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Linear Conjugated Systems Bearing Aromatic Terminal Groups. XIII.1) Syntheses of α-(*p*-Methoxyphenyl)-ω-(*p*-nitrophenyl)polyenes

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α-*p*-Methoxyphenyl-ω-*p*-nitrophenylpolyenes (III_n, $n=1$—5) were prepared by the Wittig reaction of *p*-methoxyphenylpolyenals (I, $n=1$—5) with phosphorane derived from *p*-nitrobenzyltriphenylphosphonium bromide (II). The electronic spectra of III_n showed broad and structureless absorption curves. However, the trend of bathochromic shift of long wavelength absorption maxima with increasing length of polyene chain suggests that no alternation in the type of light-absorption of polyene chromophore is caused by the introduction of electron donating and withdrawing substituents in the terminal phenyl groups.

In view of prominent effect of terminal groups of α,ω-diarylpolyenes on the electronic spectral regularity,2—5) it seemed to be of interest to prepare a series of polyenes bearing electron donating and withdrawing substituents in each of the terminal aromatic rings. The present paper deals with the syntheses of a series of α-*p*-methoxyphenyl-ω-*p*-nitrophenylpolyenes (III_n $n=1$—5).

Syntheses of III_n were performed by the Wittig reaction of ω-*p*-methoxyphenyl polyene aldehydes (I, $n=1$—5)6) with phosphorane prepared from *p*-nitrobenzyltriphenylphosphonium bromide (II).7)

The physical properties of III_n are summarized in Table 1. We see that the frequency of C–H out-of-plane deformation (δ_{C-H}) and that of C=C stretching vibration ($\nu_{C=C}$) move to higher and lower wave number, respectively, along with the increase in *n*. The absorption curves of electronic spectra of III_n in tetrahydrofuran at room temperature are illustrated in Fig. 1. Owing to the broad and structureless feature of the absorption curves, estimation of the exact wavelength of maxima of long wavelength bands was difficult and no discussion could be given on the regularity of electronic spectra. However, it was observed that the magnitude of bathochromic shift of long wavelength band between III_{n+1} and III_n ($\Delta\lambda$) decreases with the increase of n (Table 1). This indicates that the introduction of electron donating and withdrawing groups does not alter the type of light-absorption properties of α,ω-diarylpolyene system (convergent type).8)

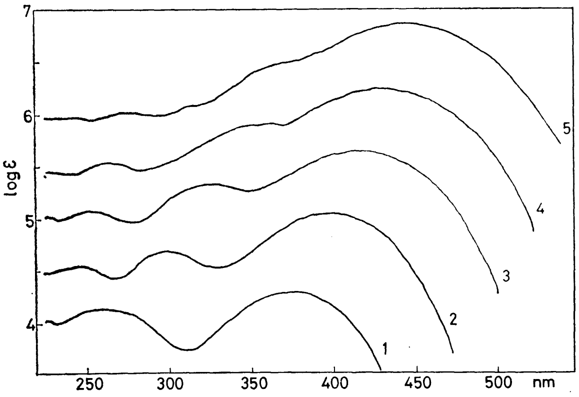

Fig. 1. Absorption curves of α-*p*-methoxyphenyl-ω-*p*-nitrophenylpolyenes (III_n) in tetrahydrofuran. Each curve, except for the lowest one, has been displaced upward by a 0.5 log ε unit increment from one immediately below it.

TABLE 1. PHYSICAL PROPERTIES OF α-*p*-METHOXYPHENYL-ω-*p*-NITROPHENYLPOLYENES (III_n)

n	Color of crystals	Mp (°C)	λ_{max} (logε) (nm)	$\Delta\lambda$	δ_{C-H} (cm^{-1})	$\nu_{C=C}$ (cm^{-1})
1	yellow	130—131	374 (4.29)		968	1587
				26		
2	yellow	173—175	400 (5.56)		993	1585
				19		
3	orange yellow	178—179	419 (4.65)		1000	1580
				11		
4	orange	204—205	430 (4.75)		1002	1565
				12		
5	reddish brown	229—231	442 (4.85)		1002	1552

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1) For Part XII of this series, see Ref. 5.

