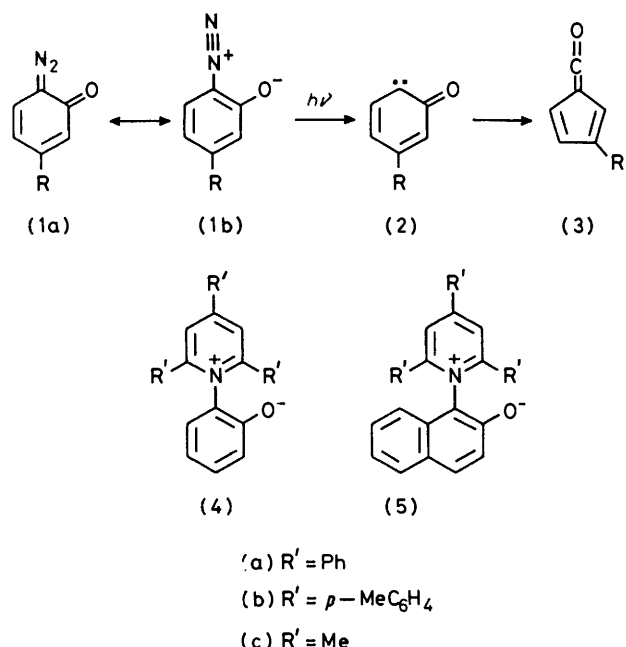


## Heterocycles in Organic Synthesis. Part 40.<sup>1</sup> Oxidation of 2,4,6-Triarylpyridinium Betaines and 2,4,6-Triarylpyridinium Perchlorates by Hydrogen Peroxide

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*N*-(2-Oxidophenyl and 2-oxido-1-naphthyl)-2,4,6-triarylpyridiniums are oxidised by hydrogen peroxide to mixtures of tetra-arylpyrroles and 3-oxidopyridinium betaines, whereas 2,4,6-triarylpyridinium salts and alkaline hydrogen peroxide give  $\beta$ -amino- and  $\beta$ -aroylamino-chalcones.

THE diazo-derivatives of general type (1a)  $\leftrightarrow$  (1b) undergo photo-elimination of nitrogen giving the ketens (3) by rearrangement of the intermediate carbenes (2).<sup>2</sup> Our studies of 2,4,6-triarylpyridines as leaving groups<sup>3</sup> led us to investigate the possibility that photolysis or



thermolysis † of the 2,4,6-trimethyl- and 2,4,6-triarylpyridinium betaines (4) and (5) might lead to similar products. The anticipated reaction did not occur but this work led to the discovery of novel oxidations of a series of pyridinium betaines (4) and (5) which we now report.

### RESULTS AND DISCUSSION

We have prepared the betaines (4a), (4b), and (5a), (5b) by deprotonation of the 1-(2-hydroxyaryl)-2,4,6-triarylpyridinium perchlorates (6b, e, j, k;  $X = ClO_4$ ) using ethanolic potassium hydroxide or ion-exchange resin. These betaines reacted with acids to re-form the pyridinium cation and chlorides and tetrafluoroborates were

† Some initial work was carried out in collaboration with Mr. J. Lewis, M.Sc.

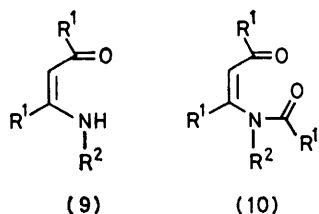
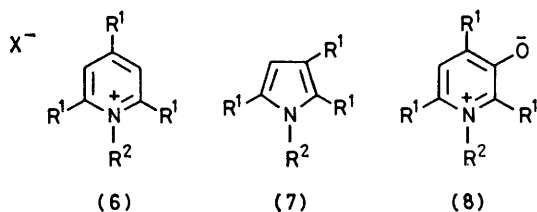
prepared in this way. Thermolysis of the betaine (4a) under a variety of conditions only led to complex mixtures of products. When this betaine (4a) was photolysed (3 000 Å) in a mixture of water and dioxan (1 : 10), however, two products were isolated by column chromatography. The first product, obtained in 19% yield, was identified as 1-(2-hydroxyphenyl)-2,3,5-triphenylpyrrole (7b). The structure of this compound is fully supported by its spectroscopic properties and has been confirmed by an X-ray structure determination (see below). The second product was obtained in 20% yield and has been shown to be a 2,4,6-triphenylpyridinium-3-olate (8b). This is the first reported example of a 2,4,6-triarylpyridinium-3-olate (8;  $R^1 = aryl$ ),<sup>4</sup> although 3-hydroxy-2,4,6-triphenylpyridine itself has been described previously<sup>5</sup> and simple pyridinium-3-olates are well known.<sup>4,6</sup>

Further investigations of the conditions necessary to achieve this novel transformation of the betaine (4a) showed that the process is not in fact photochemical, but that the products are formed by reaction between the betain (4) and peroxides generated in the dioxan solvent. We found that the same products (7b) and (8b) were formed in similar yields when the betaine (4a) was treated with an ethanolic solution of hydrogen peroxide. Furthermore, under these conditions the betaines (4b) and (5a), (5b) also gave the corresponding pyrroles (7e, j, and k) and pyridinium-3-olates (8e, j, and k) whose structures are fully supported by microanalysis and by their spectroscopic properties.

The mechanism of formation of these products (7) and (8) is not yet completely clear but we propose the oxidation sequence shown in the Scheme. Initial addition of the peroxide anion is followed by cyclisation to an epoxide intermediate (11), which in turn is hydrolysed to the 1,2-dihydroxy-derivative (12). We postulate that this intermediate (12) can either dehydrate giving the observed pyridinium-3-olate (13) or alternatively can undergo oxidative ring-opening to the acyclic aldehyde (14), which then gives the pyrrole (15) by a sequence involving recyclisation, oxidation, and decarboxylation. This mechanism leading to (15) resembles that postulated by Bristol and Dittmer to account for the slow transformation of 1-methyl-3-carbamoylpyridinium chloride to a

pyrrolidinone hydroperoxide by hydrogen peroxide and sodium hydrogen carbonate.<sup>7</sup>

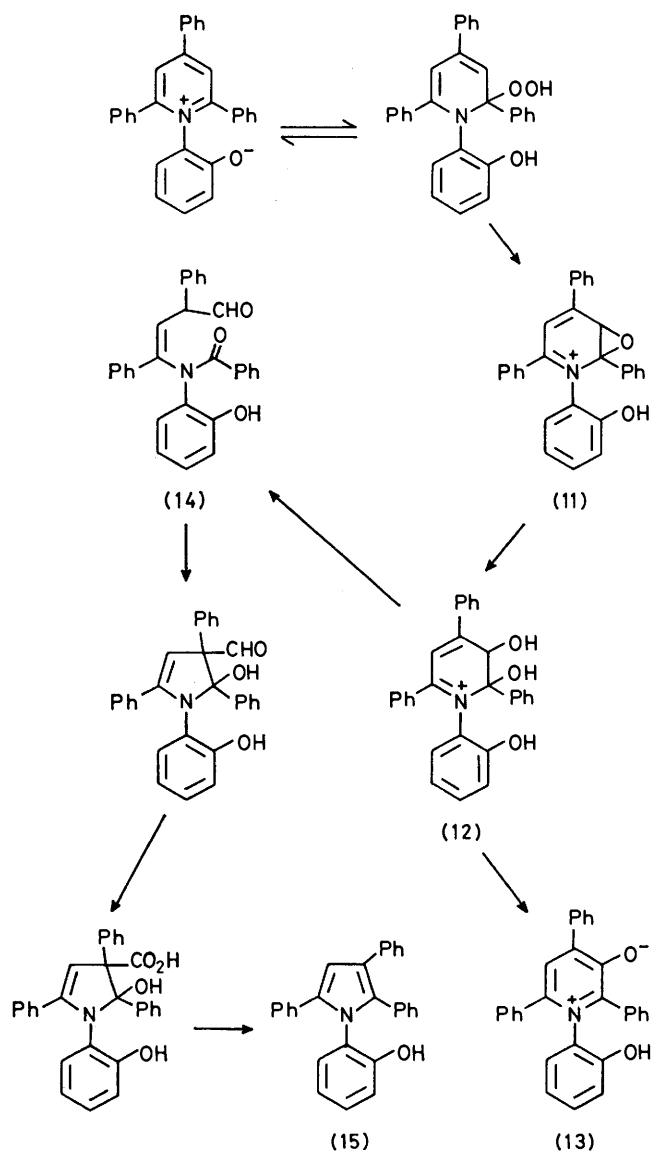
An interesting difference was observed when an ethanolic solution of the *p*-phenoxy-betaine (16) was treated with hydrogen peroxide. The pyridinium-3-olate (8d) was isolated in 14% yield but no pyrrole (7) could be detected. The structure of compound (8d) has been confirmed by *X*-ray analysis (see below). In addition to compound (8d) two other products were also isolated. A product melting at 213 °C with decomposition appears to be the hydroperoxide (18), which has



