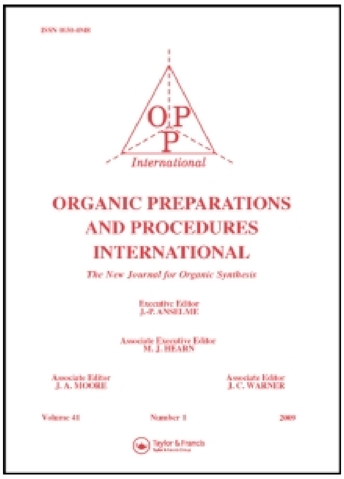

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A SIMPLE SYNTHESIS OF 1-ARYL-POLYENES

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A SIMPLE SYNTHESIS OF 1-ARYL-POLYENES

Submitted by Elena Pini*, Elisabetta Rossi, Giuseppe Celentano, Riccardo Stradi
(08/02/01)

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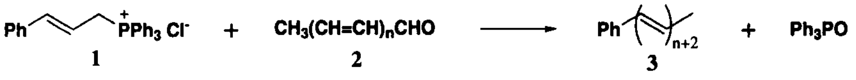
The delocalization of π electrons (conjugation) in linear molecules has been and continues to be of great interest in modern chemistry, physics and technology since these systems can display relevant and unique physical properties such as high electrical conductivity and large optical non-linearities.[1] The prototype of polyconjugated linear molecules is polyacetylene (PA) first synthesized by Natta;[2] it shows large electrical conductivity if suitably doped with electron donors or acceptors.[3] PA is however, a difficult material to handle and is totally insoluble in most common solvents; it is highly unstable and structurally very complex, possibly due to cross-linking. The interest of researchers then turned to a class of polyconjugated oligomers which could be used as model compounds whose chain-length dependent properties could be extrapolated to the "infinite" chain of PA. Very short oligoenes are chemically stable and tractable, *t*-butyl capped oligoenes[4] and α,ω-diphenylpolyenes[4,5] became available, but their chain lengths have been very limited. The stability and solubility of these materials allows the systematic characterization of their physical properties as a function of chain-length (and conjugation length, CL). The set of molecules one-ten conjugated carbon-carbon double bonds can be taken as suitable models for the entire series of polyconjugated materials.

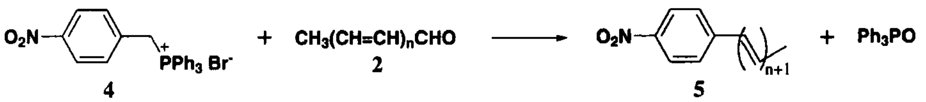
In addition physicists and chemists dealing with electrical conductivity and nonlinear optical properties of polyene-like systems also turned their attention to the class of natural and synthetic carotenoids of various lenghts.[6] The role of carotenoids in bioscience is well acknowledged and is the subject of extensive studies.[7] The idea of adopting carotenoids as model compounds for the PA system was not successful probably because of methyl groups regularly placed as substituents along the oligoene chain which greatly affects their properties compared to the corresponding demethylated polyenes. Since demethylated carotenoids are not easily available, the synthesis of 1-arylpolyenes can offer new materials with increasing CL. This work presents a general method for the synthesis of 1-arylpolyenes having with from three to nine conjugated carbon-carbon double bonds.

1-Phenylpolyenes **3** *(Eq. 1)* and 1-(*p*-nitrophenyl)polyenes **5** *(Eq. 2)* were obtained by a Wittig reaction between the appropriate phosphonium salts and crotonaldehyde or polyconjugated aldehydes **2b-g.** Aldehydes **2 a-g** were prepared by the self-condensation of crotonaldehyde and by condensation of crotonaldehyde and acetaldehyde, following literature methods.[8,9]