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

3) A. Yasuhara, S. Akiyama, and M. Nakagawa, *ibid.*, **45**, 3638 (1972).

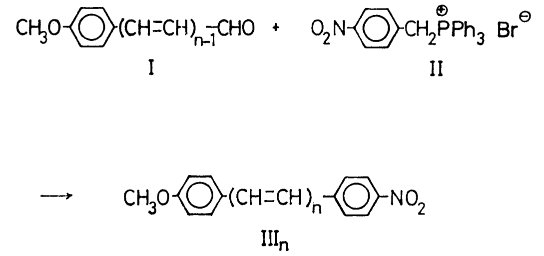
4) Y. Takeuchi, A. Yasuhara, S. Akiyama, and M. Nakagawa, *ibid.*, **46**, 909 (1973).

5) Y. Takeuchi, A. Yasuhara, S. Akiyama, and M. Nakagawa, *ibid.*, **46**, 2822 (1973).

6) D. Marshall and M. C. Whiting, *J. Chem. Soc.*, **1956**, 4082.

7) R. N. McDonald and T. W. Campbell, *J. Org. Chem.*, **24**, 1969 (1959).

8) $\Delta\lambda$ of diarylpoly-ynes was found to increase with the increase of n ($n=1-6$) [M. Nakagawa, S. Akiyama, K. Nakasuji, and K. Nishimoto, *Tetrahedron*, **1971**, 5401] and $\Delta\lambda$ of charge resonance system such as cyanine dyes has been found to be constant regardless of change of *n* (nonconvergent type).



Experimental

All melting points are not corrected. The electronic spectra in tetrahydrofuran were obtained on a Hitachi EPS-3T spectrophotometer using a well-matched pair of 1 cm quartz cells, the shoulder being denoted by an asterisk. The IR spectra were measured with a Hitachi EPI-2 spectrophotometer by the KBr-disk method. Preparation of phosphorane was performed under nitrogen atmosphere using an ethereal solution of phenyllithium as a base. The Wittig reaction was carried out under shielding from light. Initially deposited crystals in the final recrystallization were used in the measurements of electronic spectra to avoid contamination with an isomer containing *cis*-linkage.

*1-*p*-Methoxyphenyl-2-*p*-nitrophenylethylene (III_1).* To a suspension of *p*-nitrobenzyltriphenylphosphonium bromide[7] (II, 1.44 g, 3.0 mmol) in benzene (15 ml) was added a solution of phenyllithium (0.24 N, 12.5 ml). After being stirred for 2 hr at room temperature, a solution of *p*-methoxybenzaldehyde (I, n=1, 0.27 g, 2.0 mmol) in benzene (5 ml) was added and the mixture was stirred overnight. The residue obtained by evaporation of the solvent *in vacuo* was extracted with hot benzene. Crude crystals deposited on concentration of the extract were recrystallized from ethanol to give yellow plates, mp 127—128 °C, 0.124 g (24.3%) which were recrystallized from the same solvent to give pure III_1, yellow plates, mp 130—131 °C (lit,[9] mp 131—132.5 °C), UV, λ_{max} ($\log\varepsilon$): 258 (4.14), 270*, and 374 (4.29) nm.