- a: R<sup>1</sup> = R<sup>2</sup> = Ph  
 b: R<sup>1</sup> = Ph, R<sup>2</sup> = *o*-HOC<sub>6</sub>H<sub>4</sub>  
 c: R<sup>1</sup> = Ph, R<sup>2</sup> = *m*-HOC<sub>6</sub>H<sub>4</sub>  
 d: R<sup>1</sup> = Ph, R<sup>2</sup> = *p*-HOC<sub>6</sub>H<sub>4</sub>  
 e: R<sup>1</sup> = Ph, R<sup>2</sup> = 2-hydroxynaphthyl  
 f: R<sup>1</sup> = Ph, R<sup>2</sup> = Me  
 g: R<sup>1</sup> = Ph, R<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>  
 h: R<sup>1</sup> = Ph, R<sup>2</sup> = PhCH<sub>2</sub>  
 i: R<sup>1</sup> = Ph, R<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>  
 j: R<sup>1</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = *o*-HOC<sub>6</sub>H<sub>4</sub>  
 k: R<sup>1</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = 2-hydroxynaphthyl  
 l: R<sup>1</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>  
 m: R<sup>1</sup> = Me, R<sup>2</sup> = *o*-HOC<sub>6</sub>H<sub>4</sub>

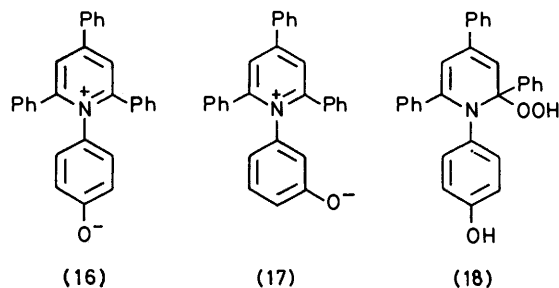
previously been described by Dilthey and Dierichs (m.p. 201 °C).<sup>8</sup> The third product has been shown to be the acylaminochalcone (10d). Similar treatment of the *m*-phenoxy-betaine (17) gave only the aminochalcone derivative (9c) (59%).

The results of the reactions described above prompted us to investigate the reaction of other pyridinium perchlorates (6; X = ClO<sub>4</sub>) with hydrogen peroxide. Treatment of an alkaline ethanolic solution of 1,2,4,6-tetra-phenylpyridinium perchlorate (6a; X = ClO<sub>4</sub>) with hydrogen peroxide gave 3-anilino-1,3-diphenylpropen-2-one (9a) in 64% yield. This product is presumably formed by an oxidative cleavage, which is initiated by



nucleophilic attack at the 2-position of the pyridinium ring. A similar treatment of 1-methyl-2,4,6-triphenylpyridinium perchlorate gave 3-(*N*-benzoyl-*N*-methylamino)-1,3-diphenylpropen-2-one (10f) (22%). Similar products or mixtures [(9) and (10)] were obtained from other perchlorates (6; X = ClO<sub>4</sub>).

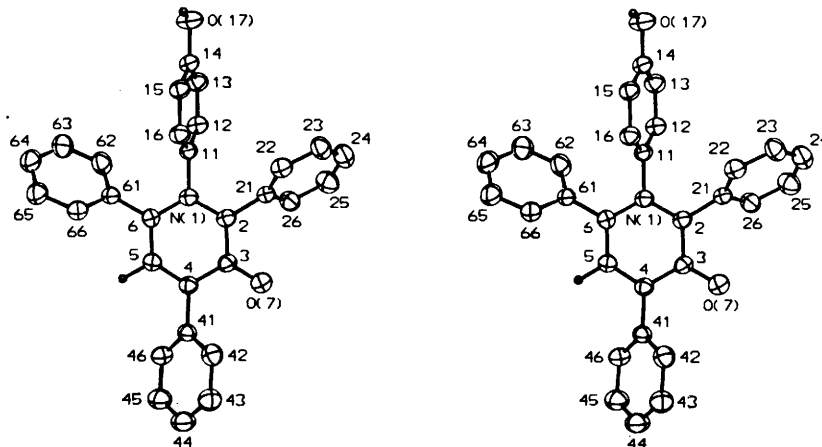
*Description of the Structures (7b) and (8d).*—The basic structure of 1-(2-hydroxyphenyl)-2,3,5-triphenylpyrrole



(7b) (*i.e.* four six-membered rings attached to a five-membered ring) was easily solved by direct methods (MULTAN). However, the structure suffers from a serious disorder problem. The molecule is *ca.* two-fold disordered with respect to rotation about the CH bond of the pyrrole ring, so that the nitrogen atom and one of the carbon atoms in the ring share sites. Also the oxygen atom of the *o*-hydroxyphenyl group, which should thus occupy two sites, does in fact occupy four sites with widely disparate occupation factors. Because the disorder could not be properly modelled and since the

singlet at  $\delta$  7.5–8.5 and the signals for the 2-, 4-, and 6-substituents remain relatively unchanged. By contrast the signals of the 1-substituent suffer a pronounced upfield shift from the influence of the oxido-group.

The structures of the tetra-arylpyrroles (7) (Table 4) and the tetra-arylpuridinium-3-olates (8) (Tables 5 and 6) are fully supported by their  $^1\text{H}$  n.m.r. and u.v. spectra. The long-wavelength absorption of the tetra-arylpyrroles (7) at 285–290 nm is consistent with the reported u.v. spectra of 1,2,5-triphenylpyrrole [ $\lambda_{\text{max}}$  (EtOH) 301 nm ( $\epsilon$  19 500)].<sup>9</sup> The absorption of the pyridinium-3-olates



Stereo-drawing of 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium-3-olate (8d) (numbers refer to carbon atoms)

structure of the product had already been solved, the refinement of this structure was halted at  $R$  0.146.

The crystal structure of 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium-3-olate (8d) consists of discrete molecules which form infinite chains parallel to the  $z$ -axis *via*  $\text{O}(17)\text{--H}(17)\cdots\text{O}(7)$  hydrogen bonds with the following bond parameters:  $\text{O}(17)\text{--H}(17)$ , 0.88(4) Å;  $\text{O}(17)\text{--O}(7)$ , 2.616(4) Å; and  $\text{O}(17)\text{--H}(17)\cdots\text{O}(7)$ , 1.68(4) Å. Selected bond lengths and bond angles are given in Table 1 and the structure is shown schematically in the Figure.

TABLE 1

Bond lengths (Å) and bond angles ( $^\circ$ ) of 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium-3-olate (8d)\*

$\text{N}(1)\text{--C}(2)$	1.373(5)	$\text{C}(2)\text{--N}(1)\text{--C}(6)$	122.8(3)
$\text{N}(1)\text{--C}(6)$	1.272(5)	$\text{N}(1)\text{--C}(2)\text{--C}(3)$	120.2(3)
$\text{C}(2)\text{--C}(3)$	1.424(5)	$\text{C}(2)\text{--C}(3)\text{--C}(4)$	117.1(3)
$\text{C}(3)\text{--C}(4)$	1.430(5)	$\text{C}(2)\text{--C}(3)\text{--O}(7)$	120.9(3)
$\text{C}(3)\text{--O}(7)$	1.279(4)	$\text{C}(4)\text{--C}(3)\text{--O}(7)$	122.0(3)
$\text{C}(4)\text{--C}(5)$	1.377(5)	$\text{C}(3)\text{--C}(4)\text{--C}(5)$	118.9(3)
$\text{C}(5)\text{--C}(6)$	1.389(5)	$\text{C}(4)\text{--C}(5)\text{--C}(6)$	123.3(3)
$\text{C}(14)\text{--O}(17)$	1.356(4)	$\text{N}(1)\text{--C}(6)\text{--C}(5)$	117.0(3)

\*Atom numbers as in the Figure.