(1)

a) n = 1 b) n = 2 c) n = 3 d) n = 4 e) n = 5 f) n = 6 g) n = 7



(2)

a) n = 2 b) n = 3 c) n = 4 d) n = 5 e) n = 6 f) n = 7

Triphenylphosphine cinnamylide or *p*-nitrobenzylide generated by deprotonation of the corresponding triphenylphosphonium salts with sodium methoxide, were treated with a methanolic solution of **2**; after stirring at room temperature, the 1-arylpolyenes precipitated from the reaction mixtures. Compound **3a**, however, was obtained using BuLi in THF instead of sodium methoxide for the deprotonation of cinnamyl triphenylphosphonium chloride, followed by reaction with a solution of crotonaldehyde in THF. Compounds **3 a-g** could also be obtained, in lower yields, starting from triphenylphosphine benzylide following the same reaction scheme. Examination of the ^{1}H-NMR spectra of compounds **3a-g** and **5a-b** made it possible to assign the proton resonance of α-, β- and ω-hydrogens of the polyene chain. The values of the vicinal coupling constants ($J = \sim 15$Hz) established the *trans* configuration for these protons. Since the resonance of the other protons of the unsaturated chain appeared as a multiplet, it was not possible to establish the stereochemistry of these double bonds. The increase in the length of the chain (compounds **3f**, **3g** and **5c-f**) caused the resonance of the α- and β-protons to appear as a multiplet; thus it was only possible to postulate the *trans* configuration in analogy with the lower homologs. The low solubility of compounds **3f**, **3g**, and **5c-f** limited their analytical studies to ^{1}H NMR, IR and mass spectroscopy. A single peak in the HPLC three-dimensional chromatograms of componds **3a-e** and **5a**, **5b** support the existence of single one isomers in each case.

EXPERIMENTAL SECTION

Melting points were determined in open capillary tubes with a Stuart Scientific apparatus and are uncorrected. IR spectra were recorded as KBr pellets with a FT-IR 16 PC Perkin-Elmer Spectrophotometer equipped with a Cambridge Instruments Microscopy for solids and recording in the range 4000- 400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 200 operating at 200 MHz and 50 MHz respectively using TMS as internal standard; chemical shifts (δ) in ppm, coupling constants (*J*) in Hz. HPLC analyses were performed using two columns, joined in sequence, Lichrocart Purospher RP 18 (250 x 4 mm I.D.) Merck mantained at 40°C with a column block heater mod. 7970 Hicrom Limited (Reading UK). Mobile phase, methanol; flow 0.6 mL/min. Mass/HPLC analyses were performed with a Finnigam TSA 700 with thermospray MS/MS tecnique. The phosphines and other reagents were obtained from by Aldrich, Milan, Italy. Thin layer chromatographies were performed on silica gel (silica gel $60F_{254}$, Merck).

Hepta-1,3,5-trienylbenzene (3a).- A solution of BuLi (3 mL; 5 mmol) in anhydrous THF (7 mL) under nitrogen was added dropwise to a suspension of **1** (1.0 g; 2.5 mmol) with stirring in THF (10 mL). After twenty min. at room temperature, crotonaldehyde (2.5 mmol) was added dropwise to the red solution and the mixture was stirred at room temperature for 24 h. After removal of the solvent under reduced pressure (30 mm Hg), the residue was treated with petroleum ether and the insoluble triphenylphosphine oxide was filtered off; the filtrate was then evaporated and the crude residue crystallized from isopropyl alcohol to give the yellowish solid product.

1-Arylpolyenes (3b-g). General Procedure.- A methanolic solution of sodium methoxide [0.047 g (2.05 mmol) of sodium in 5 mL of absolute methanol] was added dropwise to a stirred solution of cinnamyltriphenylphosphonium chloride (1.0 g, 2.05 mmol) in absolute MeOH (20 mL) under nitrogen at room temperature. After stirring at room temperature for thirty minutes, a solution of the appropriate polyenal (2.05 mmol) in absolute methanol (20 mL) was added dropwise. The yellow products **3b-g**, that precipitated (monitored by TLC) within 22-48 h in yields of 47-50% (Table1), were collected and washed twice with methanol (5 mL) and analyzed without further purification.

Table 1. Reaction Times, Yields, mps, Elemental Analyses and MH^+ of Compounds **3a-g**

Cmpd	Time (h)	Yield (%)	mp (°C)	Elemental Analyses C	H	MH^+
3a	24	47	80-81[a]	91.71 (91.73)	8.23 (8.10)	171
3b	3	45	83-85	91.78 (91.65)	8.22 (8.25)	197
3c	20	49	88-89	91.84 (91.61)	8.17 (8.20)	223
3d	27	40	120-130	91.88 (91.58)	8.12 (8.30)	249
3e	24	45	>200	91.92 (91.63)	8.08 (8.00)	275
3f	24	50	>200	91.94 (91.72)	8.06 (7.91)	301
3g	48	50	>200	91.97 (91.85)	8.03 (7.98)	327

