

## PYRROLE STUDIES—XIII<sup>1</sup>

### THE SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF *trans* 2-(*p*-SUBSTITUTEDSTYRYL)PYRROLES

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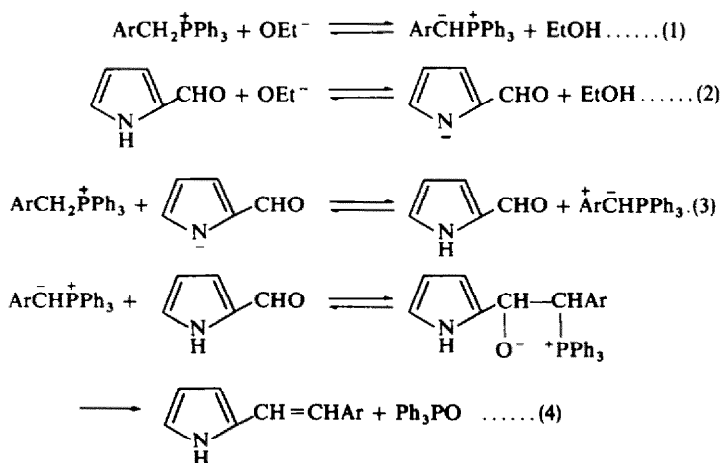
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**Abstract**—A series of *trans* 2-(*p*-substitutedstyryl)pyrroles and their N-Me derivatives have been synthesized using the Wittig reaction. The electronic absorption maxima are recorded and the frequencies of the long wavelength band are used to measure the effect of the *para*-substituent on the energy of transition from the ground to first excited state. IR measurements are used as an indication of the degree of interaction between the pyrrole ring and the aryl group in the ground state.

IN CONTINUATION of our earlier studies<sup>2,3</sup> of the interaction between the substituent and the heteroaromatic ring of substituted pyrroles, we have now investigated the electronic interaction between the pyrrole ring and an aryl group across the C=C bond of 2-(*p*-substitutedstyryl)pyrroles and their 1-Me derivatives.

In our initial attempts to synthesize the styryl pyrroles via the Wittig reaction, we generated the phosphoranes using sodium ethoxide. Although this method had been used successfully to prepare both the *cis* and *trans* isomers of 2-styrylpyrrole and their N-Me derivatives,<sup>4</sup> we have now found that the method could only be extended to the synthesis of 1-methyl-2-(*p*-substitutedstyryl)pyrroles and, in a low yield, for 2-(*p*-methylstyryl)pyrrole. The most probable cause for the failure of the reaction with 2-formylpyrrole is the possibility of the following equilibria:



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Under the conditions used, equilibria may be set up between the phosphorane and the formylpyrrole to give either the betaine and hence the styrylpyrrole (4) or, alternatively, to give the phosphonium salt and the unreactive pyrrolyl anion (3), which may also be formed from formylpyrrole and ethoxide ion (2). As styrylpyrroles can only be obtained if both equilibria (3) and (4) lie to the right, the yields will therefore depend upon the relative basicities of the phosphoranes and pyrrolyl anion and upon the nucleophilicity of the phosphorane.

Equilibria (2) and (3) are non-existent with 1-methyl-2-formylpyrrole and the styrylpyrroles were obtained in ca. 40–60% yield. A similar situation has been observed for the relative reactivity of phosphonate anions with 2-formylpyrrole and its 1-Me derivative.<sup>4</sup> Where the equilibria positions are unfavourable for the formation of the styryl compounds alternative reactions may occur. Grayson and Keough<sup>5</sup> have reported that substituted toluenes and bibenzyls are formed by decomposition of benzyltriphenylphosphonium salts in the presence of ethoxide ions and in the presence of oxygen autooxidation may occur to give stilbenes.<sup>6</sup> In all experiments where no styrylpyrroles were obtained we quantitatively recovered the formylpyrrole and isolated *p*-substituted toluenes and/or bibenzyls and, in some instances, stilbenes.

The use of sodium hydride instead of sodium ethoxide was found to virtually eliminate the side reactions and styrylpyrroles were obtained in yields of ca. 50–60%. However, 4,4'-dinitrobibenzyl was still obtained in an approximately equivalent yield to that of the *p*-nitrostyrylpyrrole. Only the *trans* isomers were obtained for the 2-styrylpyrroles and, although the unstable *cis* isomers of the 1-methyl-2-styrylpyrroles were obtained in a low yield, they were also isolated as their *trans* isomers.

