OXIDATIVE AND BASIC TRANSFORMATIONS OF SOME 1-HETEROARYLOLIGOPHENYLPYRIDINIUM SALTS. LIMITATIONS TO THE APPLICABILITY OF FERRICYANIDE OXIDATION

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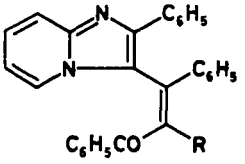
Dedicated to Professor Miloslav Ferles on the occasion of his 70th birthday.

Ferricyanide oxidation of 2,3,4,6-tetraphenyl-1-(2′-pyridyl)pyridinium perchlorate (*III*) gave, in addition to the biheterocyclic product *Ib*, two pyrrole derivatives *IIb* and *IIc* and in some conditions also the diketone *IV*. Additional pyrrole derivatives, *VII* and *IX*, were obtained analogously from the thiazole 2,4,6-triphenylpyridinium salts *V* and *VIb*. Alkalysis of the thiazole salts *V* and *VIb* and of the imidazole salts *VIc* and *VId* using alcoholic KOH afforded the biheterocyclic products *XI* – *XIV*. The mechanisms of the conversions involved are discussed.

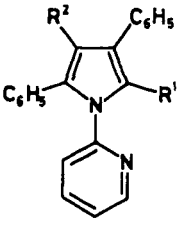
Evidence has been obtained recently[1] that ferricyanide oxidation of 1-(2′-pyridyl)-2,4,6-triphenylpyridinium perchlorate gives rise to the stereospecifically unsaturated ketone *Ia* of the *Z*-configuration, in whose molecule the six-membered fragment of the newly formed biheterocyclic system stems from the 1-substituent of the starting substrate. Previous findings[2] also suggest that conversions of this kind will be typical of quaternary 2,4,6-triphenylpyridinium salts carrying 2-pyridyl-like substituents in position 1. This course, however, is hindered by a complete substitution of the positively charged pyridinium ring; ferricyanide oxidation of 1-(2′-pyridyl)-2,3,4,5,6-pentaphenylpyridinium perchlorate gave the pentasubstituted pyrrole *IIa* solely[3].

In context with the above facts it was of interest (i) whether formation of products of type *I* is conditional on the absence of substitutents in either of the positions 3,5 of the starting pyridinium salt and (ii) whether effects analogous to that induced by 2-pyridyl-like substitutents in position 1 are caused by similar groups involving five-membered 1,3-oxazole, 1,3-thiazole or 1,3-diazole heterocycles. Experimental data obtained during the investigation into the above problems are presented in this paper.

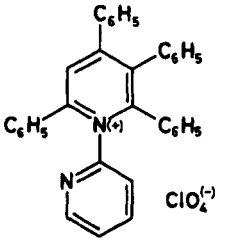
Reaction of 2,3,4,6-tetraphenylpyrylium perchlorate with 2-aminopyridine gave 1-(2'-pyridyl)-2,3,4,6-tetraphenylpyridinium perchlorate (*III*). This salt was subjected to short-run (5 min) ferricyanide oxidation to obtain a mixture of products, from which three substances could be isolated chromatographically; these were (*Z*)-1',2,2',3'-tetraphenyl-3-(3'-oxopropenyl)imidazo[1,2-*a*]pyridine (*Ib*), 2,3,5-triphenyl-1-(2'-pyridyl)pyrrole (*IIb*) and 2-benzoyl-3,4,5-triphenyl-1-(2'-pyridyl)pyrrole (*IIc*). The pyrrole derivative *IIb* appeared to be sensitive to the continuing oxidation with ferricyanide; if the reaction time was extended to 15 min, this compound transformed into (*Z*)-1,2,4-triphenyl-2-butene-1,4-dione (*IV*). The explanation of the formation of the three products *Ib*, *IIb* and *IIc* is given in Scheme 1 in agreement with the mechanisms postulated previously[4,5]. It is clear that absence of a phenyl group in position 5 is really a prerequisite for the formation of the biheterocyclic system in the molecule *Ib* in the reaction pathway beginning with the nucleophilic attack of the starting substrate *III* in position 2. Should the other reaction pathway beginning with the attack of position 6 be



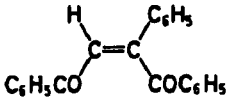
Ia, R = H
Ib, R = C_6H_5



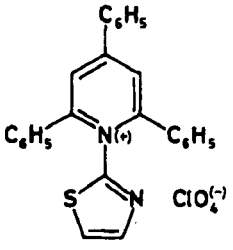
IIa, $R^1 = R^2 = C_6H_5$
IIb, $R^1 = C_6H_5$; R^2 = H
IIc, $R^1 = COC_6H_5$; $R^2 = C_6H_5$



