[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

THE PREPARATION AND ABSORPTION SPECTRA OF α-(4-PYRIMIDYL)-ω-PHENYLPOLYENES

MALCOLM KORACH AND WERNER BERGMANN

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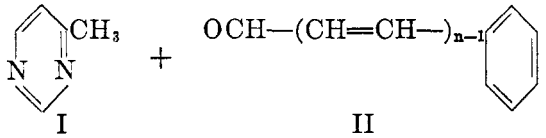
Previous work on polyenes having terminal, uncharged, aromatic groups has been restricted to the classical studies of Kuhn and Winterstein (1) on the diphenylpolyenes and the more recent studies of Compton and Bergmann (2) on the α-(α-quinolyl)-ω-phenylpolyenes. The present paper deals with an extension of such studies to a series of heterocyclic polyenes which differ from the diphenylpolyenes only in the replacement of one terminal phenyl group by the 4-pyrimidyl nucleus.

The first member of the α-(4-pyrimidyl)-ω-phenylpolyene series, (III, n = 1) is the only one which has previously been described. Its preparation was first accomplished by Gabriel and Colman (3) through the condensation of 4-methyl-



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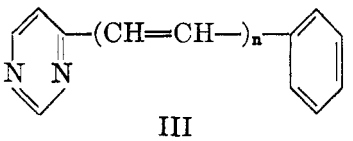

III

pyrimidine (I) with benzaldehyde (II, n = 1). The phenylpolyenealdehydes necessary for an extension of this series are available in reasonable yields through the method described by Schmitt (4). It consists in the condensation of a phenylpolyenealdehyde, such as cinnamaldehyde (IV), with crotonaldehyde (V), in the presence of piperidine acetate. Two aldehydes are the principal products of this reaction, 7-phenylheptatrienal (VI) and 11-phenylundecapentaenal (VII), of

$$\underset{\text{IV}}{C_6H_5CH{=}CHCHO} + \underset{\text{V}}{CH_3CH{=}CHCHO} \rightarrow$$

$$\underset{\text{VI}}{C_6H_5CH{=}CHCH{=}CHCH{=}CHCHO} +$$

$$\underset{\text{VII}}{C_6H_5CH{=}CHCH{=}CHCH{=}CHCH{=}CHCH{=}CHCHO}$$

which the latter is more readily isolated because of its lower solubility. In order to prepare the trienal (VI) without the simultaneous formation of substantial quantities of the pentaenal (VII) it has now been found of advantage to work in higher dilutions and to add the crotonaldehyde (V) dissolved in ethanol over a

period of seven days to a well-stirred alcoholic solution of cinnamaldehyde (IV). The condensation of the aldehydes with 4-methylpyrimidine was carried out by heating the reagents with zinc chloride at 120° for an extended period of time. The resulting zinc compounds were then decomposed by treatment with hydrochloric acid, and the free bases were liberated by addition of ammonia. A large excess of 4-methylpyrimidine was used with the higher aldehydes in order to effect their solution.

As shown in Table I, the colors of the pyrimidylphenylpolyenes show a gradation similar to that of the diphenylpolyenes. As in the case of the latter, the first member of the heterocyclic series showing definite coloration is the triene. The higher vinylogs of the heterocyclic series are, however, more deeply colored than the corresponding members of the diphenyl series. On the basis of visual evidence it appears therefore, that the chromophoric value of the 4-pyrimidyl group lies between that of a phenyl and a styryl group.

