(4) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).
(5) P. Laszlo and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2709 (1963).
(6) P. Laszlo and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).
(7) D. Van Haver, D. Tavernier, M. Anteunis, and M. Vandewalle, *Tetrahedron*, **30**, 105 (1974).
(8) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1969, p 78.
(9) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5247 (1965).
(10) M. A. Battiste and M. E. Brennan, *Tetrahedron Lett.*, 5857 (1966).
(11) D. D. Miller, J. Fowble, and P. N. Patil, *J. Med. Chem.*, **16**, 177 (1973).

Synthesis and Spectral Properties of a Series of New α,ω-Diphenylpolyenes

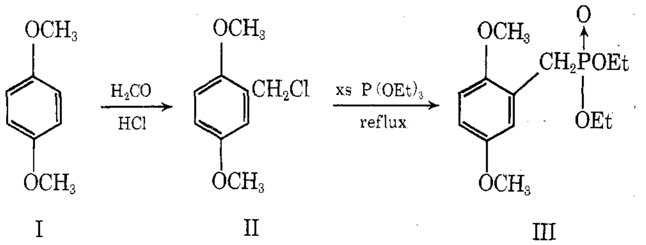
Gerret M. Peters, Jr.,* Fred A. Stuber, and Henri Ulrich

The Upjohn Company,
Donald S. Gilmore Research Laboratories,
North Haven, Connecticut 06473

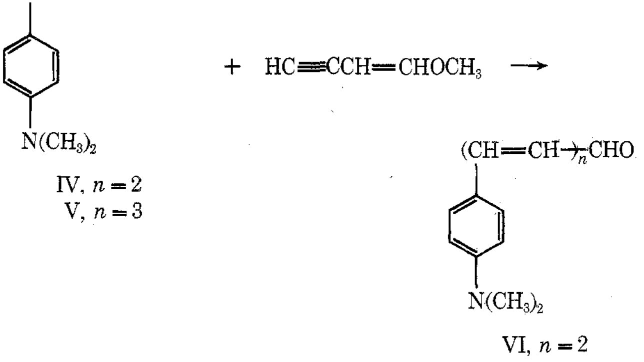
Received January 15, 1975

It has been determined that substituted *trans*-stilbenes act as sensitizers for the photochemical decomposition of arenesulfonyl azides.[1] A series of new α,ω-diphenylpolyenes has been synthesized which extend the spectral sensitivity of the azide-sensitizer system into the visible region of the electromagnetic spectrum. The study of energy transfer and quantum yield determination will be the topic of a forthcoming paper.

The synthesis involves formation of aromatic polyenals (IV → VII) which are subsequently converted to α,ω-diphenylpolyenes (VIII → XI) via a phosphonate carbanion reaction with 2,5-dimethoxybenzyl phosphonate (III). Several methods are available for the extension of double bond conjugation in systems containing an aldehyde function: multiple aldol condensations with paraldehyde;[2] aldol condensation with crotonaldehyde[3] or acetaldehyde;[4] reaction of 1-methylaniline penta-1,3-dienal (Zincke aldehyde) with dimethylaniline in the presence of $POCl_3$[5] and condensation of methoxybutenyne with either benzaldehyde or cinnamaldehyde followed by reduction with $LiAlH_4$.[6] The last method is a stepwise approach and was selected as being the most appropriate for the current work.