**Spectroscopy.**— $^1\text{H}$  N.m.r. spectra of the pyridinium salts are collected in Table 2. The 3,5 protons of the central ring appear as a singlet at  $\delta$  7.7–8.65: the other aromatic protons appear in the expected regions, with the 2',6'-protons of the 4-aryl group being shifted downfield (to *ca.*  $\delta$  8.0) as expected.

$^1\text{H}$  N.m.r. spectra of the betaines are given in Table 3. Again the 3,5-protons of the pyridinium ring appear as a

(8) in the region 310–325 nm is in good agreement with the spectra of simpler derivatives: *N*-methylpyridinium-3-olate has  $\lambda_{\text{max}}$  320 nm in aqueous solution.<sup>10</sup> The 5-proton of the pyridinium-3-olate ring appears as a singlet at  $\delta$  7.5–8.0 and the protons of the aromatic substituents appear in the usual regions. Table 7 shows the  $^1\text{H}$  n.m.r. and u.v. spectra of the 3-aminoprop-2-en-1-ones (9) and (10).

#### EXPERIMENTAL

Unless otherwise stated, i.r. spectra were measured for Nujol mulls, u.v. spectra for solutions in ethanol, and n.m.r. spectra (60 MHz) for solutions in deuteriochloroform (tetramethylsilane as internal reference). Only significant i.r. bands are quoted.

Evaporation refers to the removal of volatile materials under reduced pressure. When substances are stated to be identical, this refers to their m.p.s and i.r. spectra.

**Preparation of Pyridinium Perchlorates.**—1-(2-Hydroxyphenyl)-2,4,6-triphenylpyridinium perchlorate (6b;  $\text{X} = \text{ClO}_4$ ). 2,4,6-Triphenylpyrylium perchlorate<sup>11</sup> (8.17 g, 0.02 mol) and 2-aminophenol (2.18 g, 0.02 mol) in absolute EtOH (100 ml) were heated under reflux (48 h). The cooled solution was then filtered and addition of  $\text{Et}_2\text{O}$  (500 ml) to the filtrate gave a solid. Recrystallisation from EtOH– $\text{Et}_2\text{O}$  gave compound (6b;  $\text{X} = \text{ClO}_4$ ) (7.5 g; 81%) as a brown microcrystalline solid, m.p. 253  $^\circ\text{C}$  (Found: C, 69.3; H, 4.5; N, 2.5. Calc. for  $\text{C}_{29}\text{H}_{22}\text{ClNO}_5$ : C, 69.6; H, 4.4; N, 2.8%);  $\nu_{\text{max}}$  1 050–1 100  $\text{cm}^{-1}$  ( $\text{ClO}_4^-$ ).

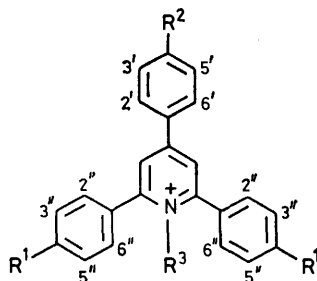
The following compounds were similarly prepared from the appropriate pyrylium salt and amine: 1-(2-hydroxyphenyl)-2,4,6-tri-*p*-tolylpyridinium perchlorate (6j;  $\text{X} = \text{ClO}_4$ )

(81%), brown needles (from EtOH-Et<sub>2</sub>O), m.p. 289—292 °C (Found: C, 71.0; H, 5.5; N, 2.3. C<sub>32</sub>H<sub>28</sub>ClNO<sub>5</sub> requires C, 70.9; H, 5.2; N, 2.6%);  $\nu_{\max}$ . 1 050 cm<sup>-1</sup> (ClO<sub>4</sub><sup>-</sup>); 1-(2-hydroxynaphthyl)-2,4,6-triphenylpyridinium perchlorate (6e);

*ium perchlorate* (6k, X = ClO<sub>4</sub>) (86%), a brown microcrystalline solid (from EtOH-Et<sub>2</sub>O), m.p. 292—296 °C (Found: C, 73.0; H, 5.2; N, 2.5. C<sub>30</sub>H<sub>30</sub>ClNO<sub>5</sub> requires C, 73.0; H, 5.1; N, 2.4%);  $\nu_{\max}$ . 1 040 cm<sup>-1</sup> (ClO<sub>4</sub><sup>-</sup>); 1-(3-hydroxyphenyl)-

TABLE 2

N.m.r. spectra of pyridinium salts

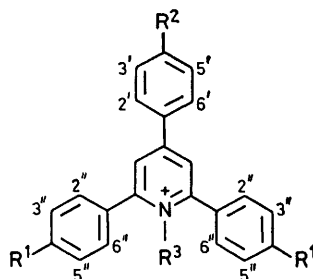


Compound	Substituents			Solvent	3-H, 5-H (2 H, s)	Other aromatic protons			
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>			1-Substituent	2,6-Substituents	4-Substituent	
(6a)	H	H	Ph	(CD <sub>3</sub> ) <sub>2</sub> SO	8.65	7.4 (5 H, m)	7.4 (10 H, m)	8.4 (m)	7.4 (3 H, m)
(6b)	H	H	<i>o</i> -HOC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub> CO <sub>2</sub> H	8.35	7.0 (4 H, m)	7.45 (10 H, m)	8.1 (m)	7.8 (3 H, m)
(6c)	H	H	<i>m</i> -HOC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub> CO <sub>2</sub> H	8.3	6.9 (4 H, m)	7.4 (10 H, m)	8.0 (m)	7.7 (3 H, m)
(6d)	H	H	<i>p</i> -HOC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub> CO <sub>2</sub> H	8.3	7.0 (4 H, AB system, <i>J</i> 8 Hz)	7.4 (10 H, m)	8.0 (m)	7.75 (3 H, m)
(6e)	H	H	HOC <sub>10</sub> H <sub>6</sub>	CF <sub>3</sub> CO <sub>2</sub> H	8.43	7.3 (6 H, m)	7.3 (10 H, m)	8.05 (m)	7.3 (3 H, m)
(6f)	H	H	Me	CDCl <sub>3</sub>	7.7 (m)	3.8 (3 H, s)	7.6 (10 H, m)	7.7 (m)	7.6 (3 H, m)
(6g)	H	H	<i>o</i> -MeC <sub>6</sub> H <sub>4</sub>	CDCl <sub>3</sub>	8.0	7.1 (4 H, m), 1.95 (3 H, s, Me)	7.35 (10 H, m)	7.8 (m)	7.6 (3 H, m)
(6h)	H	H	CH <sub>2</sub> Ph	CF <sub>3</sub> CO <sub>2</sub> H	8.2	5.8 (2 H, s, CH <sub>2</sub> ), 6.6 (2 H, m), 7.3 (3 H, m)	7.6 (10 H, m)	7.9 (m)	7.6 (3 H, m)
(6i)	H	H	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	CF <sub>3</sub> CO <sub>2</sub> H	8.15	2.3 (3 H, s, Me), 5.72 (2 H, s, CH <sub>2</sub> ), 6.45 (2 H, d, <i>J</i> 7 Hz), 7.05 (2 H, d, <i>J</i> 7 Hz)	7.6 (10 H, m)	7.9 (m)	7.6 (3 H, m)
(6j)	Me	Me	<i>o</i> -HOC <sub>6</sub> H <sub>4</sub>	CF <sub>3</sub> CO <sub>2</sub> H	8.25	7.35 (4 H, m)	7.35 (8 H, m), 2.33 (6 H, s, 2 × 4''-Me)	7.9 (d, <i>J</i> 8 Hz)	7.5 (2 H, d, <i>J</i> 8 Hz, 3',5'-H), 2.48 (3 H, s, 4'-Me)
(6k)	Me	Me	HOC <sub>10</sub> H <sub>7</sub>	CF <sub>3</sub> CO <sub>2</sub> H	8.3	7.3 (6 H, m)	2.15 (6 H, s, 2 × 4''-Me), 7.3 (4 H, d, <i>J</i> 8 Hz, 2''-,6''-H), 6.95 (4 H, d, <i>J</i> 8 Hz, 3''-,5''-H)	7.95 (d, <i>J</i> 8 Hz)	7.6 (2 H, d, <i>J</i> 8 Hz, 3',5'-H), 2.5 (3 H, s, 4'-Me)
(6l)	Me	Me	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	CDCl <sub>3</sub>	7.95	2.35 (3 H, s, Me), 5.70 (2 H, s, CH <sub>2</sub> ), 6.30 (2 H, d, <i>J</i> 7 Hz), 6.9 (2 H, d, <i>J</i> 7 Hz)	2.35 (6 H, s, 2 × 4''-Me), 7.55 (4 H, d, <i>J</i> 8 Hz, 2''-,6''-H), 7.2 (4 H, d, <i>J</i> 8 Hz, 3''-,5''-H)	7.7 (d, <i>J</i> 8 Hz)	7.45 (2 H, d, <i>J</i> 8 Hz), 2.2 (3 H, s, 4'-Me)