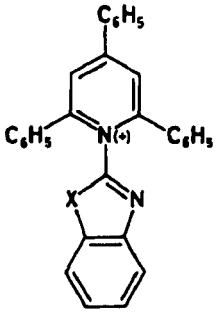
III



IV

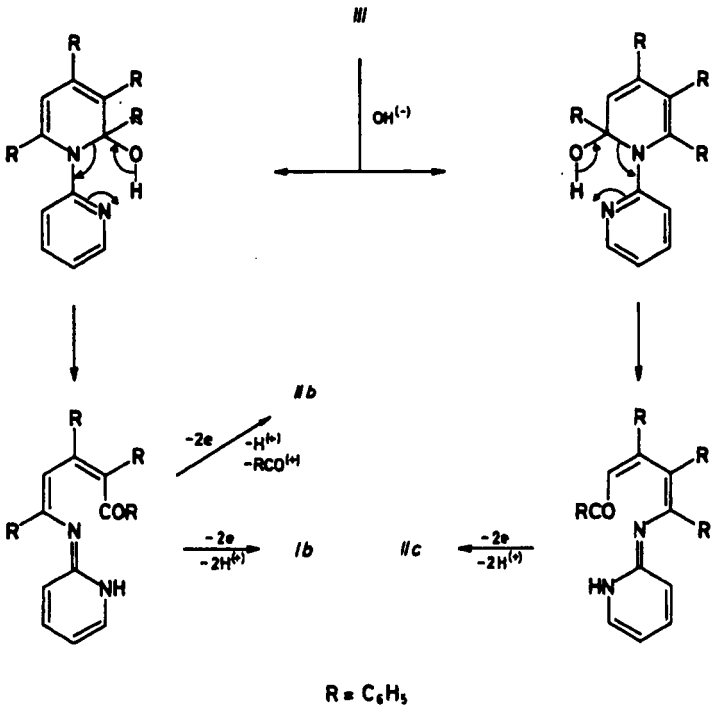


V



VIa, X = O
VIb, X = S
VIc, X = NH
VId, X = NCH_3

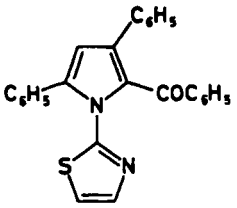
used for such a conversion, only compound *Ia* could be the product; this, however, has not been observed in the reaction mixture. Apparently, such conversion requiring detachment of the $C_6H_5^+$ group is energetically highly unfavourable and therefore does not occur here.



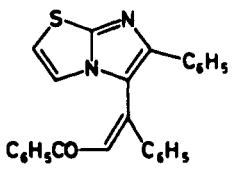
SCHEME 1

For gaining insight into the effect of the 1-substituent on the ferricyanide oxidations, quaternary salts *V* and *VIb – VId* were prepared by reacting 2,4,6-triphenylpyrylium perchlorate with 2-amino derivatives of the corresponding 1,3-thiazole and 1,3-diazole heterocycles[6 - 10]. Attempted analogous preparation of the salt *VIa* failed, presumably because of the low nucleophilicity of 2-aminobenzoxazole. Ferricyanide oxidation products, however, were only obtained in the case of the 1,3-thiazole substrates *V* and *VIb*. Of the two assumed products of salt *V*, viz. *VII* and *VIII*, only the former, i.e. 2-benzoyl-3,5-diphenyl-1-(1′,3′-thiazol-2′-yl)pyrrole, was obtained in a low yield. The heteropentalene derivative *VIII* is probably too labile under the experimental conditions applied[11] and thus cannot be detected. For analogous reasons, oxidation of the salt *VIb* gave 2-benzoyl-3,5-diphenyl-1-(benz-1′,3′-thiazol-2′-yl)pyrrole (*IX*) only.

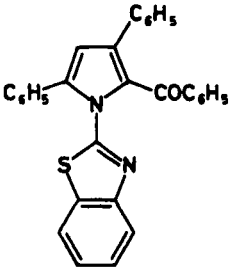
The imidazole derivative *VIc* reacted much faster with the alcoholic potassium hydroxide than with potassium ferricyanide, and only its alkalysis products could be identified in its reaction mixture. Therefore, isolation of the same reaction products was successful in an experiment conducted in the absence of the oxidant. In agreement with published data[10], the quaternary salt *VIc* exposed to the effect of potassium hydroxide gave the betaine derivative *X*; however, at elevated temperature and in the presence of excess reagent, 2,4-diphenylbenzimidazo[1,2-*a*]pyrimidine (*XI*) (which is available by