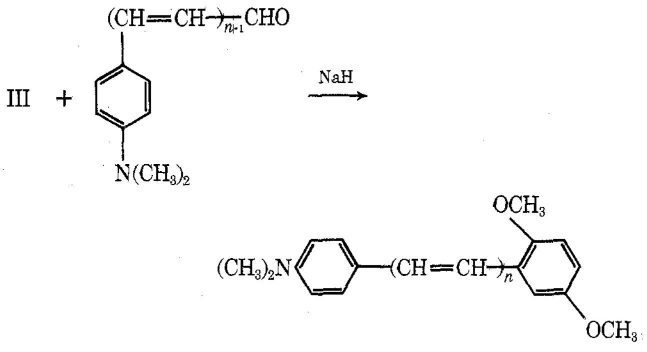


I II III



IV, $n=2$
V, $n=3$

VI, $n=2$
VII, $n=3$



VIII, $n=1$
IX, $n=2$
X, $n=3$
XI, $n=4$

It was desired to obtain the α,ω-diphenylpolyenes in the all-trans configuration to ensure the highest extinction coefficients and the longest wavelength absorption maxima. Several criteria were utilized in assigning the all-trans stereochemical configuration to the compounds synthesized: known stereochemistry of the chemical reactions involved; comparison of physical properties to those of similar compounds with known stereochemistry; analysis of the ultraviolet absorption spectra and analysis of the infrared spectra.

The reaction of the benzyl phosphonate III with an aldehyde produces an exclusively trans double bond.[9] The intermediate step in which $LiAlH_4$ is used to reduce the acetylenic bond of methoxybutenyne also results in formation of an exclusively trans double bond.[8] Finally, the *p*-dimethylaminocinnamaldehyde (V) was known to be the trans isomer. From these considerations we can assign the trans configuration to the stilbene VIII, both olefinic bonds in the butadiene IX, two of the three olefinic bonds in the hexatriene X, and three of the four olefinic bonds in the octatetraiene XI. The double bonds remaining unassigned are due to the methoxybutenyne for which the configuration of the double bond is not certain.

Table I compares some physical properties of known isomers with those of the first two members of the α,ω-diphenylpolyene series. Only the all-trans isomers are crystalline, high melting point solids.

In a review by Lewis and Calvin[7] it is reported that for a series of all-trans diphenylpolyenes the square of the ultraviolet absorbance maximum (λ^2_{max}) is related in a linear fashion to the number of olefinic bonds separating the aromatic rings (n). Plotting λ^2_{max} vs. n for the current series of diphenylpolyenes (Figure 1) gives the linear relationship expected if the members of the homologous series are in the all-trans configuration.

The 650–1050-cm^{-1} region of the infrared spectrum has been used by some researchers[6,11] to distinguish the out-of-plane vinyl C–H bonding of cis olefins (650–850 cm^{-1}) from that of trans olefins (950–1050 cm^{-1}). The presence of aromatic C–H bonding absorbances in the 700–800-cm^{-1} range[12] in the infrared spectra of the compounds under discussion, however, precludes the unambiguous assignment of any cis bond. The infrared spectrum of each α,ω-diphenylpolyene does contain a strong absorbance in the 950–1050-cm^{-1} region which could be assigned to a trans vinyl C–H bond.

In the present homologous α,ω-diphenylpolyene series each successive olefinic bond introduced into the system resulted in a bathochromic shift in the position of the ultraviolet absorbance maximum by about 17 nm and in an increase in the intensity of the absorption maximum.

Table I
Comparison of Physical Properties between α,ω-Diphenylpolyenes and Known Cis,Trans Isomers

Compd	Isomer	Mp (bp), °C	λ_{max}, nm	ϵ_{max}
4-Methoxystilbene[9]	Trans	136	306[a]	29,000
	Cis	(98–100, 2 mm)	270[a]	11,700
Diphenylbutadiene[10,16]	Trans,trans	152–153	328[b]	56,200
	Trans,cis	Oil	312[b]	31,600
	Cis,cis	70.5	299[b]	29,500
2,5-Dimethoxy-4′-dimethylaminostilbene (VIII)	Trans	120–121	363[b]	32,350
1-(2,5-Dimethoxyphenyl)-4(4′-dimethylaminophenyl)buta-1,3-diene (IX)	Trans,trans	121–121.5	380[c]	49,500
1-(2,5-Dimethoxyphenyl)-6(4′-dimethylaminophenyl)hexa-1,3,5-triene (X)	All-trans	123–123.5	397[c]	54,600
1-(2,5-Dimethoxyphenyl)-8-(4′-dimethylaminophenyl)octa-1,3,5,7-tetraene (XI)	All-trans	146–147	413[c]	70,150

[a] 95% ethanol. [b] Hexane. [c] Acetonitrile.