TABLE I

COMPARISON OF DIPHENYL- AND α-PYRIMIDYL-ω-PHENYLPOLYENES

n	C_6H_5-(CH=CH—)$_n$$C_6H_5$		$C_4H_3N_2$-(CH=CH—)$_n$$C_6H_5$	
	M.p, °C.	Color	M.p., °C.	Color
1	124	colorless	72	colorless
2	153	colorless	101	colorless
3	200	light-yellow	155	light-yellow
4	232	golden-yellow	194	golden
5	253	orange	218	orange-red
6	267	orange-red	239	red
7	279	bronze-red	—	dark red

A comparison of the absorption spectra maxima of the members of the two series indicates a similar relationship. Table II records the wave lengths of the absorption maxima of both series, which were measured in a chloroform solution, using a Beckman spectrophotomometer. Figure 1 shows the spectra of the members of the heterocyclic series. Like those of the diphenyl series, they show the typical increase of absorption intensity and curve character with the lengthening of the exocyclic chain. The fact that the heterocyclic polyenes exhibit less curve character than the diphenylpolyenes may be attributed to the presence of the nitrogen atoms which tend to stabilize one or more of the polar resonance forms. An increase in the contribution of polar resonance forms is usually associated with a loss of curve character, as is well shown by a comparison of the absorption spectra of cyanine dyes with those of diphenylpolyenes (6).

From a consideration of the electronic oscillation concept, Lewis and Calvin (5) have formulated the equation $\lambda^2 = kn$, which relates λ, the wavelength of the absorption maximum, to n, the number of double bonds in the exocyclic chain. The data for the diphenylpolyene series are in excellent agreement with this relationship, and the data for the α-(α-quinolyl)-ω-phenylpolyene series (2) also

follows it closely. As shown by Figure 2, there is an increasing deviation from this relationship in the case of the α-(4-pyrimidyl)-ω-phenylpolyenes as the length of the exocyclic polyene chain is increased. This divergence indicates that

TABLE II

ABSORPTION MAXIMA IN CHLOROFORM AT 25°C.

COMPOUND	MAX. (mμ)		
	(a)	(b)	(c)
Diphenylethylene	299	310	—
Diphenylbutadiene	319	333	350
Diphenylhexatriene	342	357	377
Diphenyloctatetraene	361	379	401.5
Diphenyldecapentaene	379	399	424
Diphenyldodecahexaene	396.5	417.5	444.5
Diphenyltetradecaheptaene	411	434	462
Pyrimidylphenylethylene	—	316	—
Pyrimidylphenylbutadiene	—	344	—
Pyrimidylphenylhexatriene	—	370.5	—
Pyrimidylphenyloctatetraene	—	393.5	—
Pyrimidylphenyldecapentaene	—	414.5	—
Pyrimidylphenyldodecahexaene	—	432	—
Pyrimidylphenyltetradecaheptaene	—	447	471

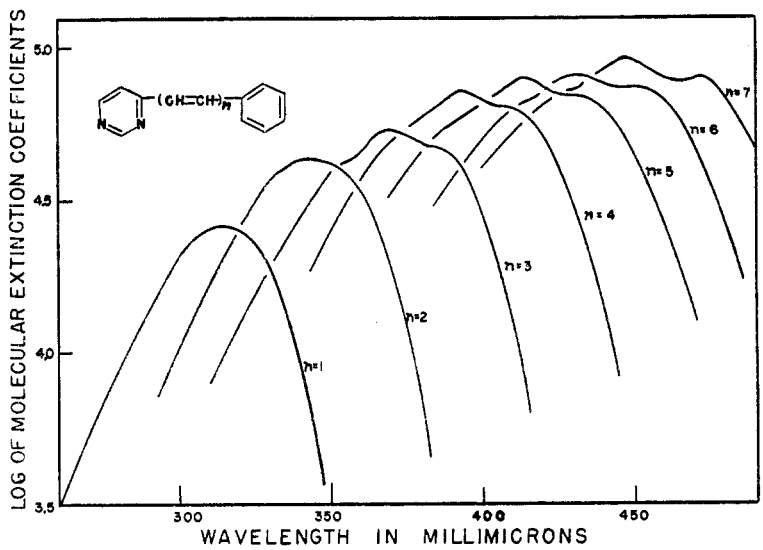

FIGURE 1. ABSORPTION CURVES OF α-(4-PYRIMIDYL)-ω-PHENYLPOLYENES IN CHLOROFORM AT 25°

the absorption maxima of the pyrimidyl-phenylpolyene series converge more rapidly than those of the diphenyl or the quinolyl-phenyl series. According to Brooker (6) rapid convergence of absorption maxima in a vinylogous series can be attributed to a considerable difference in the energies of the extreme resonance

structures involved, and to an increase in this difference as the chain is lengthened. Figure 2, therefore, indicates that the structures of the pyrimidyl-phenylpolyenes either differ somewhat more in energy, or show larger increases in energy difference with increasing chain lengths, than do the structures of the diphenylpolyenes or the quinolyl-phenylpolyenes.