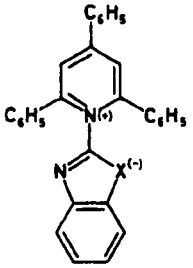
VII



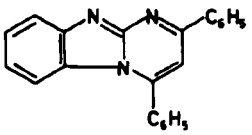
VIII



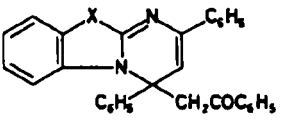
IX



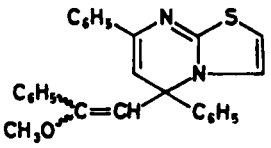
X, X = N



XI



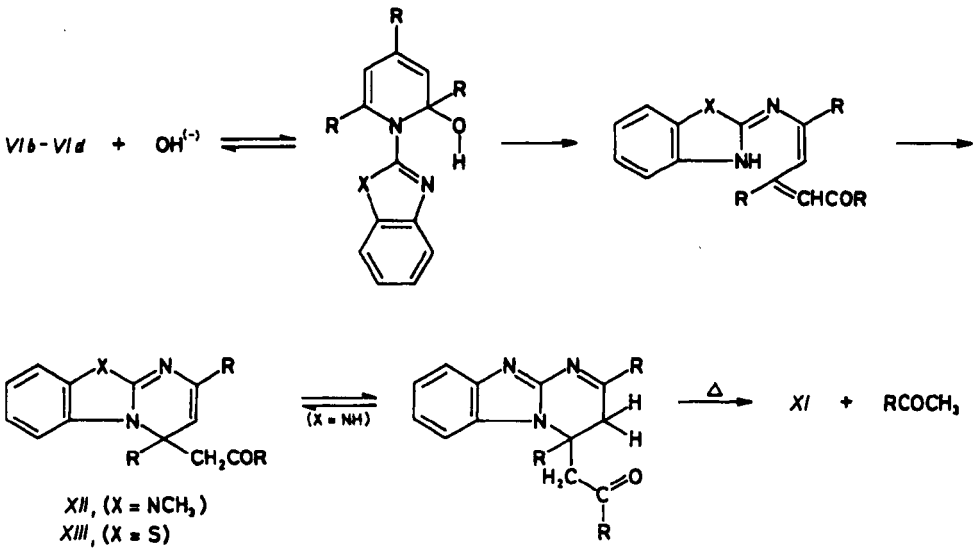
XII, X = NCH$_3$
XIII, X = S



XIV

a different route[10]) and acetophenone emerge. In the case of the N-methylated starting salt *VId*, the 4-benzoylmethyl-2,4-diphenyl-10-methylbenzimidazo[1,2-*a*]-4,5-dihydropyrimidine (*XII*), formed under the same conditions, is relatively stable and isolable. The formation of the two products *XI* and *XII* is interpreted in Scheme 2. Quite analogous is the explanation of the formation of 4-benzoylmethyl-2,4-diphenylbenz-10,5-

thiazolo[1,2-*a*]-4,5-dihydropyrimidine (*XIII*) during the reaction of the salt *VIb* with methanolic potassium hydroxide, as well as of the formation of the product whose formula is probably *XIV* during the conversion of the salt *V*.



SCHEME 2

Empirical interpretation of the mass spectra and of the ^{1}H and ^{13}C NMR spectra is consistent with the suggested formulas *Ib*, *IIb*, *IIc*, *III*, *IV*, *VIb – VId*, *VII* and *IX – XIV*. The spectral characteristics are given in Tables I – IV and in the Experimental.

EXPERIMENTAL

Temperature data are not corrected. Melting temperatures were determined on a Boetius apparatus. NMR spectra were scanned on a Varian VXR-400 (400 MHz) instrument, mass spectra were measured on a Finnigan MAT 90 spectrometer.

In the NMR spectra, the CH groups at N-substituents are distinguished by the symbols A, B, C, D, A′ and B′. Phenyls are denoted Ph1, Ph2 and Ph3.

The proton and carbon signals were assigned based on COSY and HETCOR experiments; the assignment appeared to be unambiguous at this level of interpretation.

Preparation of Pyridinium Salts

Elemental analysis data, melting temperatures and pyridinium salt yields are given in Table I.

TABLE I
Pyridinium salts

Substance	Formula (M. w.)	M. t.[a], °C	Yield %	Calculated/Found			
				% C	% H	% N	% S
III	$C_{34}H_{25}ClN_2O_4$	265 – 267	86	72.79	4.49	4.99	–
	(561.0)			72.97	4.69	5.14	–
V	$C_{26}H_{19}ClN_2O_4S$	233 – 235[b]	89	63.60	3.90	5.71	6.53
	(491.0)			63.49	4.14	5.88	6.63
VIb	$C_{30}H_{21}ClN_2O_4S$	288 – 290	74	66.60	3.91	5.18	5.93
	(541.0)			66.58	4.08	5.29	6.17
VIc	$C_{30}H_{22}ClN_3O_4$	237 – 239[c]	74	68.77	4.23	8.02	–
	(524.0)			68.32	4.78	7.78	–
VId	$C_{31}H_{24}ClN_3O_4$	226 – 228	73	69.21	4.50	7.82	–
	(538.0)			69.26	4.80	7.84	–

[a] Crystallized from ethanol; [b] ref.[9]: 226 °C; [c] ref.[6]: 255 °C, ref.[10]: 236 – 237 °C.