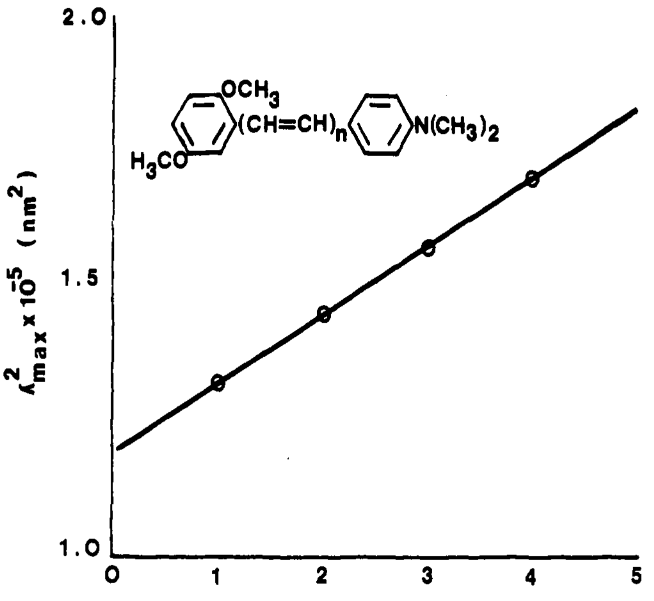


Figure 1. Linear relationship between λ^2_{max} and n for the trans polyene series.

These shifts were accompanied by a decrease in the energy of the lowest lying excited state singlet ($E_{0\rightarrow0}$) energy levels. A comparison of the ultraviolet absorbance spectra of these α,ω-diphenylpolyenes is shown in Figure 2.

Experimental Section

General. Melting points were measured on a Thomas-Hoover capillary apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer using KBr pellets. NMR spectra were measured on a Varian T-60 spectrometer. Ultraviolet absorption spectra were recorded on a Cary Model 14 spectrophotometer. Emission–excitation spectra were determined on an Aminco-Bowman spectrophotofluorometer. The NaH (50% in mineral oil) was washed with n-hexane prior to use. The elemental analyses were performed in these laboratories.

Starting Materials. The 2,5-dimethoxybenzyl phosphonate (III) was prepared by the Michaelis–Arbuzov reaction.[13] The 2,5-dimethoxybenzyl chloride (II) was prepared by chloromethylation of hydroquinone dimethyl ether (I) according to the method of Mel'nikov and Prilutskaya.[14]

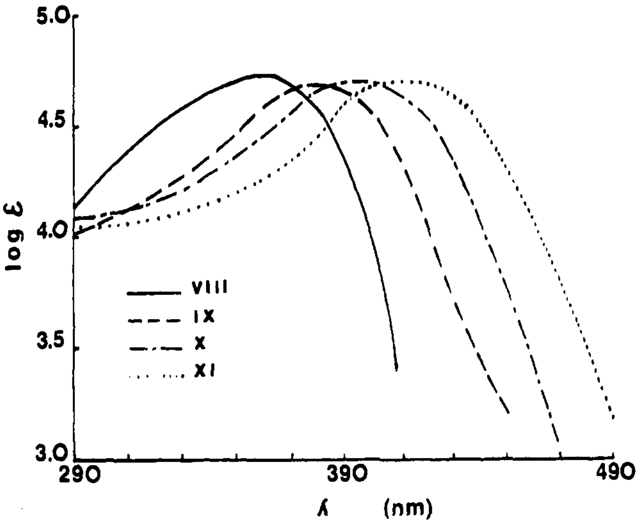


Figure 2. Ultraviolet absorbtion curves for the homologous polyene series.