The electronic absorption maxima of the *trans* styrylpyrroles, measured in ethanol, are recorded in Table 1. The values given are those observed within 5 minutes of preparation of the solutions. The spectra changed markedly with time and after

TABLE 1. ELECTRONIC ABSORPTION MAXIMA

<i>p</i> -Substituent	$m\mu$	$10^{-3}\epsilon$	$m\mu$	$10^{-3}\epsilon$	$m\mu$	$10^{-3}\epsilon$
<i>2-(p-Substituted styryl)pyrroles.</i>						
OMe	234	7.2			335	29.8
Me	237	9.8	243sh	9.3	333.5	30.2
H	236	10.8	242sh	10.3	333	31.2
F			238	6.0	332	18.6
Cl			241	8.2	341	27.9
Br			246	9.1	343	31.3
NO <sub>2</sub>			279	10.0	418	25.4
<i>1-Methyl-2-(p-substituted styryl)pyrroles.</i>						
OMe	234.5	8.5			342	22.9
Me	239	10.1	245sh	9.7	341	22.0
H	239	10.4	244	9.6	339.5	22.5
F			244	8.7	338	22.1
Cl	240.5sh	10.4	246	10.7	349	28.8
Br	232	9.1	246sh	8.8	350	21.6
NO <sub>2</sub>			269	8.3	423	23.4

24 hours they closely resembled the spectra one would expect for the *cis* isomers.<sup>4</sup> The long wavelength band had shifted hypsochromically and its intensity was approximately half of the original value, whereas the intensity of the band near 240 m $\mu$  had increased two to three fold. We are at present investigating the exact nature of the structural change.

The long wavelength band is a result of through conjugation between the two rings; the energy of the electronic transition from the ground to the first excited state being proportional to the frequency of this band. These frequencies, together with those of the substituted stilbenes, are given in Table 2. It has been shown for other unsaturated heterocyclic systems<sup>7</sup> that a measure of the interaction between the *para*-substituent and heterocyclic ring is given by the expression:

$$\nu_{\text{interact}} = \nu_{\text{subst. het}} + \nu_{\text{benz}} - \nu_{\text{het}} - \nu_{\text{subst. benz}}$$

where  $\nu_{\text{het}}$  and  $\nu_{\text{benz}}$  are the frequencies of the long wavelength band of styrylpyrrole and stilbene respectively, and  $\nu_{\text{subst. het}}$  and  $\nu_{\text{subst. benz}}$  the frequencies of their *para*-substituted derivatives. The interaction values are listed in Table 3. Electron withdrawing substituents have negative interaction values, i.e. they lower the energy of transition from the ground to excited state, whereas electron donating substituents increase the transition energy. This was to be expected as the pyrrole ring is strongly electron donating.

TABLE 2. FREQUENCY OF LONGEST WAVELENGTH BAND (cm<sup>-1</sup>).

R	Ar CH = CHC <sub>6</sub> H <sub>4</sub> R		
	Phenyl <sup>a</sup>	2-Pyrrolyl	1-Methyl-2-pyrrolyl
OMe	32,500 <sup>b</sup>	29,830	29,280
Me	33,000 <sup>b</sup>	29,980	29,310
H	33,440 <sup>b</sup>	30,020	29,450
F	33,650	30,120	29,550
Cl	32,800 <sup>b</sup>	29,340	28,660
Br	32,610	29,150	28,540
NO <sub>2</sub>	28,100 <sup>b</sup>	23,900	23,650

<sup>a</sup> Measured in 50% aqueous ethanol; <sup>b</sup> ref. 7.

A measure of the interaction between the *para*-substituent and the pyrrole ring in the ground state may be obtained from the IR spectra of the compounds. The magnitude of the charge asymmetry in the C=C bond, as measured by the intensity of the C=C stretching frequency near 1630 cm<sup>-1</sup>, is proportional to the electronic interaction between the two rings in the ground state.

Whereas the intensities of the C=C stretching bands for *p*-substituted stilbenes depend upon the conjugative power of the substituent, but not on whether the substituent is electron withdrawing or donating, the intensities for the styrylpyrroles drop smoothly as the *p*-substituent changes from the strongly electron withdrawing NO<sub>2</sub> group to the electron donating OMe group.

Thus, the results obtained for the styrylpyrroles are similar to those observed for the pyrrolylmethyleneimines,<sup>2</sup> in that, the interaction between the *para*-substituent

and the heterocyclic ring is qualitatively similar in both the ground and excited state of the molecule, but that it is quantitatively greater in the excited state than in the ground state.