[a] *lit.*[10] mp. 81°C

Table 2. Retention Time(t_R), UV/vis Absorption and Spectral Data of Compounds **3a-g**

Cmpd	IR (cm^{-1})	^{1}H NMR (δ)	^{13}C NMR	t_R (min)	UV/vis (nm)
3a	3012, 2926, 1636, 1000, 750, 690	7.44-7.18 (m, 5 H, $H_{arom.}$), 6.83 (dd, 1 H, J = 15.6, 4 , H_2), 6.54 (d, 1 H, , J = 15.6, H_1), 6.43-6.12 (m, 3 H, CH=), 5.8 (dq, 1 H, J = 6.4, 13, $H_{6.}$), 1.84 (d, 3 H, J = 6.4, CH_3)	137.72, 133.7, 131.95, 131.54, 130.609, 130.395, 129.44, 128.66, 127.3, 126, 18.4	6.248	314.1; 327.3
3b	3010, 2924, 1636, 1000, 750, 690	7.44 -7.18 (m, 5 H, H_{arom}), 6.85 (ddd, 1 H, J = 15.4, 6.6, 3.7, H_2), 6.52 (d, 1 H, J = 15.4, H_1), 6.47-6.09 (m, 5 H, CH=), 5.81 (dq, 1 H, J = 6.6, $11_{.8}$), 1.81 (d, 3 H, J = 6.6, CH_3)	138.02, 134.24, 134.123, 132.824, 132.46, 132.377, 130.996, 130.899, 129.81, 129.104, 127.83, 126.78, 18.9	6.935	323.4; 335.5; 343.7 nm.
3c	3010, 2922 , 1636, 1004, 746, 690	7.4 -7.2 (m, 5 H, H_{arom}), 6.87 (ddd, 1 H, J = 15.4, 10, 6.2, H_2), 6.56 (d, 1 H, J = 15.4, H_1), 6.45-6.1(m, 7H, CH=), 5.79 (dq, 1 H, J = 6.6,13.5, H_{10}), 1.82 (d, 3 H, J = 6.6, CH_3)	137.6, 134.512, 134.221, 133.153, 132.104, 130.764, 130.628, 130.356, 129.307, 128.7, 127.676, 127.5, 126.6, 124.51, 18.5	7.309	342.9; 359.7; 378.9
3d	3010, 2910, 1600, 1004, 744, 690	7.48 - 7.25 (m, 5 H, $H_{arom),}$ 6.8 (m,1 H, H_2), 6.6 (d, 1 H , J = 15.4, H_1), 6.35-6.1(m, 9 H, CH=), 5.79 (dq, 1 H, J = 7.3, 14.6, H_{12}), 1.82 (d, 3 H, J = 7.3, $CH_{3,}$)	137.6, 134.5, 134.251, 134.08, 133.254, 132.461, 132.372, 130.723, 130.614, 130.314, 128.9, 128.573, 128.17, 127.6, 126.6, 124.5, 18.5	11.644	378.1; 398.5; 422.5
3e	3008,2920, 1636, 1004, 744, 690	7.5 -7.24 (m, 5 H, H_{arom}), 6.8 - 6.65 (m, 1 H, H_2), 6.6 (d, 1 H, J = 15.4, H_1), 6.35 - 6.13 (m, 11 H, CH=), 5.76 (dq, 1H, J = 7,14.6, H_{14}), 1.81 (d, 3H, J = 7, CH_3)	137.6, 134.493, 134.260, 134.007, 133.871, 133.386, 132.764, 132.415, 132.123, 130.686, 130.584, 130.298 129.754, 128.725, 128.200, 127.715, 126.7, 124.5, 18.4	-	-
3f	3010, 2920, 1636, 1006, 746, 690	7.8-7.2 (m, 5 H, $H_{arom),}$ 6.56 (m, 15 H, CH=), 5.8 (m, 1 H, H_{16}), 1.81 (d, 3 H, J = 7, CH_3).	-	-	-
3g	3010, 2922, 1630, 1000, 740, 690	7.7 - 7.15 (m, 5 H H_{arom}), 6.8-6 (m, 17 H, CH=), 5.8 (m, 1H, H_{18}), 1.81(d, 3 H, J =7, $CH_{3,}$)	-	-	-