TABLE II
Pyridinium salt oxidation products

Substance	Formula (M. w.)	M. t.[a], °C	Yield %	Calculated/Found			
				% C	% H	% N	% S
Ib	$C_{34}H_{24}N_2O$	199 – 201	11	85.69	5.08	5.87	–
	(476.6)	E + D		85.84	5.30	5.82	–
IIc	$C_{34}H_{24}N_2O$	229 – 231	29	85.69	5.08	5.87	–
	(476.6)	M + B		85.54	5.02	5.77	–
VII	$C_{26}H_{18}N_2OS$	160 – 162	11	76.82	4.47	6.89	7.89
	(406.5)	E		76.39	4.73	6.81	8.45
IX	$C_{30}H_{20}N_2OS$	170 – 172	52	78.91	4.42	6.14	7.02
	(456.6)	E		79.37	4.62	5.96	7.34
X	$C_{30}H_{21}N_3$	265 – 268[b]	75	85.08	5.00	9.93	–
	(423.5)	B		85.13	5.11	9.74	–
XI	$C_{22}H_{15}N_3$	312 – 315[c]	4	82.22	4.70	13.08	–
	(321.4)	E + C		82.04	5.17	13.03	–

[a] B benzene, C chloroform, D diethyl ether, E ethanol, M methanol; [b] ref.[10]: 255 – 257 °C; [c] ref.[10]: 308 – 310 °C.

2,3,4,6-Tetraphenyl-1-(2'-pyridyl)pyridinium Perchlorate (*III*)

A mixture of 2,3,4,6-tetraphenylpyrylium perchlorate (10 mmol) and 2-aminopyridine (10 mmol) in 180 ml of ethanol was refluxed for 5 h. After cooling, crystals were collected and recrystallized from ethanol.

^{1}H NMR ($CDCl_3$): 6.88 – 7.03 ddd, 1 H (A, J = 7.8, 4.8 and 0.9); 7.10 – 7.14 m, 1 H; 7.19 – 7.34 m, 7 H; 7.36 dd, 1 H (B, J = 7.8 and 1.9); 7.38 – 7.44 m, 3 H; 7.55 – 7.58 m, 2 H; 7.64 – 7.67 m, 1 H (C); 8.02 s, 1 H (at the pyridinium ring); 8.22 ddd, 1 H (D, J = 4.8, 1.9 and 0.9).

^{13}C NMR ($CDCl_3$): 124.82, CH; 125.15, CH; 127.02, CH; 127.50, CH (broadened); 127.92, CH; 127.96, CH; 128.29, CH (broadened); 128.38, 2 CH; 128.40, 2 CH; 129.23, CH; 129.59, 2 CH; 129.87, CH; 130.03, 2 CH; 130.10, CH (broadened); 130.31, CH; 130.52, CH; 131.04, CH; 131.41, C; 131.74, CH (broadened); 132.37, C; 134.01, C; 136.50, C; 138.71, CH; 140.22, C; 148.17, CH; 152.19, C; 154.33, C; 155.36, C; 160.09, C.

2,4,6-Triphenyl-1-(1',3'-thiazol-2'-yl)pyridinium Perchlorate (*V*)

To a boiling solution of 2,4,6-triphenylpyrylium perchlorate (1.5 mmol) in ethanol (30 ml) was added 2-aminothiazole (2.0 mmol) and the whole was refluxed for 4 h. Thereafter the mixture was allowed to cool down, and crystals were filtered out and recrystallized from ethanol.

^{1}H NMR ($CDCl_3$): 7.26 – 7.45 m, 8 H; 7.55 – 7.62 m, 7 H; 7.92 d, 1 H (J = 6.9); 8.13 s, 2 H (hydrogen atoms at the pyridinium ring).

^{13}C NMR ($CDCl_3$): 125.55, CH; 126.56, 2 CH; 128.56, 4 CH; 128.77, 2 CH; 129.86, 2 CH; 129.94, 4 CH; 130.83, 2 CH; 131.95, 2 C; 132.67, CH; 134.45, C; 139.50, CH; 156.90, C; 157.46, 2 C; 159.70, C.

1-(Benz-1',3'-thiazol-2'-yl)-2,4,6-triphenylpyridinium Perchlorate (*VIb*)

2,4,6-Triphenylpyrylium perchlorate was reacted with 2-aminobenzthiazole using the same procedure as in the preparation of substance *V*.

^{1}H NMR ($CDCl_3$): 7.24 – 7.34 m, 6 H; 7.35 – 7.40 m, 1 H (A); 7.43 – 7.48 m, 1 H (B); 7.54 – 7.64 m, 4 H; 7.69 d, 4 H (J = 6.7); 7.87 d, 1 H (C, J = 8.1); 7.90 – 7.95 m; 8.13 s, 2 H.