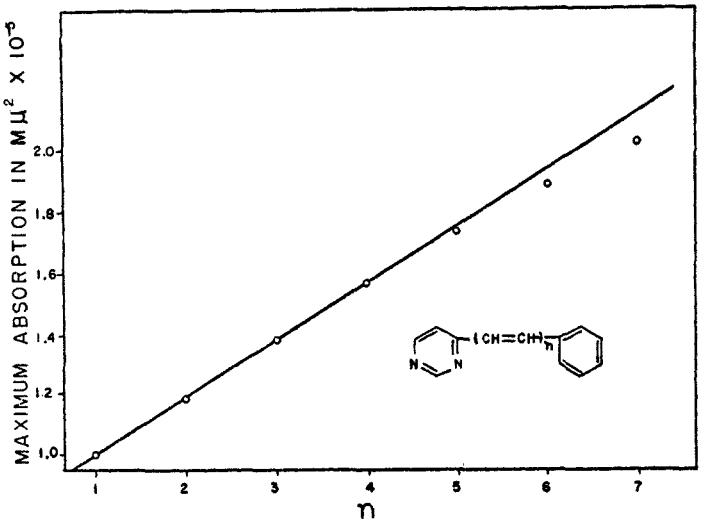

FIGURE 2. PLOT OF THE SQUARE OF THE WAVE LENGTH AGAINST THE NUMBER OF EXOCYCLIC DOUBLE BONDS

EXPERIMENTAL

All melting points are corrected.

7-Phenylheptatrien-2,4,6-al (VI). A mixture of 25 g. of piperidine, 25 g. of glacial acetic acid, and 132 g. (one mole) of freshly distilled cinnamaldehyde was dissolved in 600 cc. of 65% ethanol contained in a 2-liter, three-neck flask. The flask was equipped with a stirrer, a CO_2-inlet tube, and a one-liter dropping-funnel. The latter contained a solution of 35 g. (0.5 mole) of freshly distilled crotonaldehyde in 400 cc. of 65% ethanol under an atmosphere of CO_2. Through a capillary tube, attached to the dropping-funnel, the crotonaldehyde was added slowly over a period of a week to the solution containing the cinnamaldehyde. During the addition, the reaction mixture was stirred continuously and kept under an atmosphere of CO_2. The color of the solution slowly turned deep red, and crystals began to form after about one-half of the crotonaldehyde had been added.

After seven days the crystalline precipitate was collected and washed well with cold 70% ethanol. The mother liquor was kept under CO_2 for a week when a second crop of precipitate was obtained. The weight of the combined fractions was 49.5 g. The low melting point of the product, 108–112°, at once indicated that the material consisted chiefly of the *trienal*. The condensation product was then refluxed with one liter of 95% ethanol, and the solution filtered while still hot. There remained undissolved 6.4 g. of material, m.p. 173–178°, which consisted mainly of the *pentaenal* (VII).

The crude trienal obtained by cooling the filtrate was purified by three successive recrystallizations from ethanol containing small amounts of activated charcoal. The final product was obtained in form of nice yellow leaves; m.p. 116°. Yield, 32.6 g., or 35.5%.

1-(4-Pyrimidyl)-2-phenylethylene (III, n = 1). This compound was prepared by the procedure of Gabriel and Colman (3) with slight modifications. It melted at 71.5–72°.