The out-of-plane CH deformation of the *trans* CH=CH group absorbs with fairly constant frequency and intensity at  $951 \pm 2 \text{ cm}^{-1}$  ( $190 \pm 35$ ). All of the compounds showed absorption bands characteristic of the aryl group<sup>8,9</sup> and of the 2-mono-substituted<sup>10</sup> or 1,2-disubstituted pyrrole rings.<sup>11</sup>

TABLE 3. INTERACTION BETWEEN PYRROLE RING AND *para*-SUBSTITUENT ( $\text{cm}^{-1}$ )

<i>para</i> -substituent	2-Pyrrolyl	1-Methyl-2-pyrrolyl
OMe	+750	+770
Me	+400	+300
F	-110	-110
Cl	-40	-150
Br	-40	-80
NO <sub>2</sub>	-780	-460

TABLE 4. IR ABSORPTION OF *trans* CH=CH GROUP.

<i>para</i> -substituent	2-Pyrrolyl compounds				1-Methyl-2-pyrrolyl compounds			
	$\nu\text{C}=\text{C}$		$\gamma\text{CH}$		$\nu\text{C}=\text{C}$		$\gamma\text{CH}$	
	$\text{cm}^{-1}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$
OMe	1637	75	950	195	1631	65	951	100
Me	1636	75	952	200	1632	75	954	150
H	1637	90	950	210	1632	110	951	210
F	1637	140	950	220	1633	120	952	210
Cl	1637	170	953	190	1630	150	953	170
Br	1636	170	952	195	1629	125	953	155
NO <sub>2</sub>	1633	360	947	240	1627	300	946	200

## EXPERIMENTAL

Electronic spectra were measured for ca.  $3 \times 10^{-5}$  M ethanolic solns in 10 mm cells using a Unicam SP700 spectrometer. IR spectra were measured in the region  $2000\text{--}800 \text{ cm}^{-1}$  for 0.202 M solns in chloroform in 0.099 mm compensated cells on a Perkin-Elmer 125 spectrometer.

*Styrylpyrroles.* The phosphonium chloride (0.01 mole) was added with stirring to NaH (50% dispersion in mineral oil, 0.01 mole) in benzene (30 ml) under N<sub>2</sub>. When the colour of the soln appeared to be orange, the formylpyrrole (0.01 mole) in benzene (10 ml) was added. The soln was refluxed for 3 hr and then poured into water (200 ml). The organic layer was collected and the aqueous layer extracted with ether ( $2 \times 100$  ml). The combined organic layer and extracts were dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residual oil was absorbed on silica gel and eluted with benzene to give the styrylpyrroles, which were recrystallized from hexane.

The *p*-nitrostyrylpyrroles obtained by this method contained 4,4'-dinitrobiphenyl, which was removed by Soxhlet extraction with pet. ether (b.p.  $40\text{--}60^\circ$ ). The nitrostyrylpyrroles were recrystallized from CHCl<sub>3</sub>:pet. ether.

TABLE 5.

<i>para</i> -Substituent	m.p. °C	Required			Found		
		C	H	N	C	H	N
<i>trans</i> 2-( <i>p</i> -Substituted styryl)pyrroles							
OMe	169–170	78.4	6.1	7.0	78.6	6.5	7.0
Me	162–164	85.2	7.15	7.6	85.2	6.8	7.4
H	140–141 <sup>a</sup>						
F	147–149	77.0	5.4	7.5	77.0	5.5	7.2
Cl	200–201	70.8	4.95	6.9	71.15	4.8	6.55
Br	185–186	58.1	4.1	5.6	58.0	4.4	5.3
NO <sub>2</sub>	167–169 <sup>b</sup>	67.3	4.7	13.1	67.0	4.75	12.7
<i>trans</i> 1-Methyl-2-( <i>p</i> -substituted styryl)pyrroles							
OMe	90–91	78.8	7.1	6.6	78.6	7.1	6.4
Me	58–59	85.2	7.7	7.1	84.7	7.9	7.1
H	70–72 <sup>c</sup>						
F	101–102	77.6	6.0	7.0	77.7	6.2	6.7
Cl	86–87	71.7	5.6	6.4	72.2	5.5	6.6
Br	95–96	59.5	4.6	5.3	59.75	4.6	5.3
NO <sub>2</sub>	148–149	68.4	5.3	12.3	68.5	5.3	12.3

<sup>a</sup> lit.<sup>4</sup> m.p. 140–142°. <sup>b</sup> Dimorphic, transition temperature ca. 148°. <sup>c</sup> lit.<sup>4</sup> m.p. 70–73.

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