5-(p-Dimethylaminophenyl)penta-2,4-dienal (VI). Using the method of Marshall and Whiting,[8] 1.6 g (66.6 mmol) of magnesium turnings plus 45 ml of tetrahydrofuran (THF) (dried over tosyl isocyanate and distilled) together with a crystal of iodine were placed in a 250-ml three-neck flask fitted with a thermometer, reflux condenser, and addition funnel both topped with $CaCl_2$ drying tubes. To this mixture was added dropwise 7.2 g (66.0 mmol) of ethyl bromide in 10 ml of THF at a rate fast enough to ensure continued refluxing.[15] The water-white reaction mixture was allowed to cool to 34–45°, then 7.3 g (89.0 mmol) of freshly distilled 1-methoxybut-1-en-3-yne in 10 ml of THF was added dropwise maintaining a temperature of 40–45°. Upon completion of this addition, the reaction mixture was stirred at room temperature for 1 hr followed by cooling on an ice–salt bath and dropwise addition of 10 g (67.1 mmol) of p-dimethylaminobenzaldehyde in 10 ml of THF. A temperature of 0–5° was maintained during the aldehyde addition, then the mixture was allowed to warm to room temperature and was stirred for an additional 2 hr. After this time the mixture was cooled to 0° and 5 ml of absolute ethanol was added followed by stirring for 20 min. Then 2.0 g (52.6 mmol) of $LiAlH_4$ powder was added to the cold solution over a 30-min period followed by stirring at room temperature for 3 hr. The mixture was again cooled to 0° and the following were added consecutively: 3 ml of ethyl acetate, 15 ml of H_2O, 75 ml of 4 N H_2SO_4, and 100 ml of benzene. After stirring for 5–10 min the red benzene layer was separated, dried (sodium sulfate), and evaporated in vacuo to yield a reddish-brown solid which after recrystallization from isopropyl alcohol afforded 6.7 g (50%) of yellow plates of VI: mp 153–155°; NMR ($CDCl_3$) 3.0 (s, W = 1.0 Hz, 2 CH_3), 9.58 (d, J = 8 Hz, 1 CHO), 6.0–7.5 ppm (m, 8 H); uv (acetonitrile) λ_{max} 405 nm (ϵ 24,500); ir ($CHCl_3$) 3025, 1665, 1590 cm^{-1}.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.40; H, 7.44; N, 6.81.

7-(*p*-Dimethylaminophenyl)hepta-2,4,6-trienal (VII) was prepared similarly to IV from *p*-dimethylaminocinnamaldehyde. Recrystallization from ligroin (bp 90–120°) gave VII (2%) as a red powder: mp 177–179°; NMR ($CDCl_3$) 3.0 (s, W = 1.0 Hz, 2 CH_3), 5.9–7.4 (m, 10 H), 9.56 ppm (d, J = 8 Hz, 1 CHO); uv (acetonitrile) λ_{max} 425 nm (ϵ 36,260); ir ($CHCl_3$) 3020, 1665, 1560 cm^{-1}.

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.17; H, 7.49; N, 6.03.

General Procedure for Synthesis of α,ω-Diphenylpolyenes (VIII $\rightarrow$ XI).[13] Into the reaction vessel were charged 7 mmol of 2,5-dimethoxybenzyl phosphonate (III), 7 mmol of the appropriate aldehyde (IV $\rightarrow$ VII), and 25 ml of 1,2-dimethoxyethane (dried over Na). To this stirred solution was added in several portions 7 mmol of NaH followed by refluxing of the mixture for 0.5–1.5 hr. The reaction mixture was then cooled to room temperature and drowned in 150 ml of cold water followed by filtration (in the case of VIII) or extraction with benzene (in the case of IX, X, and XI) of the α,ω-diphenylpolyene.