Table 3. Reaction Times, Yields, mps and Elemental Analyses of Compounds **5a-f**

Cmpd	Reaction time (h)	Yield (%)	mp (°C)	Elemental Analyses C	H	N	MH^+
5a	22	40	82-84	72.53 (72.33)	6.09 (5.85)	6.51 (6.34)	216
5b	22	53	127-130	74.66 (74.36)	6.27 (6.62)	5.81 (5.93)	242
5c	27	47	>200	76.38 (76.21)	6.41 (6.32)	5.24 (5.17)	268
5d	24	45	>200	77.79 (77.61)	6.52 (6.67)	4.77 (4.55)	294
5e	30	45	>200	78.97 (78.70)	6.63 (6.54)	4.36 (4.33)	320
5f	48	40	>200	79.97 (79.67)	6.71 (6.64)	4.06 (4.10)	346

Table 4. Retention Time(t_R), UV/vis Absorption and Spectral Data of Compds **5a-f**

Cmpd	IR (cm^{-1})	^1H NMR (d)	^{13}C NMR	t_R (min)	UV/vis (nm)
5a	3014, 2924, 1586, 1507, 1340, 1108, 996	8.2 (m, 2 H, $H_{arom.}$), 7.5 (m, 2 H H_{arom}), 6.97 (dd, 1H, J =10, 15.7, H_2), 6.76 - 6.06 (m, 4 H, CH=), 5.82 (dq, 1H, J = 6.9, 13.7, $H_{6.}$), 1.81 (d, 3 H, J = 6.9, CH_3)	146.5, 144.6, 138.513, 133.93, 133.056, 131.619, 129.51, 126.4, 125.2, 124, 18.5	3.486	276.5; 374.5
5b	3010, 2926, 1590, 1508, 1438, 1108, 996	8.2 (m, 2 H $H_{arom.}$), 7.5 (m, 2H, H_{arom}), 6.96 (dd, 1 H, J = 10.05, 15, 6, H_2), 6.75 - 6.06 (m, 6 H, CH=), 5.81 (dq, 1 H, J = 14,7, 6.1, H_8), 1.82 (d, 3H, J = 6.15, CH_3)	146.5, 144.6, 138.611, 133.891, 133.368, 132.104, 131.81, 130.045, 129.171, 126.530, 124.1, 123.7, 18.5.	3.789	304.5; 390.5
5c	3010, 2928, 1588, 1508, 1340, 1108, 996	8.18 (m, 2 H, $H_{arom.}$), 7.6 (m, 2H, H_{arom}), 6.7-6.1(m, 9 H, CH=), 5.8 (m, 1H, H_{10}), 1..82 (d, 3 H, J= 6.1, CH_3)	----	----	----
5d	3010, 2926, 1590, 1340, 1108, 1004	8.1 (m, 2 H, $H_{arom.}$), 7.54 (m, 2 H, H_{arom}), 6.7 - 5.85 (m, 12 H, CH=), 1.83 (d, 3 H, J = 7.3, CH_3)	----	----	----
5e	3010, 2932, 1590, 1362, 1118, 1006.	8.2 (m, 2 H, $H_{arom.}$), 7.5 (m, 2 H, H_{arom}), 6.8-5.8 (m, 14 H, CH=), 1.84 (d, 3 H, J=6.2, CH_3)	----	----	----
5f	3008, 2924, 1576, 1006.	8.14 (m, 2 H, $H_{arom.}$), 7.5 (m, 2 H, H_{arom}), 6.6 - 5.8 (m, 16 H, CH=), 1.81 (d, 3 H, J = 6.2, CH_3)	----	----	----

1-(*p*-Nitrophenyl)polyenes (5a-f). General procedure.- A methanolic solution of sodium methoxide (sodium 0.047 g; 2.05 mmol dissolved in 5 mL of absolute methanol) was added dropwise to a stirred solution of p nitrobenzyltriphenylphosphonium bromide (1.0 g; 2.05 mmol) dissolved in anhydrous MeOH (15 mL) under nitrogen at room temperature. The yellow solution was stirred at room temperature for a few minutes before a methanolic solution (20 mL) of the appropriate polyenal (2.05 mmol) was added. After stirring at room temperature under nitrogen, the precipitated product was collected from the reaction medium and washed twice with methanol (Table 3) and analyzed without further purification.

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