^{13}C NMR ($CDCl_3$): 121.9, CH; 124.11, 2 CH; 126.35, 2 CH; 127.19, CH; 127.35, CH; 128.53, 4 CH; 128.79, 3 CH; 129.85, 4 CH; 130.96, 2 CH; 131.66, 2 C; 132.72, CH; 134.34, C; 136.34, C; 136.52, C; 147.73, C; 156.79, C; 156.96, 2 C; 159.69, C.

1-(1*H*-Benzimidazol-2-yl)-2,4,6-triphenylpyridinium Perchlorate (*VIc*)

A mixture of 2,4,6-triphenylpyrylium perchlorate (6.0 mmol) and 2-aminobenzimidazole (6.0 mmol) in ethanol (20 ml) was refluxed for 5 h. Substance *VIc* was isolated after acidification with a drop of 70% perchloric acid and cooling to room temperature, and recrystallized from ethanol also acidified with a drop of perchloric acid.

^{1}H NMR (hexadeuteriodimethyl sulfoxide): 5.85 s, 1 H (NH, broadened); 7.10 – 7.19 m, 2 H (A and A'); 7.26 – 7.44 m, 8 H (*m*-Ph1, *p*-Ph1, B and B'); 7.55 d, 4 H (*o*-Ph1, J = 7.7); 7.67 dd, 2 H (*m*-Ph2, J = 7.7 and 7.1); 7.72 dd, 1 H (*p*-Ph2, J = 7.1 and 7.1); 8.31 d, 2 H (*o*-Ph2, J = 7.7); 8.64 s, 2 H (at the pyridinium ring).

^{13}C NMR (hexadeuteriodimethyl sulfoxide): 116.59, 2 CH (B and B'); 124.03, 2 CH (A and A'); 125.49, 2 CH (at the pyridinium ring); 128.82, 4 CH (*m*-Ph1); 129.56, 4 CH (*o*-Ph1); 129.62, 2 CH (*o*-Ph2); 130.26, 2 CH (*m*-Ph2); 131.40, 2 CH (*p*-Ph1); 131.95, 2 C (Ph1); 133.49, C (Ph2); 133.71, CH (*p*-Ph2); 142.58, C (at the pyridinium ring); 157.16, 2 C (at the pyridinium ring); 158.48, C (between nitrogen atoms).

1-(1-Methylbenzimidazol-2-yl)-2,4,6-triphenylpyridinium Perchlorate (*VId*)

The compound was prepared by reacting 2,4,6-triphenylpyrylium perchlorate with 2-amino-1-methylbenzimidazole by the same route as substance *VIc*. The product was filtered out from the hot system and recrystallized from ethanol without addition of acid.

^{1}H NMR (hexadeuteriodimethyl sulfoxide): 3.47 s, 3 H (methyl); 7.22 – 7.42 m, 9 H (A, B, C, *m*- and *p*-Ph1); 7.52 – 7.58 m, 5 H (D, *o*-Ph1); 7.64 – 7.76 m, 3 H (*m*- and *p*-Ph2); 8.34 d, 2 H (*o*-Ph2, J = 7.2); 8.71 s, 2 H (at the pyridinium ring).

^{13}C NMR (hexadeuteriodimethyl sulfoxide): 30.64, CH_3; 111.64, CH (C); 120.38, CH (D); 124.39, CH (A); 125.44, CH (B); 126.13, 2 CH (at the pyridinium ring); 129.07, 4 CH (*m*-Ph1); 129.46, 4 CH (*o*-Ph1); 129.79, 2 CH (*o*-Ph2); 130.24, 2 CH (*m*-Ph2); 131.46, 2 C; 131.75, 2 CH (*p*-Ph1); 133.59, C; 133.84, CH (*p*-Ph2); 133.86, C; 139.27, C; 141.82, C (at the pyridinium ring); 133.86, C; 139.27, C; 141.82, C (at the pyridinium ring); 157.01, 2 C (at the pyridinium ring); 159.35, C (betwen the nitrogen atoms).

Oxidation of Pyridinium Salts

Elemental analysis data, melting temperatures and yields for the products of pyridinium salt oxidations are given in Table II; mass spectral data are given in Table IV.

Oxidation of Salt *V*

To a boiling suspension of salt *V* (0.021 mol) in ethanol (1 000 ml) was added a solution of potassium ferricyanide (0.061 mol) and potassium hydroxide (0.089 mol) in water (100 ml). The mixture was refluxed for 20 min and thereafter diluted with ice-cool water (1 500 ml) and extracted with 4 × 200 ml of chloroform. The combined extracts were washed with 2 × 200 ml of water, dried with sodium sulfate, and evaporated to dryness. The reaction mixture was separated by column chromatography (SiO_2, $CHCl_3$), and the product, viz. 2-benzoyl-3,5-diphenyl-1-(1',3'-thiazol-2'-yl)pyrrole, was recrystallized from ethanol.