X = ClO<sub>4</sub>) (71%), light brown microcrystals (from EtOH-Et<sub>2</sub>O), m.p. 170—175 °C (Found: C, 72.1; H, 4.4; N, 2.3. C<sub>33</sub>H<sub>24</sub>ClNO<sub>5</sub> requires C, 72.1; H, 4.4; N, 2.6%);  $\nu_{\max}$ . 1 090 cm<sup>-1</sup> (ClO<sub>4</sub><sup>-</sup>); 1-(2-hydroxynaphthyl)-2,4,6-tri-*p*-tolylpyridin-

ium perchlorate (6c; X = ClO<sub>4</sub>) (56%), prisms (from MeOH), m.p. 173 °C (Found: C, 69.7; H, 4.4; N, 3.0. C<sub>29</sub>H<sub>22</sub>ClNO<sub>5</sub> requires C, 69.7; H, 4.4; N, 2.8%);  $\nu_{\max}$ . (CHBr<sub>3</sub>) 1 100 cm<sup>-1</sup> (ClO<sub>4</sub><sup>-</sup>); 1-(*p*-methylbenzyl)-2,4,6-

TABLE 3  
N.m.r. spectra of pyridinium betaines



Compd.	Substituents			Solvent	3-H and 5-H (2 H, s)	Other protons			
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>			1-Substituent	2,6-Substituents	4-Substituent	
(4a)	H	H	2-Oxidophenyl	(CD <sub>3</sub> ) <sub>2</sub> SO	8.35	5.6 (1 H, m) 6.15 (1 H, d, J 8 Hz) 6.6 (2 H, m) 5.6 (1 H, m)	7.6 (4 H, m) 7.35 (6 H, m) 2.25 (6 H, s, 2 Me)	8.2 (m)	7.6 (3 H, m) 2.40 (3 H, s, Me)
(4b)	Me	Me	2-Oxidophenyl	(CD <sub>3</sub> ) <sub>2</sub> SO	8.2	6.0 (1 H, d, J 8 Hz) 6.55 (2 H, m)	7.6 (4 H, d, J 8 Hz) 7.1 (4 H, d, J 8 Hz)	8.1 (d, J 8 Hz)	7.4 (2 H, d, J 8 Hz)
(5a)	H	H	2-Oxido-1-naphthyl	(CD <sub>3</sub> ) <sub>2</sub> SO	8.5	6.55 (6 H, m)	7.7 (4 H, m) 7.2 (6 H, m) 2.15 (6 H, s, 2 Me)	8.2 (m)	7.7 (3 H, m)
(5b)	Me	Me	2-Oxido-1-naphthyl	CDCl <sub>3</sub>	8.0	6.4 (1 H, d, J 8 Hz) 6.7 (3 H, m) 7.4 (2 H, m)	7.4 (4 H, d, J 8 Hz) 6.8 (4 H, d, J 8 Hz) 7.4 (10 H, m)	7.7 (d, J 8 Hz)	7.2 (2 H, d, J 8 Hz) 2.45 (3 H, s, Me) 7.6 (3 H, m)
(16)	H	H	4-Oxidophenyl	(CD <sub>3</sub> ) <sub>2</sub> SO	8.5	5.9 (2 H, d, J 8 Hz) 6.7 (2 H, d, J 8 Hz)	7.4 (10 H, m)	8.4 (m)	7.6 (3 H, m)
(17)	H	H	3-Oxidophenyl	(CD <sub>3</sub> ) <sub>2</sub> SO	8.5	6.3 (4 H, m)	7.5 (10 H, m)	8.3 (m)	7.5 (3 H, m)

*tri-p-tolylpyridinium perchlorate* (61; X = ClO<sub>4</sub>) (98%), needles (from EtOH), m.p. 179 °C (Found: C, 72.7; H, 6.2; N, 2.2. C<sub>34</sub>H<sub>32</sub>ClNO<sub>4</sub>·0.5 EtOH requires C, 72.9; H, 6.1; N, 2.4%);  $\nu_{\max}$ , 1 080 cm<sup>-1</sup> (ClO<sub>4</sub><sup>-</sup>); 1-(2-hydroxyphenyl)-2,4,6-trimethylpyridinium perchlorate (6m; X = ClO<sub>4</sub>) (92%), plates (from H<sub>2</sub>O), m.p. 156 °C (Found: C, 51.3; H, 5.4; N, 4.1. Calc. for C<sub>14</sub>H<sub>16</sub>ClNO<sub>5</sub>·0.75H<sub>2</sub>O: C, 51.4; H, 5.4; N, 4.3%);  $\nu_{\max}$ , 3 475 (OH), and 1 120 cm<sup>-1</sup> (ClO<sub>4</sub><sup>-</sup>);  $\delta$  (CF<sub>3</sub>-CO<sub>2</sub>H) 2.5 (6 H, s), 2.7 (3 H, s), 7.35 (4 H, m), and 7.75 (2 H, s).

*Preparation of Pyridinium Betaines.*—1-(2-Oxidophenyl)-2,4,6-triphenylpyridinium betaine (4a). (a) The perchlorate (6b; X = ClO<sub>4</sub>) (1.0 g) in EtOH (5 ml) was eluted through a

column of Amberlite Resin IRA-401 (70 g) which had been treated with NaOH (300 ml, 4%). When the eluant was neutral to litmus, the aqueous solution (300 ml) was extracted with CHCl<sub>3</sub> (3 × 100 ml) and the combined extracts dried (MgSO<sub>4</sub>). Evaporation gave the betaine (4a) (830 mg, 97%) as a purple solid, m.p. 188 °C (decomp.) (lit.,<sup>12</sup> m.p. 188 °C) (Found: C, 83.2; H, 5.6; N, 3.2. Calc. for C<sub>29</sub>H<sub>21</sub>NO·H<sub>2</sub>O: C, 83.4; H, 5.5; N, 3.4%);  $\lambda_{\max}$ , 208 ( $\epsilon$  15 500) and 306 nm (18 300);  $m/e$  399 ( $M^{+}$ );

(b) The perchlorate (6b; X = ClO<sub>4</sub>) (7.5 g) in EtOH (25 ml) was treated with ethanolic KOH (40 ml; 3%) and the mixture was stirred (15 min). KClO<sub>4</sub> was filtered off and the filtrate evaporated until nearly dry. Water (20 ml) was