1-(4-Pyrimidyl)-4-phenylbutadiene-1,3 (III, n = 2). A mixture of 4 g. (0.043 mole) of

freshly distilled 4-methylpyrimidine, 8 g. (0.061 mole) of freshly distilled cinnamaldehyde, and 0.5 g. of zinc chloride was heated for 10 hours in an oil-bath at 120° in a test tube fitted with a stopper containing a capillary. The mixture was then cooled, extracted with ether, and the ether extract washed with dilute hydrochloric acid. Upon addition of ammonia to the acid solution, a curdy, yellow product was precipitated, which after four recrystallizations from ethanol, including three treatments with Norit, gave 0.7 g. (8%) of a colorless, crystalline material, m.p. 100–101°.

Anal. Calc'd for $C_{14}H_{12}N_2$: C, 80.7; H, 5.8.

Found: C, 80.5; H, 5.9.

1-(4-Pyrimidyl) 6-phenylhexatriene-1,3,5 (III, n = 3). A mixture of 2 g. (0.021 mole) of freshly distilled 4-methylpyrimidine, 5 g of pentadienal, and 0.2 g. of zinc chloride was treated as described above. There was eventually obtained 0.08 g. (1.6%) of bright yellow needles, m.p. 154.8–155.3°. The product was soluble in ethanol, ether and chloroform, but only slightly soluble in dilute hydrochloric acid.

Anal. Calc'd for $C_{16}H_{14}N_2$: C, 82.0; H, 6.0.

Found: C, 81.8; C, 6.2.

1-(4-Pyrimidyl)-8-phenyloctatetraene-1,3,5,7 (III, n = 4). A mixture of 1 g. (0.005 mole) of 7-phenylheptatrienal, 3 g. (0.031 mole) of freshly distilled 4-methylpyrimidine, and 0.4 g. of zinc chloride was heated for eight hours at 125° as described above. After cooling the reaction product was filtered and washed with ethanol. This zinc compound was then digested with dilute hydrochloric acid for one hour, and the insoluble material was transferred to a thimble in a Soxhlet apparatus. The crude octatetraene hydrochloride was then extracted for eight hours with ethanol, and the resulting extract was made basic with ammonia. Upon dilution with water the octatetraene precipitated as an amorphous, yellow product, which after three recrystallizations from a mixture of toluene and ethanol gave 0.19 g. (21%) of bright golden crystals, m.p. 193–194°. The product is only slightly soluble in ethanol, but soluble in toluene and chloroform.

Anal. Calc'd for $C_{18}H_{16}N_2$: C, 83.0; H, 6.2.

Found: C, 82.9; H, 5.9.

1-(4-Pyrimidyl)-10-phenyldecapentaene-1,3,5,7,9 (III, n = 5). This compound was prepared from 4-methylpyrimidine and 9-phenylnonatetraenal (4) by a method analogous to the one described above, giving an orange-red, crystalline material; m.p. 217–218°, yield 1.25%. It is somewhat less soluble in all solvents tested than the preceding compound.

Anal. Calc'd for $C_{20}H_{18}N_2$: C, 83.9; H, 6.3.

Found: C, 83.5; H, 6.6.

1-(4-Pyrimidyl)-12-phenyldodecahexaene-1,3,5,7,9,11 (III, n = 6). This compound was prepared from 4-methylpyrimidine and 11-phenylundecapentaenal (4) by the procedure described above. Yield, 3.8%; fine, red crystals, m.p. 238–240°. The hexaene is practically insoluble in ethanol, moderately soluble in toluene and chloroform.

Anal. Calc'd for $C_{22}H_{20}N_2$: C, 84.6; H, 6.5.

Found: C, 84.2; H, 6.6.

1-(4-Pyrimidyl)-14-phenyltetradecaheptaene-1,3,5,7,9,11,13 (III, n = 7). This compound was prepared as described above from 4-methylpyrimidine and 13-phenyltridecahexaenal (4). Its great insolubility made purification exceedingly difficult, and it has not yet been possible to obtain an ash-free product. The crude product was a dark red, microcrystalline powder which upon heating began to decompose above 250°.

SUMMARY

A series of α-(4-pyrimidyl)-ω-phenylpolyenes has been prepared, and their absorption spectra have been measured and compared with those of the diphenylpolyene series.

NEW HAVEN, CONN.

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