline precipitate was formed. This was filtered and the filtrate was concentrated to yield a second crop. The combined precipitate was digested with hot benzene. The extract was filtered and the filtrate gave yellow crystals (0.360 g, quantitative) on concentration. After the crystals had been recrystallized three times from benzene, a benzene solution of the crystals was percolated through a short column of alumina. Pure I_4, mp 225.7—225.8°C was obtained from the filtrate.

Found: C, 93.84; H, 6.13%. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19%.

(b) From 5-(1-Naphthyl)-2,4-pentadienal (VI). To a stirred suspension of 3-(1-naphthyl)-2-propen-1-yltriphenylphosphonium bromide (XI, 1.28 g, 0.0025 mol) in benzene (20 m*l*) was added over a 10-min period an ethereal solution of phenyllithium (10 m*l*, 0.0025 mol) under nitrogen atmosphere to give a deep red solution of phosphorane. After 35 min, a solution of slightly crude 5-(1-naphthyl)-2,4-pentadienal (VI, 0.455 g, 0.0022 mol) in benzene (10 m*l*) was added over a period of 15 min to the solution of phosphorane. After stirring for 24 hr, the orange red precipitate formed was filtered and washed with benzene. The precipitate was digested with hot benzene and toluene and the combined extract was concentrated to half its original volume and treated with alumina (2 g). The concentrated solution was passed through a short column of alumina (5 g). Yellow crystals (0.505 g, 64.5%) obtained by concentration of the filtrate were recrystallized from toluene to give pure I_4, 222.4—225.1°C.

Found: C, 93.88; H, 6.38%. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19%.

1,12-Di(1-naphthyl)-1,3,5,7,9,11-dodecahexaene (I_6). A solution of 3-(1-naphthyl)-2-propenylidenetriphenylphosphorane was prepared from 3-(1-naphthyl)propenyltriphenylphosphonium bromide (XI, 1.528 g, 0.003 mol) in benzene (40 m*l*) and an ethereal solution of phenyllithium (5.8 m*l*, 0.003 mol) under nitrogen atmosphere. To this was added repidly a solution of muconaldehyde (0.11 g, 0.001 mol) in benzene (10 m*l*) and the mixture was stirred for 48 hr at room temperature. Crystalline solid deposited was collected by filtration and the filtrate was evaporated to give second crop of crystalline solid. The combined material was extracted with hot benzene (total 500 m*l*). Brown crystals (0.563 g, quantitative) obtained by evaporation of the extract were recrystallized from toluene. Crude I_6 thus obtained was dissolved in hot toluene and passed through a thin layer of alumina (1.5 g). The crystals obtained by concentration of the filtrate were recrystallized twice from the same solvent, yielding pure I_6 as orange crystals, mp 240—242°C.

Found: C, 93.44; H, 6.32%. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38%.

1,2-Di(2-naphthyl)ethylene (I_1'). To a stirred suspension of 2-naphthylmethyltriphenylphosphonium bromide (IV′, 2.321 g, 0.0048 mol) in benzene (40 m*l*) was added an ethereal solution of phenyllithium (0.635 N, 7.5 m*l*, 0.0048 mol). After stirring for 1 hr, a solution of 2-naphthaldehyde (III′, 0.726 g, 0.0047 mol) in benzene (15 m*l*) was added dropwise to the deep red solution of phosphorane and the mixture was stirred overnight. Crystalline solid deposited was digested with hot benzene and the hot extract was percolated through a short column of alumina. The crystals obtained from the filtrate were recrystallized from benzene

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[16] J. H. Wood, J. A. Bacon, A. W. Meibohm, W. H. Throckmorton, and G. P. Turner, *J. Amer. Chem. Soc.*, **63**, 1334 (1941).

to afford pure I_1' as pale yellow crystals, 0.968 g (74.3%), mp 258—259°C (lit, 257—258°C,[12] 255°C[16]).

1,4-Di(2-naphthyl)-1,3-butadiene (I_2'). A solution of 2-naphthylmethylidenetriphenylphosphorane was prepared by the reaction of phosphonium bromide (IV′, 1.049 g, 0.00217 mol) in benzene (40 m*l*) with an ethereal solution of phenyllithium (0.53 N, 4.05 m*l*, 0.00215 mol) under nitrogen atmosphere. To this was added a solution of 3-(2-naphthyl)-propenal (V′, 0.383 g, 0.0021 mol) in benzene (15 m*l*) and the mixture was stirred overnight. The residue obtained by evaporation of the solvent was digested with hot toluene. Crude crystals deposited on concentration of the filtrate were recrystallized from toluene, and the crystals were dissolved in the same solvent. The toluene solution was refluxed for several min with alumina (2 g) and filtered. The crystals deposited on cooling the filtrate were recrystallized from toluene, yielding pure I_2' as pale yellow needles, 0.208 g (32.3%), mp 271—273°C (lit,[14]: 268°C).