TABLE 4  
N.m.r. and u.v. spectra of tetra-arylpyrroles

Compound	Substituents		$\delta$ (CDCl <sub>3</sub> )	$\lambda_{\max}$ (EtOH)/nm ( $\epsilon$ in parentheses)
	R <sup>1</sup>	R <sup>2</sup>		
(7b)	Ph	<i>o</i> -HOC <sub>6</sub> H <sub>4</sub>	5.3 (1 H, br s, exchanges with D <sub>2</sub> O) and 6.9—7.9 (20 H, m)	217 (29 000), 258 (21 700), and 285 (22 800)
(7e)	Ph	2-hydroxynaphthyl	7.0—8.0 (24 H, m)	230 (61 200), 280 (26 200), and 290 (26 600)
(7j)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	<i>o</i> -HOC <sub>6</sub> H <sub>4</sub>	2.2 (9 H, s), 6.8 (1 H, s), 7.1 (16 H, m), and 9.8 (1 H, br s, exchanges with D <sub>2</sub> O)	210 (25 000), 258 (14 600), and 278 (13 700)
(7k)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	2-hydroxynaphthyl	2.05 (3 H, s), 2.1 (3 H, s), 2.2 (3 H, s), 5.6 (1 H, br s), 7.0 (16 H, m), and 7.5 (2 H, d, J 9 Hz)	232 (43 100), 281 (18 900), and 291 (19 600)

added and the solution extracted with  $\text{CHCl}_3$  ( $3 \times 25$  ml). The dry extracts ( $\text{MgSO}_4$ ) were evaporated to give a purple solid. Recrystallisation from  $\text{EtOH-Et}_2\text{O}$  gave the betaine (4a) (6.3 g, 97%), m.p. 188 °C (decomp.), identical with an authentic sample.

The following compounds were similarly prepared by method (b): 1-(2-oxidophenyl)-2,4,6-tri-*p*-tolylpyridinium

TABLE 5

U.v. spectra of 1,2,4,6-tetra-arylpyridinium-3-olates

Compd.	Substituents		$\lambda_{\text{max.}}(\text{EtOH})/\text{nm}$ ( $\epsilon$ in parentheses)
	R <sup>1</sup>	R <sup>2</sup>	
(8b)	Ph	2-Hydroxyphenyl	212 (33 400) 302 (25 400) and 318 (8 000)
(8d)	Ph	4-Hydroxyphenyl	230 (19 000) 276 (19 800) and 390 (8 100)
(8e)	Ph	2-Hydroxynaphthyl	230 (22 000) and 312 (13 300)
(8j)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	2-Hydroxyphenyl	209 (14 000) and 325 (13 200)
(8k)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	2-Hydroxynaphthyl	210 (30 400) 231 (33 500) and 324 (19 800)

betaine (4b) (83%) as red prisms (from  $\text{EtOH-Et}_2\text{O}$ ), m.p. 203–205 °C (decomp.) (Found: C, 85.8; H, 6.6; N, 3.0.  $\text{C}_{32}\text{H}_{27}\text{NO}\cdot 0.5\text{H}_2\text{O}$  requires C, 85.3; H, 6.2; N, 3.1%);  $\lambda_{\text{max.}}$  208 ( $\epsilon$  17 000) and 322 nm (13 200);  $m/e$  429 ( $M^{+}$ ); 1-(2-naphthylloxy)-2,4,6-triphenylpyridinium betaine (5a) (88%) as a blue microcrystalline solid (from  $\text{EtOH-Et}_2\text{O}$ ), m.p. 150 °C (decomp.) (Found: C, 81.2; H, 5.4; N, 2.9.  $\text{C}_{33}\text{H}_{23}\text{NO}\cdot 2\text{H}_2\text{O}$  requires C, 81.7; H, 5.6; N, 2.9%);  $\lambda_{\text{max.}}$  210 ( $\epsilon$  25 100),

manner, compound (5a) gave 1-(2-hydroxynaphthyl)-2,4,6-triphenylpyridinium chloride (6e; X = Cl) (68%) as yellow prisms, m.p. 228–230 °C (Found: C, 78.1; H, 5.5; N, 2.9; Cl, 7.0.  $\text{C}_{33}\text{H}_{24}\text{ClNO}\cdot \text{H}_2\text{O}$  requires C, 78.4; H, 5.0; N, 2.8; Cl, 7.0%).

(b) With tetrafluoroboric acid. Compound (4a) was treated with concentrated  $\text{HBF}_4$  and the product recrystallised from  $\text{EtOH-Et}_2\text{O}$  to give 1-(2-hydroxyphenyl)-2,4,6-triphenylpyridinium tetrafluoroborate (6b; X =  $\text{BF}_4$ ) (89%) as prisms, m.p. 160–162 °C (Found: N, 2.7.  $\text{C}_{29}\text{H}_{22}\text{BF}_4\text{NO}$  requires N, 2.9%).

In a similar manner, compound (5a) gave 1-(2-hydroxynaphthyl)-2,4,6-triphenylpyridinium tetrafluoroborate (6e; X =  $\text{BF}_4$ ) (78%) as yellow prisms, m.p. 175–178 °C (Found: C, 73.7; H, 4.3; N, 2.5.  $\text{C}_{33}\text{H}_{24}\text{BF}_4\text{NO}$  requires C, 73.7; H, 4.5; N, 2.5%).

Reaction of Pyridinium Betaines with Hydrogen Peroxide.—1-(2-Oxidophenyl)-2,4,6-triphenylpyridinium betaine (4a). The betaine (4a) was generated *in situ* by treatment of an  $\text{EtOH}$  solution of the perchlorate (6b; X =  $\text{ClO}_4$ ) (2.0 g) with ethanolic  $\text{KOH}$  to pH 10 and removal of  $\text{KClO}_4$ . The betaine solution was then treated with  $\text{H}_2\text{O}_2$  (3 ml, 30%) and the mixture stirred under nitrogen (24 h). Evaporation gave a residue which was purified by column chromatography (silica gel:  $\text{CHCl}_3$  as eluant). The main band ( $R_F$  0.54) was collected and recrystallised from benzene giving 1-(2-hydroxyphenyl)-2,3,5-triphenylpyrrole (7b) (0.23 g; 20%) as prisms, m.p. 166 °C (Found: C, 86.6; H, 5.4; N, 3.3.  $\text{C}_{28}\text{H}_{21}\text{NO}$  requires C, 86.8; H, 5.4; N, 3.5%);  $m/e$  387 ( $M^{+}$ ). A second product was then obtained by eluting the column with  $\text{MeOH}$ . Recrystallisation of this fraction from  $\text{EtOAc}$  gave 1-(2-hydroxyphenyl)-2,4,6-triphenylpyridinium-

TABLE 6

N.m.r. spectra of 1,2,4,6-tetra-arylpyridinium-3-olates

Compound	Substituents		Solvent	$\delta$
	R <sup>1</sup>	R <sup>2</sup>		
(8b)	Ph	2-Hydroxyphenyl	( $\text{CD}_3$ ) <sub>2</sub> SO	6.5 (4 H, m), 7.2 (13 H, m), 7.5 (1 H, s), and 8.0 (2 H, m)
(8d)	Ph	4-Hydroxyphenyl	( $\text{CD}_3$ ) <sub>2</sub> SO	6.4 (2 H, d, $J$ 10 Hz), 7.0 (2 H, d, $J$ 10 Hz), 7.2 (10 H, m), 7.45 (3 H, m), 7.6 (1 H, s), and 8.2 (2 H, m)
(8e)	Ph	2-Hydroxynaphthyl	( $\text{CD}_3$ ) <sub>2</sub> SO	7.5 (16 H, m), 8.35 (2 H, m), and 8.6 (2 H, s)
(8j)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	2-Hydroxyphenyl	$\text{CDCl}_3$	2.15 (6 H, s), 2.35 (3 H, s), 7.0 (15 H, m), 7.7 (2 H, d, $J$ 8 Hz), and 7.9 (1 H, s)
(8k)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	2-Hydroxynaphthyl	$\text{CDCl}_3$	2.0 (6 H, s), 2.3 (3 H, s), 4.8 (1 H, br s, exchanged by $\text{D}_2\text{O}$ ), 7.0 (16 H, m), 7.7 (2 H, d, $J$ 9 Hz), and 8.0 (1 H, s)