^{1}H NMR ($CDCl_3$): 6.61 s, 1 H (hydrogen at the pyrrole ring); 7.06 – 7.34 m, 14 H; 7.58 d, 1 H (J = 3.6); 7.65 dd, 1 H (J = 7.6 and 1.2).

^{13}C NMR ($CDCl_3$): 112.42, CH; 121.07, CH; 126.95, CH; 127.72, 2 CH; 127.94, 2 CH; 128.30, CH; 128.34, 2 CH; 129.05, 2 CH; 129.35, 2 CH; 129.96, 2 CH; 130.93, C; 132.18, CH; 133.91, C; 134.54, C; 138.17, C; 140.05, CH; 140.45, C; 159.37, C; 187.54, CO.

Oxidation of Salt *VIb*

Salt *VIb* was oxidized and the product purified in the same manner as in the case of salt *V*. The reaction time was 10 min. White needles of 2-benzoyl-1-(benz-1',3'-thiazol-2'-yl)-3,5-diphenylpyrrole (*IX*) were obtained.

^{1}H NMR ($CDCl_3$): 6.64 s, 1 H (hydrogen at the pyrrole ring); 7.07 – 7.13 m, 5 H; 7.20 – 7.31 m, 6 H; 7.34 – 7.41 m, 3 H; 7.44 ddd, 1 H (A, J = 7.9, 7.7 and 1.2); 7.66 dd, 2 H (J = 8.2 and 1.2); 7.72 d, 1 H (B, J = 7.9); 7.92 d, 1 H (C, J = 8.1).

^{13}C NMR ($CDCl_3$): 112.97, CH; 121.55, CH; 123.87, CH; 125.77, CH; 126.34, CH; 127.03, CH; 127.72, 2 CH; 127.95, 2 CH; 128.42, 2 CH; 128.45, CH; 129.10, 2 CH; 129.34, 2 CH; 129.84, 2 CH; 130.63, C; 130.90, C; 132.20, CH; 134.15, C; 134.32, C; 135.92, C; 137.98, C; 140.10, C; 149.63, C; 158.79, C; 187.40, CO.

Oxidation of Salt *VIc*

Oxidation of salt *VIc* was performed by the same procedure as the oxidation of salt *V*. The reaction time was 15 min. The reaction mixture was separated by column chromatography (SiO_2, $CHCl_3$ + $CH_3COOC_2H_5$ 9 : 1). Obtained were 1-(2-benzimidazolyl)-2,4,6-triphenylpyridinium betaine (*X*) and 2,4-diphenylbenzimidazo[1,2-*a*]pyrimidine (*XI*).

Substance X: ^{1}H NMR ($CDCl_3$): 6.93 – 6.97 m, 2 H (A and A'); 7.17 – 7.28 m, 6 H; 7.38 – 7.42 m, 2 H (B and B'); 7.49 dd, 4 H (J = 7.7 and 0.8); 7.59 – 7.66 m, 3 H; 7.83 – 7.97 m, 2 H; 8.05 s, 2 H (at the pyridinium ring).

^{13}C NMR ($CDCl_3$): 117.43, 2 CH; 119.19, 2 CH; 124.42, 2 CH; 127.88, 2 CH; 128.32, 4 CH; 128.87, 4 CH; 129.99, 2 CH; 130.39, 2 CH; 132.34, CH; 133.08, 2 C; 134.30, C; 144.79, 2 C; 151.14, C; 156.06, 2 C; 157.96, C.

Substance XI: ^{1}H NMR ($CDCl_3$): 6.69 dd, 1 H (A, J = 8.4 and 1.0); 7.03 ddd, 1 H (B, J = 8.4, 7.2 and 1.0); 7.27 s, 1 H (hydrogen at the pyrimidine ring); 7.46 ddd, 1 H (C, J = 8.2, 7.2 and 1.0); 7.52 – 7.58 m, 3 H; 7.63 – 7.75 m, 5 H; 7.97 dd (D, J = 8.2 and 1.0); 8.30 – 8.34 m, 2 H.

^{13}C NMR ($CDCl_3$): 105.29, CH; 114.52, CH; 120.25, CH; 121.16, CH; 125.91, CH; 127.46, C; 127.84, 2 CH; 128.40, 2 CH; 128.94, 2 CH; 129.42, 2 CH; 131.06, CH; 131.28, CH; 132.64, C; 136.71, C; 145.57, C; 149.35, C; 152.17, C; 161.11, C.