2,5-Dimethoxy-4′-dimethylaminostilbene (VIII): yield 70%; yellow hexagonal crystals (acetone), mp 120–121°; NMR ($CDCl_3$) 2.90 (s, 2 NCH_3), 3.73 (s, $-OCH_3$), 3.77 (s, $-OCH_3$), 6.6–7.5 ppm (m, 9 H); ir 705 (m), 800 (s), 840 (m), 1045 cm^{-1} (s); $E_{o\rightarrow o}$ = 70.6 ± 0.6 kcal/mol.

Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.28; H, 7.48; N, 4.94. Found: C, 76.50; H, 7.36; N, 4.84.

1-(2,5-Dimethoxyphenyl)-4-(4′-dimethylaminophenyl)buta-1,3-diene (IX): yield 52%; yellow needles (ethanol), mp 121–121.5°; NMR ($CDCl_3$) 2.93 (s, 2 NCH_3), 3.73 (s, $-OCH_3$), 3.78 (s, $-OCH_3$), 6.6–7.4 ppm (m, 11 H); ir 715 (m), 810 (m), 860 (m), 985 cm^{-1} (s); $E_{o\rightarrow o}$ = 66.0 ± 0.6 kcal/mol.

Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.62; H, 7.51; N, 4.53. Found: C, 77.80; H, 7.67; N, 4.45.

1-(2,5-Dimethoxyphenyl)-6-(4′-dimethylaminophenyl)hexa-1,3,5-triene (X): yield 40%; orange needles (isopropyl alcohol), mp 123–123.5°; NMR ($CDCl_3$) 2.90 (s, 2 NCH_3), 3.77 (s, OCH_3), 3.80 (s, OCH_3), 6.6–7.4 ppm (m 13 H); ir 800 (s), 820 (s), 995 (s), 1045 cm^{-1} (s); $E_{o\rightarrow o}$ = 61.2 ± 0.6 kcal/mol.

Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.76; H, 7.53; N, 4.18. Found: C, 79.08; H, 7.78; N, 4.08.

1-(2,5-Dimethoxyphenyl)-8-(4′-dimethylaminophenyl)octa-1,3,5,7-tetraene (XI): yield 25%; shiny copper plates (acetone), mp 146–147°; NMR ($CDCl_3$) 2.95 (s, 2 NCH_3), 3.78 (s, OCH_3), 3.80 (s, OCH_3), 6.4–7.4 ppm (m, 15 H); ir 810 (s), 1000 cm^{-1} (vs); $E_{o\rightarrow o}$ = 58.0 ± 0.6 kcal/mol.

Anal. Calcd for $C_{24}H_{27}NO_2$: C, 79.73; H, 7.54; N, 3.88. Found: C, 79.61; H, 7.72; N, 3.73.

Registry No.—**III**, 55298-76-5; **IV**, 100-10-7; **V**, 20432-35-3; **VI**, 20432-36-4; **VII**, 55298-77-6; **VIII**, 55298-78-7; **IX**, 55298-79-8; **X**, 55298-80-1; **XI**, 55298-81-2; 1-methoxybut-1-en-3-yne, 2798-73-4.

References and Notes

(1) F. A. Stuber et al., *Photogr. Sci. Eng.*, **17**, 446 (1973).
(2) W. König, W. Schramek, and G. Rösch, *Chem. Ber.*, **61**, 2074 (1928).
(3) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **12**, 496 (1929).
(4) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 113 (1928).
(5) C. Jutz, *Chem. Ber.*, **91**, 850 (1958).
(6) D. Marshall and M. C. Whiting, *J. Chem. Soc.*, 4082 (1956).
(7) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).
(8) E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954).
(9) O. H. Wheeler and H. N. Battle DePabon, *J. Org. Chem.*, **30**, 1473 (1965).
(10) J. H. Pinckard, B. Wille, and L. Zechmeister, *J. Am. Chem. Soc.*, **70**, 1938 (1948).
(11) J. L. H. Allan, G. D. Meakins, and M. C. Whiting, *J. Chem. Soc.*, 1874 (1955).
(12) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1965, p 52.
(13) S. R. Sandler and W. Karo, "Organic Functional Group Preparations", Vol. 12, Academic Press, New York, N.Y., 1968, p 50.
(14) N. N. Mel'nikov and M. V. Pritlutskaya, *Zh. Obshch. Khim.*, **29**, 3746 (1959); *Chem. Abstr.*, **54**, 19566*d* (1960).
(15) It may be necessary to heat the reaction mixture until the orange iodine color disappears in order to initiate the reflux.
(16) M. J. Kamlet, Ed., "Organic Electronic Spectral Data", Vol. I, Interscience, New York, N.Y., 1960, p 669.