240 (30 900), and 303 nm (20 600); 1-(2-oxidonaphthyl)-2,4,6-tri-*p*-tolylpyridinium betaine (5b) (96%) as a dark blue microcrystalline solid (from  $\text{EtOH-Et}_2\text{O}$ ), m.p. 270 °C (decomp.) (Found: C, 85.3; H, 6.2; N, 2.8.  $\text{C}_{36}\text{H}_{29}\text{NO}\cdot \text{H}_2\text{O}$  requires C, 84.9; H, 6.1; N, 2.8%);  $\lambda_{\text{max.}}$  209 ( $\epsilon$  25 000), 240 (30 900), and 303 nm (20 600). 1-(2-Oxidophenyl)-2,4,6-trimethylpyridinium betaine (4c) crystallised from  $\text{EtOH-Et}_2\text{O}$  as brown microcrystals (0.85 g, 29%), m.p. 110 °C (decomp.) (Found: N, 6.6.  $\text{C}_{14}\text{H}_{15}\text{NO}$  requires N, 6.6%);  $\nu_{\text{max.}}$  (Nujol) 3 480br, 1 645s, 1 595s, 1 565w, 1 340s, 1 290m, 1 105w, 1 100br, 850m, and 760s  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 2.51 (6 H, s), 2.85 (3 H, s), 7.44 (2 H, s), and 6.2–7.4 (4 H, m);  $\lambda_{\text{max.}}(\text{EtOH})$  220 ( $\epsilon$  18 400), 288 (15 000), and 305 (sh) nm (7 100).

Reaction of Pyridinium Betaines with Acids.—(a) With hydrochloric acid. Compound (4a) was treated with concentrated  $\text{HCl}$  and the product recrystallised from  $\text{EtOH}$  giving 1-(2-hydroxyphenyl)-2,4,6-triphenylpyridinium chloride (6b; X = Cl) (55%) as needles, m.p. 279 °C (Found: C, 77.4; H, 5.3; N, 2.9; Cl, 7.7.  $\text{C}_{29}\text{H}_{22}\text{ClNO}\cdot 0.75\text{H}_2\text{O}$  requires C, 77.5; H, 5.2; N, 3.1; Cl, 7.5%). In a similar

3-olate (8b) (0.33 g; 26%), orange microcrystals, m.p. 294 °C (Found: C, 83.5; H, 5.6; N, 3.2.  $\text{C}_{29}\text{H}_{21}\text{NO}_2$  requires C, 83.8; H, 5.1; N, 3.4%);  $m/e$  415 ( $M^{+}$ ).

In a similar manner, the following betaines gave corresponding products: betaine (5b) gave 1-(2-hydroxyphenyl)-2,3,5-tri-*p*-tolylpyrrole (7j) (43%) as colourless microcrystals [from light petroleum (b.p. 40–60 °C)], m.p. 148–150 °C (Found: C, 86.5; H, 6.5; N, 3.1.  $\text{C}_{31}\text{H}_{27}\text{NO}$  requires C, 86.7; H, 6.3; N, 3.3%);  $m/e$  429 ( $M^{+}$ ) and 1-(2-hydroxyphenyl)-2,4,6-tri-*p*-tolylpyridinium-3-olate (8j) (25%) as yellow prisms (from  $\text{EtOAc-Et}_2\text{O}$ ), m.p. 312 °C (decomp.) (Found: C, 79.1; H, 6.1; N, 3.0.  $\text{C}_{32}\text{H}_{27}\text{NO}_2\cdot 1.5\text{H}_2\text{O}$  requires C, 79.3; H, 6.2; N, 2.9%); betaine (5a) gave 1-(2-hydroxynaphthyl)-2,3,5-triphenylpyrrole (7e) (24%) as microcrystals (from  $\text{MeOH-H}_2\text{O}$ ), m.p. 105–110 °C (Found: C, 87.2; H, 5.3; N, 3.2.  $\text{C}_{32}\text{H}_{23}\text{NO}$  requires C, 87.8; H, 5.3; N, 3.2%);  $m/e$  437 ( $M^{+}$ ) and 1-(2-hydroxynaphthyl)-2,4,6-triphenylpyridinium-3-olate (8e) (23%) as yellow prisms (from  $\text{CHCl}_3\text{-EtOAc}$ ), m.p. 167 °C (Found: C, 85.0; H, 5.2; N, 2.7.  $\text{C}_{33}\text{H}_{23}\text{NO}_2$  requires C, 85.2; H, 5.0; N, 3.0%);

betaine (4b) gave *N*-(2-hydroxynaphthyl)-2,3,5-tri-*p*-tolylpyrrole (7k) (41%) as prisms [from light petroleum (b.p. 40–60 °C)], m.p. 200–201 °C (Found: C, 87.1; H, 6.2; N, 3.1.  $C_{35}H_{29}NO$  requires C, 87.7; H, 6.1; N, 2.9%); and 1-(2-hydroxynaphthyl)-2,4,6-tri-*p*-tolylpyridinium-3-olate (8k) (22%), purple microcrystals (from EtOAc–Et<sub>2</sub>O), m.p. 198 °C (decomp.) (Found: N, 2.8.  $C_{36}H_{29}NO_2$  requires N, 2.8%).

1-(3-Oxidophenyl)-2,4,6-triphenylpyridinium Betaine (17).—Compound (17)<sup>9</sup> (2.0 g) in EtOH (100 ml) was treated with H<sub>2</sub>O<sub>2</sub> (2 ml, 30%) and stirred at room temperature under nitrogen (24 h). Evaporation and recrystallisation of the residue from MeOH gave 3-[*N*-(3-hydroxyphenyl)amino]-1,3-diphenylprop-2-en-1-one (9c) (0.92 g; 59%) as yellow needles, m.p. 172–174 °C (Found: C, 80.1; H, 5.6;

Reaction of Pyridinium Perchlorates with Potassium Hydroxide and Hydrogen Peroxide.—1,2,4,6-Tetraphenylpyridinium perchlorate (6a; X = ClO<sub>4</sub>). Compound (6a; X = ClO<sub>4</sub>)<sup>8</sup> (1.0 g) in EtOH (40 ml) was treated with ethanolic KOH until pH 10. After stirring at room temperature (15 min) the KClO<sub>4</sub> was filtered off and H<sub>2</sub>O<sub>2</sub> (2 ml; 30%) was added to the filtrate which was then stirred under a nitrogen atmosphere (24 h). Evaporation gave a residue which was extracted with Et<sub>2</sub>O. The insoluble PhCO<sub>2</sub>K was removed and the Et<sub>2</sub>O solution dried (MgSO<sub>4</sub>) and evaporated. Recrystallisation of the residue from EtOH gave 3-anilino-1,3-diphenylprop-2-en-1-one (9a) (0.4 g, 64%) as yellow prisms, m.p. 100–101 °C (lit.,<sup>13</sup> m.p. 102–103 °C) (Found: C, 84.1; H, 5.6; N, 4.9. Calc. for C<sub>21</sub>H<sub>17</sub>NO: C, 84.3; H, 5.7; N, 4.7%).