Oxidation of Salt *III*

The oxidation procedure was identical with that for salt *V*. The reaction time was 15 min and the reaction mixture was separated by column chromatography (SiO_2, $CHCl_3$). The product comprised 2-benzoyl-3,4,5-triphenyl-1-(2'-pyridyl)pyrrole (*IIc*) (29%), (*Z*)-1',2,2',3'-tetraphenyl-3-(3'-oxopropenyl)imidazo[1,2-*a*]pyridine (*Ib*) (11%), and (*Z*)-1,2,4-triphenyl-2-butene-1,4-dione (*IV*) of m.t. 129-131 °C (ref.[13]: 128 – 130 °C) (10%). If the oxidation was conducted for 5 min only, a small amount (5%) of 2,3,5-triphenyl-1-(2'-pyridyl)pyrrole (*IIb*), m.t. 210 – 212 °C, was obtained in place of substance *IV*. Molecular weight calculated for $C_{27}H_{20}N_2$: 372.5, *m/z* found from MS: 372.

Substance IIc: ^{1}H NMR ($CDCl_3$): 6.85 – 7.35 m, 20 H; 7.56 ddd, 1 H (A, J = 7.7, 7.7 and 1.8); 7.65 d, 2 H (J = 7.8); 8.42 dd, 1 H (B, J = 5.5 and 1.8).

^{13}C NMR ($CDCl_3$): 122.54, CH; 122.87, CH; 123.92, C; 125.98, CH; 126.26, CH; 127.33, 2 CH; 127.48, 2 CH; 127.51, CH; 127.68, 2 CH; 127.85, 2 CH; 129.97, 2 CH; 130.08, C; 130.98, 2 CH; 131.02, 4 CH; 131.55, C; 131.79, CH; 133.95, 2C; 134.05, C; 135.99, C; 137.32, CH; 138.28, C; 148.82, CH; 151.87, C; 188.21, CO.

Substance Ib: ^{1}H NMR ($CDCl_3$): 6.54 ddd, 1 H (C, J = 6.8, 6.8 and 1.2); 6.91 dddd, 2 H (J = 8.0, 8.0, 1.0 and 1.0); 7.02 – 7.08 m, 2 H (B and *p*-Ph); 7.18 – 7.39 m, 16 H; 7.42 ddd, 1 H (D, J = 6.8, 1.2 and 1.1); 7.84 ddd, 2 H (J = 7.0, 1.5 and 1.5).

^{13}C NMR ($CDCl_3$): 112.05, CH (C); 117.02, CH (A); 119.39, C; 124.52, CH (D); 125.11, CH (B); 127.09, 2 CH (broadened); 127.44, 2 CH; 127.65, 2 CH; 128.04, CH; 128.14, CH; 128.40, 2 CH; 128.67, 2 CH; 128.82, 2 CH; 128.85, CH; 129.83, 2 CH; 130.04, 2 CH; 131.14, CH; 132.29, C; 133.64, C; 136.48, C, 137.86, C; 145.41, C; 145.50, C; 147.12, C; 196.39, C (CO).

Substance IIb: ^{1}H NMR (CD_2Cl_2): 6.69 s, 1 H (at the pyrrole ring); 6.95 d, 1 H (A, J = 7.9); 7.08 – 7.35 m, 16 H; 7.52 ddd, 1 H (B, J = 7.9, 7.7 and 1.9); 8.38 dd, 1 H (C, J = 4.8 and 1.9).

^{13}C NMR (CD_2Cl_2): 110.72, CH; 123.14, CH; 124.26, C; 124.44, CH; 126.05, CH; 126.86, CH; 127.51, CH; 128.25, 2 CH; 128.50, 2 CH; 128.52, 2 CH; 128.54, 2 CH; 128.62, 2 CH; 131.74, 2 CH; 132.88, C; 133.01, C; 133.37, C; 135.53, C; 136.52, C; 137.84, CH; 149.22, CH; 152.57, C.

Substance IV: ^{1}H NMR ($CDCl_3$): 7.38 – 7.50 m, 7 H; 7.53 dddd, 1 H (J = 7.1, 7.1, 1.4 and 1.4); 7.58 dddd, 1 H (J = 7.5, 7.5, 1.0 and 1.0); 7.62 – 7.65 m, 2 H; 7.67 s, 1 H; 8.02 d, 4 H (J = 7.8).

^{13}C NMR ($CDCl_3$): 120.86, CH (=CH); 127.19, 2 CH; 128.53, 2 CH; 128.62, 2 CH; 128.65, 2 CH; 128.70, 2 CH; 129.14, 2 CH; 130.66, CH; 133.23, CH; 133.27, CH; 134.71, C; 136.00, C; 137.21, C; 156.30, C; 188.12, CO; 197.50, CO.

Absorption maxima of substance *IV* (5 . 10^{-5}M solution in ethanol) lie at 235 and 258 nm, in agreement with ref.[12].

Alkalysis of Pyridinium Salts

Elemental analysis data, melting temperatures and yields of alkalysis products of the salts are summarized in Table III.