*1-*p*-Methoxyphenyl-4-*p*-nitrophenyl-1,3-butadiene (III_2).* A solution of *p*-methoxycinnamaldehyde (I, n=2, 0.32 g, 2.0 mmol) in benzene (6 ml) was added to a solution of phosphorane prepared from II[7] (1.44 g, 3.0 mmol), benzene (15 ml) and phenyllithium (0.28N, 11.5 ml). After the mixture had been stirred for 21 hr at room temperature, the solvent was removed under reduced pressure. The residue was digested with boiling benzene and the extract was passed through a short column of alumina. Yellow needles, mp 169—178 °C, 0.292 g (42.6%) obtained on concentrating the filtrate were recrystallized from benzene to give pure III_2, yellow needles, mp 173—175 °C, UV, λ_{max} ($\log\varepsilon$): 248 (4.06), 295 (4.21), and 400 (4.56) nm.

Found: C, 72.77; H, 5.40%. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37%.

*1-*p*-Methoxyphenyl-6-*p*-nitrophenyl-1,3,5-hexatriene (III_3).* A solution of phosphorane was prepared from II[7] (1.44 g, 3.0 mmol), benzene (15 ml) and phenyllithium (0.24N, 8.4 ml). A solution of 5-*p*-methoxyphenyl-2,4-pentadienal[6] (I, n=3, 0.38 g, 2.0 mmol) in benzene (6 ml) was added to the solution and the mixture was stirred overnight at room temperature. The residue obtained by evaporating the solvent under reduced pressure was extracted with hot benzene, and the extract was percolated through a short column of alumina. Concentration of the filtrate afforded orange yellow plates, mp 175—180 °C, 0.235 g (38.2%) which were recrystallized from benzene to give pure III_3, orange yellow plates, mp 178—179 °C, UV, λ_{max} ($\log\varepsilon$): 254 (4.14), 325 (4.32), 336 (4.32), and 419 (4.06) nm.

Found: C, 74.29; H, 5.56%. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.57%.

*1-*p*-Methoxyphenyl-8-*p*-nitrophenyl-1,3,5,7-octatetraene (III_4).* A solution of 7-*p*-methoxyphenyl-2,4,6-heptatrienal[6] (I, n=4, 0.43 g, 2.0 mmol) in benzene (35 ml) was added to a solution of phosphorane prepared from II[7] (1.44 g, 3.0 mmol), benzene (20 ml) and phenyllithium (0.24N, 12.5 ml), and the mixture was stirred for 21 hr at room temperature. Brown powder deposited was digested with boiling benzene. Concentration of the extract, after being filtered, afforded fine orange crystals, mp 200—202 °C, 0.222 g (33.3%). Recrystallization of this material from benzene afforded pure III_4, orange plates, mp 204—205 °C, UV, λ_{max} ($\log\varepsilon$): 265 (4.06), 360 (4.41), 430 (4.75), and 445* nm.

Found: C, 75.81; H, 5.72%. Calcd for $C_{21}H_{19}NO_3$: C 75.65; H, 5.74%.

*1-*p*-Methoxyphenyl-10-*p*-nitrophenyl-1,3,5,7,9-decapentaene (III_5).* To a solution of phosphorane prepared from II[7] (0.94 g, 1.95 mmol), benzene (15 ml) and phenyllithium (0.24N, 8.2 ml) was added a solution of 9-methoxyphenyl-2,4,6,8-nonatetraenal[6] (I, n=5, 0.32 g, 1.3 mmol) in benzene (60 ml) and tetrahydrofuran (10 ml). After the mixture had been stirred for 21 hr, reddish brown solid deposited was collected by filtration. The soild was extracted with boiling benzene. The extract was filtered and concentrated. Reddish brown crystals, mp 229—230 °C, 0.123 g (26.3%) thus obtained were recrystallized from benzene to give pure III_5, reddish brown rods, mp 229—230 °C, UV, λ_{max} ($\log\varepsilon$): 277 (4.01), 370 (4.49), 442 (4.85), and 455* nm.

Found: C, 76.86; H, 5.89%. Calcd for $C_{23}H_{21}NO_3$: C, 77.01; H, 5.83%.

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[9] R. Ketcham, D. Jambotkar, and L. Martinelli, *J. Org. Chem.*, **27**, 4666 (1962).