TABLE 7

N.m.r. and u.v. spectra of 3-aminoprop-2-en-1-ones

Compound	R <sup>1</sup>	R <sup>2</sup>	δ(CDCl <sub>3</sub> )	λ <sub>max</sub> (EtOH)/nm (ε in parentheses)
(9a)	Ph	Ph	6.0 (1 H, s), 6.6–7.5 (13 H, m), and 7.9 (2 H, m)	210 (20 600), 252 (15 200), and 380 (23 600)
(9h)	Ph	PhCH <sub>2</sub>	4.3 (2 H, d, <i>J</i> 6 Hz), 5.8 (1 H, s), 6.8–7.5 (13 H, m), and 7.8 (2 H, m)	210 (20 700), 248 (13 800), and 358 (24 400)
(9i)	Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	2.3 (3 H, s), 4.3 (2 H, d, <i>J</i> 6 Hz), 5.8 (1 H, s), 7.1 (5 H, s), 7.4 (8 H, s), and 7.9 (2 H, m)	210 (19 600), 246 (14 400), and 356 (21 800)
(9l)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	2.25 (3 H, s), 2.30 (6 H, s), 4.2 (2 H, d, <i>J</i> 6 Hz), 5.65 (1 H, s), 7.0 (4 H, m), 7.15 (7 H, m), and 7.7 (2 H, d, <i>J</i> 8 Hz)	
(10d)	Ph	<i>p</i> -HOC <sub>6</sub> H <sub>4</sub>	6.5–8.0 (21 H, m) *	212 (10 400), 246 (9 600), 285 (7 500), and 366 (7 200)
(10f)	Ph	Me	3.25 (3 H, s), 6.7 (1 H, s), and 6.9–7.65 (15 H, m)	212 (13 600), 252 (10 230), and 315 (6 700)
(10g)	Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	2.45 (3 H, s), 6.8 (1 H, s), and 6.9–7.8 (19 H, m)	210 (21 500), 265sh (14 200), and 335 (sh) (7 500)
(10h)	Ph	PhCH <sub>2</sub>	5.0 (2 H, s), 6.75 (1 H, s), and 6.9–7.8 (20 H, m)	210 (20 700), 248 (13 800), and 354 (24 400)
(10i)	Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	2.25 (3 H, s), 5.0 (2 H, s), 6.8 (1 H, s), and 6.9–7.8 (19 H, m)	208 (18 500), 250 (10 300), and 325 sh (6 000)
(10l)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	2.25 (3 H, s), 2.30 (6 H, s), 2.35 (3 H, s), 4.8 (2 H, s), 6.05 (1 H, s), and 6.9–8.0 (16 H, m)	

\* In (CD<sub>3</sub>)<sub>2</sub>SO.

N, 4.5.  $C_{21}H_{17}NO$  requires C, 80.0; H, 5.4; N, 4.4%); δ (CDCl<sub>3</sub>) 6.1 (1 H, s), 6.5 (4 H, m), 7.4 (9 H, m), and 8.0 (2 H, m).

1-(4-Oxidophenyl)-2,4,6-triphenylpyridinium Betaine (16).—Compound (16)<sup>12</sup> (1.5 g) in EtOH (40 ml) was treated with H<sub>2</sub>O<sub>2</sub> (3 ml, 30%) and stirred under a nitrogen atmosphere (4 d). Evaporation gave a residue which was fractionally crystallised from MeOH–Et<sub>2</sub>O. Recrystallisation of the first fraction from MeOH–Et<sub>2</sub>O gave 1,2-dihydro-2-hydroperoxy-1-(*p*-hydroxyphenyl)-2,4,6-triphenylpyridine (18) (0.44 g, 22%) as needles, m.p. 213 °C (decomp.) (Found: C, 80.3; H, 5.4; N, 2.9.  $C_{29}H_{23}NO_3$  requires C, 80.4; H, 5.3; N, 3.2%); δ[(CD<sub>3</sub>)<sub>2</sub>SO] 6.5 (2 H, d, *J* 9 Hz), 7.3 (15 H, m), 7.7 (3 H, m), 8.3 (2 H, m), and 8.5 (1 H, s). The second fraction was recrystallised from MeOH giving 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium-3-olate (8d) (0.22 g; 14%) as yellow microcrystals, m.p. 330 °C (decomp.) (Found: C, 81.8; H, 5.3; N, 3.0.  $C_{29}H_{21}NO_2$ , 0.5 H<sub>2</sub>O requires C, 82.0; H, 5.2; N, 3.3%). The third product was purified by column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>). Evaporation of the solvent and recrystallisation from EtOH gave 3-[[*N*-benzoyl-*N*-(4-hydroxyphenyl)amino]-1,3-diphenylprop-2-en-1-one (10d) (28%) as yellow prisms, m.p. 218–220 °C (Found: C, 79.7; H, 5.0; N, 3.4.  $C_{28}H_{21}NO_3$  requires C, 80.2; H, 5.0; N, 3.3%).

In a similar manner the following transformations were achieved: in each case the products were purified or separated by column chromatography (silica gel: CHCl<sub>3</sub> as eluant). 1-Methyl-2,4,6-triphenylpyridinium perchlorate (6f; X = ClO<sub>4</sub>)<sup>14</sup> gave 3-(*N*-benzoyl-*N*-methylamino)-1,3-diphenylprop-2-en-1-one (10 f) (22%), as prisms from EtOH, m.p. 138–140 °C (lit.,<sup>15</sup> m.p. 136–138 °C) (Found: C, 80.6; H, 5.7; N, 4.2. Calc. for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub>: C, 80.9; H, 5.6; N, 4.1%); *m/e* 341 (*M*<sup>+</sup>). 1-(2-Tolyl)-2,4,6-triphenylpyridinium perchlorate (6g; X = ClO<sub>4</sub>)<sup>8</sup> gave 3-[[*N*-benzoyl-*N*-(2-tolyl)amino]-1,3-diphenylprop-2-en-1-one (10 g) (69%) as pale yellow prisms (from EtOH), m.p. 179–181 °C (Found: C, 83.7; H, 5.6; N, 3.6.  $C_{29}H_{23}NO_2$  requires C, 83.5; H, 5.5; N, 3.4%). 1-Benzyl-2,4,6-triphenylpyridinium perchlorate<sup>3</sup> (6h; X = ClO<sub>4</sub>) gave 3-benzylamino-1,3-diphenylprop-2-en-1-one (9h), prisms (from EtOH), m.p. 97 °C (lit.,<sup>13</sup> m.p. 98–99 °C) (Found: C, 84.0; H, 6.0; N, 4.4. Calc. for C<sub>22</sub>H<sub>19</sub>NO: C, 84.4; H, 6.1; N, 4.5%); and 3-(*N*-benzoyl-*N*-benzylamino)-1,3-diphenylprop-2-en-1-one (10h) (26%) as yellow prisms (from EtOH), m.p. 117 °C (Found: N, 3.8.  $C_{29}H_{23}NO_2$  requires N, 3.4%); *m/e* 417 (*M*<sup>+</sup>). 1-(4-Methylbenzyl)-2,4,6-triphenylpyridinium perchlorate (6i; X = ClO<sub>4</sub>)<sup>3a</sup> gave 3-[[4-methylbenzylamino]-1,3-diphenylprop-2-en-1-one (9i) (40%) as prisms [from light petroleum (b.p. 40–60 °C)], m.p. 88–90 °C (Found: C,

84.9; H, 6.4; N, 4.5.  $C_{23}H_{21}NO$  requires C, 84.4; H, 6.4; N, 4.3%; and 3-[*N*-benzoyl-*N*-(4-methylbenzyl)amino]-1,3-diphenylprop-2-en-1-one (10i) (46%) as yellow prisms (from EtOH), m.p. 152–153 °C (Found: C, 83.0; H, 5.8; N, 3.5.  $C_{30}H_{25}NO_2$  requires C, 83.5; H, 5.8; N, 3.2%); 1-(4-methylbenzyl)-2,4,6-tri-*p*-tolylpyridinium perchlorate (6l; X = ClO<sub>4</sub>) gave 3-[(4-methylbenzyl)amino]-1,3-di-*p*-tolylprop-2-en-1-one (9l) (22%) as an oil which was characterised by the n.m.r. spectrum, and 3-[*N*-*p*-toluoyl-*N*-(4-methylbenzyl)amino]-1,3-di-*p*-tolylprop-2-en-1-one (10l) (44%) as prisms (from EtOH), m.p. 135 °C (Found: C, 83.4; H, 6.6; N, 2.9.  $C_{33}H_{31}NO_2$  requires C, 83.7; H, 6.6; N, 3.0%).

**Crystal Structure Information.**—Both sets of data were collected on a Syntex P2<sub>1</sub> diffractometer, with the crystal cooled to –35 °C, using Mo- $K_{\alpha}$  radiation,  $\lambda = 0.71069$  Å.