Carbon-13 Nuclear Magnetic Resonance Spectra of 4-Phosphorinanones. Carbonyl Hydration in Oxides, Sulfides, and Quaternary Salts[1]

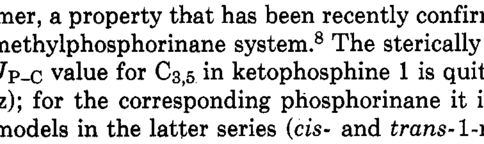
Joseph J. Breen, Shin Ok Lee, and Louis D. Quin*

Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

Received February 28, 1975

We recently reported on the ^{13}C NMR spectra of phosphorinanes[2] and their 4-hydroxy derivatives,[2,3] pointing out especially the value of the technique for gaining information on conformational aspects of this ring system. The effect of a covalence change (addition of sulfur) at the phosphorus atom was also considered.[2,4] We have extended our study to include some 4-keto derivatives of this series. On conducting ^{13}C NMR measurements on the tetracovalent species in water solution, we noted an important effect: extensive covalent hydration occurred at the carbonyl group. The present paper summarizes our observations on these compounds.

^{13}C NMR Spectra of Keto Derivatives. The ^{13}C NMR spectra of a family of *P*-methyl 4-phosphorinanone derivatives are given in Table I. In the trivalent compound **1**, assignment of the ring carbons was easily made, since their signals were separated by 12.5 ppm through the shielding effect of the phosphino group on attached carbons,[2] and the deshielding effect of carbonyl on carbons attached to it.[5] The carbonyl carbon was located in the same far-downfield position as seen for 4-methylcyclohexanone (δ 209[6]). The PCH_3 signal was in its expected high-field position. This carbon is particularly sensitive to conformational properties; the chemical shift observed is determined by the relative amounts at equilibrium of the conformer with axial (upfield) and with equatorial (downfield) methyl. Previous studies[7] on this 4-phosphorinanone have indicated that the equilibrium lacks the very strong bias to the equatorial side that is so well known for 4-methylcyclohexanone. Indeed, there seems to be a small excess of the axial conformer, a property that has been recently confirmed for the 1-methylphosphorinane system.[8] The sterically dependent $^2J_{P-C}$ value for $C_{3,5}$ in ketophosphine 1 is quite small (<2 Hz); for the corresponding phosphorinane it is 3 Hz. Rigid models in the latter series (*cis*- and *trans*-1-methyl-4-*tert*-butyl-4-phosphorinanols) have provided[3] values for the axial methyl case of 1 Hz, and for the equatorial of 7 Hz. The small $^2J_{PC}$ value for **1** therefore is qualitatively consistent with some excess of **1a** over **1b**.



1a **1b**

When sulfur or oxygen are added to phosphorus of **1**, it is likely that these substituents adopt the axial position in preference to methyl, as has been demonstrated for the phosphorinane compounds.[2] These atoms generally cause downfield shifts at α carbons;[2,9] this is seen in the spectrum for the sulfide (**2**) at both CH_3 and $C_{2,6}$, and in that of the oxide (**3**) at CH_3. On the other hand, quaternization of phosphines causes upfield shifts of attached carbons, and this is noted on comparing the data for the methiodide (**4**) to those for the phosphine (**1**).

We detect a small but significant upfield shift at C_4 on converting 1-methyl-4-phosphorinanone to any of its tetra-