Found: C, 94.32; H, 5.90%. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

1,6-Di(2-naphthyl)-1,3,5-hexatriene (I_3'). To a stirred suspension of 3-(2-naphthyl)-2-propenyltriphenylphosphonium bromide (XI′, 0.764 g, 0.0015 mol) in benzene (50 m*l*) was added under nitrogen atmosphere an ethereal solution of phenyllithium (0.336 N, 4.5 m*l*, 0.0015 mol). After stirring for 30 min, 3-(2-naphthyl)propenal (V′, 0.182 g, 0.0010 mol) in benzene (20 m*l*) was added to the resulting deep red solution of phosphorane and the mixture was stirred overnight. The precipitate formed was digested with hot benzene and toluene. The combined extract was passed through a short column of alumina. The crystals obtained by evaporation of the filtrate were recrystallized from toluene to yield pure I_3' as yellow crystals, 0.121 g, (36.4%), mp 251—262°C (decomp.).

Found: C, 93.82; H, 5.99%. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06%.

1,8-Di(2-naphthyl)-1,3,5,7-octatetraene (I_4'). To a stirred solution of 2-naphthylidenetriphenylphosphorane prepared from phosphonium bromide (IV′, 1.450 g, 0.003 mol) and phenyllithium (0.003 mol) according to the procedure for the preparation of I_1' and I_2' was added a solution of muconaldehyde (0.110 g, 0.001 mol) in benzene (12 m*l*) and the mixture was stirred overnight. Yellow crystalline solid deposited was digested with hot benzene. The filtrate obtained by percolation of the extract through a short column of alumina (5 g) was evaporated to yield yellow crystals. Recrystallization of the crystals from toluene afforded pure I_4' as yellow crystals, 0.330 g, (92.1%), mp 266—267°C.

Found: C, 93.47; H, 6.11%. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19%.

1,10-Di(2-naphthyl)-1,3,5,7,9-decapentaene (I_5'). An ethereal solution of phenyllithium (0.277 N, 9.0 m*l*, 0.0025 mol) was added under nitrogen atmosphere to a stirred suspension of 5-(2-naphthyl)-2,4-pentadienyltriphenylphosphonium bromide (XII′, 1.338 g, 0.0025 mol) in benzene (40 m*l*) to give a deep red solution of phosphorane. To this was added after stirring for 30 min a solution of 5-(2-naphthyl)-2,4-pentadienal (VI′, 0.416 g, 0.0020 mol) in benzene (60 m*l*). After the mixture had been stirred overnight, the solid deposited was digested with hot benzene and toluene. The filtrate obtained by percolation of the combined extract through a thin layer of alumina (5 g) was concentrated to yield crystals. The crystals were recrystallized from toluene to give pure I_5' as yellowish orange needles, 0.252 g (32.8%), mp 268—269°C (decomp.).

Found: C, 93.66; H, 6.38%. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29%.

1,12-Di(2-naphthyl)-1,3,5,7,9,11-dodecahexaene (I_6'). A solution of 3-(2-naphthyl)-2-propenylidenetriphenylphosphorane was prepared under nitrogen atmosphere from 3-(2-naphthyl)-2-propenyltriphenylphosphonium bromide (XI′, 1.273 g, 0.0025 mol) in benzene (50 m*l*) and an ethereal solution of phenyllithium (0.336 N, 7.45 m*l*, 0.0025 mol). To the resulting deep red solution was added a solution of muconic aldehyde (0.110 g, 0.001 mol) in benzene (20 m*l*). After the mixture had been stirred overnight at room temperature, the precipitate formed was digested with hot benzene and toluene. The extract was passed through a short column alumina. The crystals obtained by concentration of the filtrate were recrystallized from toluene to afford pure I_6' as orange crystals, 0.142 g (34.5%), mp 265—273°C decomp.), rate of temperature increase: 10°C/min).

Found: C, 93.64; H, 6.25%. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38%.