**Pyrrrole crystal data.** Triclinic, space group  $P\bar{1}$ ,  $a = 10.374(1)$ ,  $b = 12.195(1)$ ,  $c = 9.876(1)$  Å,  $\alpha = 114.19(1)$ ,  $\beta = 112.45(1)$ ,  $\gamma = 88.41(1)^\circ$ ,  $Z = 2$ . The refinement of the structure was halted at  $R = 0.146$  [isotropic thermal parameters for O, N, and C; 133 variables, 3 279 reflections with  $I > 2\sigma(I)$ ]. The atomic co-ordinates are given in Table 8.

TABLE 8

1-(2-Hydroxyphenyl)-2,3,5-triphenylpyrrole (7b): \* atomic co-ordinates with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
CN(1)	0.239 4(5)	0.351 8(4)	0.433 4(5)
CN(2)	0.260 5(5)	0.477 6(4)	0.501 7(6)
C(3)	0.301 5(5)	0.521 9(5)	0.667 3(6)
C(4)	0.302 7(6)	0.418 9(5)	0.700 3(6)
C(5)	0.264 5(6)	0.315 2(5)	0.554 8(6)
C(11)	0.181 1(6)	0.275 5(5)	0.261 0(6)
C(12)	0.262 0(7)	0.257 1(6)	0.171 5(8)
C(13)	0.204 1(7)	0.185 0(6)	0.004 0(8)
C(14)	0.064 7(7)	0.131 1(6)	–0.072 0(8)
C(15)	–0.016 5(7)	0.148 5(6)	0.014 1(8)
C(16)	0.041 7(6)	0.221 3(5)	0.181 4(7)
C(21)	0.232 5(6)	0.539 8(5)	0.397 0(6)
C(22)	0.339 9(7)	0.578 2(5)	0.368 4(7)
C(23)	0.311 7(7)	0.630 9(6)	0.259 6(8)
C(24)	0.176 2(8)	0.642 8(6)	0.179 6(8)
C(25)	0.069 0(7)	0.607 0(6)	0.205 7(8)
C(26)	0.095 7(7)	0.554 2(6)	0.317 1(7)
C(31)	0.337 4(5)	0.649 5(5)	0.788 6(6)
C(32)	0.416 9(6)	0.675 3(6)	0.951 8(7)
C(33)	0.452 6(7)	0.797 1(6)	1.072 8(8)
C(34)	0.410 2(7)	0.892 0(6)	1.033 0(8)
C(35)	0.333 4(7)	0.866 3(6)	0.870 9(9)
C(36)	0.297 2(7)	0.744 7(6)	0.748 1(8)
C(41)	0.255 4(6)	0.186 7(5)	0.529 0(6)
C(42)	0.185 7(6)	0.148 2(5)	0.599 2(7)
C(43)	0.181 7(7)	0.027 1(6)	0.581 5(8)
C(44)	0.247 7(7)	–0.054 3(6)	0.491 5(7)
C(45)	0.314 0(7)	–0.015 6(6)	0.417 8(8)
C(46)	0.320 3(6)	0.105 2(5)	0.436 7(7)
O	0.394(1)	0.291(1)	0.258(1)
O	–0.022(2)	0.248(1)	0.282(2)
O	0.011(2)	0.524(2)	0.376(2)
O	0.447(3)	0.570(2)	0.434(3)

\* Atom numbering uses the same convention used as in the Figure.

**Pyridinium crystal data.** Monoclinic, space group  $P2_1/n$ ,  $a = 14.231(4)$ ,  $b = 14.577(3)$ ,  $c = 10.186(2)$  Å,  $\beta = 93.06(2)^\circ$ ,  $Z = 4$ ; 1 617 reflections with  $I > 2\sigma(I)$ , 297 variables [O, N, and C with anisotropic thermal parameters; H(5) and H(17), attached to C(5) and O(17) respectively, with isotropic thermal parameters; other hydrogen positions calculated, not refined],  $R = 0.048$ . As the refinement converged, the thermal parameter of H(5) became negative [–1.0(6) Å<sup>2</sup>] and the C–H distance increased to 1.10 Å; the

additional density at this site is caused by a small amount of disordering of the oxygen atom O(7). No attempt was made to model the disordering. The atomic co-ordinates are given in Table 9.

TABLE 9

1-(4-Hydroxyphenyl)-2,4,6-triphenylpyridinium-3-olate (8d): \* atomic co-ordinates with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	0.400 8(2)	0.168 7(2)	0.009 7(3)
C(2)	0.389 4(2)	0.102 5(3)	0.103 3(3)
C(3)	0.428 2(2)	0.115 0(3)	0.233 8(3)
C(4)	0.483 8(2)	0.195 4(3)	0.258 9(3)
C(5)	0.486 4(2)	0.261 6(3)	0.162 7(3)
C(6)	0.446 4(2)	0.250 1(3)	0.036 5(3)
O(7)	0.414 5(2)	0.055 7(2)	0.323 3(2)
C(11)	0.370 2(2)	0.149 5(2)	–0.127 7(3)
C(12)	0.276 1(2)	0.150 0(3)	–0.165 7(3)
C(13)	0.249 5(2)	0.131 4(3)	–0.295 1(3)
C(14)	0.316 4(3)	0.110 4(3)	–0.385 5(3)
C(15)	0.410 8(2)	0.109 6(3)	–0.345 1(3)
C(16)	0.437 6(2)	0.129 3(3)	–0.215 4(3)
O(17)	0.285 4(2)	0.092 3(2)	–0.511 0(3)
C(21)	0.337 5(2)	0.016 6(3)	0.070 2(3)
C(22)	0.365 1(2)	–0.046 2(3)	–0.023 1(3)
C(23)	0.315 7(3)	–0.127 8(3)	–0.042 9(4)
C(24)	0.239 8(3)	–0.147 9(3)	0.030 5(4)
C(25)	0.212 5(3)	–0.086 0(3)	0.122 9(4)
C(26)	0.260 8(3)	–0.004 5(3)	0.143 2(3)
C(41)	0.538 5(2)	0.207 6(3)	0.386 5(3)
C(42)	0.599 5(3)	0.138 8(3)	0.433 1(4)
C(43)	0.653 1(3)	0.151 8(3)	0.549 1(4)
C(44)	0.645 8(3)	0.231 7(3)	0.619 6(4)
C(45)	0.584 8(3)	0.299 5(3)	0.574 5(4)
C(46)	0.531 7(2)	0.286 7(3)	0.458 3(3)
C(61)	0.452 6(2)	0.323 8(3)	–0.061 2(3)
C(62)	0.375 8(3)	0.357 6(3)	–0.135 8(4)
C(63)	0.384 2(3)	0.432 3(3)	–0.218 4(4)
C(64)	0.469 4(4)	0.475 2(3)	–0.225 3(4)
C(65)	0.546 9(3)	0.444 9(3)	–0.151 0(4)
C(66)	0.538 8(3)	0.368 6(3)	–0.071 5(3)
H(5)	0.515(2)	0.330(2)	0.190(2)
H(12)	0.228	0.164	–0.101
H(13)	0.181	0.133	–0.324
H(15)	0.459	0.095	–0.409
H(16)	0.506	0.129	–0.186
H(17)	0.334(3)	0.081(3)	–0.557(5)
H(22)	0.421	–0.033	–0.076
H(23)	0.335	–0.172	–0.111
H(24)	0.205	–0.207	0.017
H(25)	0.157	–0.100	0.176
H(26)	0.240	0.040	0.211
H(42)	0.605	0.080	0.383
H(43)	0.698	0.103	0.582
H(44)	0.685	0.241	0.703
H(45)	0.579	0.358	0.626
H(46)	0.488	0.336	0.426
H(62)	0.313	0.327	–0.130
H(63)	0.328	0.455	–0.273
H(64)	0.475	0.529	–0.285
H(65)	0.609	0.478	–0.155
H(66)	0.596	0.345	–0.020

\* The positions of the hydrogen atoms attached to the benzene rings were calculated and not refined. Each hydrogen atom is numbered in accord with the non-hydrogen atom to which it is bonded. Atoms are numbered as in the Figure.

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