Alkalysis of Salt *V*

To a mixed suspension of salt *V* (0.91 g, 1.85 mmol) in methanol (30 ml) was added a solution of KOH (0.35 g, 5.35 mmol) in water (10 ml). The red-violet mixture was stirred at room temperature for 1 h. Thereafter it was diluted with 400 ml of water and extracted with 4 × 50 ml of chloroform. The combined extracts were washed

TABLE III
Products of reactions of pyridinium salts in alkaline solutions

Sub-stance	Formula (M. w.)	M. t.[a], °C	Yield %	Calculated/Found		
				% C	% N	% S
X	$C_{30}H_{21}N_3$	265 – 268[b]	93	85.08	5.00	9.93
	(423.5)	B		84.95	5.22	9.73
XI	$C_{22}H_{15}N_3$	312 – 315[c]	95	82.22	4.70	13.08
	(321.4)	E + C		82.04	5.17	13.03
XII	$C_{31}H_{25}N_3O$	201 – 204[d]	68	81.74	5.54	9.23
	(455.6)	A + C		81.56	5.90	9.23

[a] A acetone, B benzene, C chloroform, E ethanol; [b] ref.[10]: 255 – 257 °C; [c] ref.[10]: 308 – 310 °C; [d] decomposition.

TABLE IV
Mass spectra of reaction products

Substance	*m* / *z* (relative intensity, %)
IIb	372 (100), 293 (6), 269 (7), 189 (6), 137 (11), 95 (14), 83 (14), 81 (43), 78 (10)
IIc	476 (100), 448 (12), 399 (79), 382 (6), 371 (12), 293 (10), 267 (31), 265 (16), 199 (10), 189 (10), 165 (16), 105 (84), 89 (14), 78 (59), 77 (86)
IV	417 (9), 312 (70), 296 (14), 283 (10), 235 (4), 207 (13), 178 (14), 105 (100), 77 (23)
VII	406 (27), 377 (4), 329 (7), 301 (5), 202 (4), 191 (11), 105 (100), 77 (74)
IX	456 (100), 105 (91)
X	425 (37), 424 (41), 423 (59), 422 (100), 348 (46), 346 (24), 344 (7), 334 (5), 322 (25), 321 (39), 307 (24), 293 (4), 246 (9), 232 (5), 230 (8), 219 (4), 215 (5), 210.5 (25), 202 (7), 196 (6), 188 (4), 173.5 (7), 161 (5), 133 (5), 125 (4), 118 (5), 115 (4), 111 (7), 109 (5), 102 (4), 97 (10), 95 (8), 91 (8), 82 (10), 78 (47), 77 (17)
XI	321 (100), 244 (2), 218 (3), 160.6 (5), 77 (3)

with 100 ml of water, dried with sodium sulfate, and evaporated in a vacuum evaporator to a volume of 5 ml. Methanol (40 ml) was added and the product was allowed to crystallize in a refrigerator. The yellow crystals of substance *XIV* (40%), which melts over the 127 – 135 °C range with decomposition, were not refined further because of their lability; the structure of the substance was verified by means of its spectral data.

^{1}H NMR (hexadeuterioacetone): 3.62 s, 3 H (CH_3); 5.45 d, 1 H (A, J = 1.7); 5.83 d, 1 H (B, J = 1.7); 6.97 s, 2 H (two mixed singlets); 7.11 tt, 1 H (*p*-Ph1, J = 7.5 and 1.4); 7.15 – 7.23 m, 5 H (*m*-Ph1, *m*- and *p*-Ph2); 7.31 – 7.34 m, 5 H (*o*-Ph1, *m*- and *p*-Ph3); 7.51 – 7.55 m, 2 H (*o*-Ph2); 7.61 – 7.65 m, 2 H (*o*-Ph3).

^{13}C NMR (hexadeuterioacetone): 50.35, CH_3; 93.10, C; 102.72, CH (B); 115.19, CH (A); 119.48, CH (in ^{1}H NMR, signal at 6.97 ppm); 126.78, 2 CH (*o*-Ph3); 128.09, C; 128.19, C; 128.22, 2 CH; 128.28, 2 CH; 128.40, 2 CH; 128.59, 2 CH; 128.87, CH (*p*-Ph3); 129.47, 2 CH (*m*-Ph3); 136.96, C; 138.91, CH (in ^{1}H NMR, signal at 6.97 ppm); 138.98, C; 139.35, C; 145.49, C; 145.79, C; 163.78, C.

Alkalysis of Salt *VIb*

The reaction was conducted as with salt *V*. The product was substance *XIII* (30%); the crystals, m.t. 156 – 160 °C (decomposition), are labile, and therefore the substance was characterized by its spectral data solely.

^{1}H NMR ($CDCl_3$): 3.94 d, 1 H (CH_2, J = 14.1); 4.33 d, 1 H (CH_2, J = 14.1); 5.20 s, 1 H (pyrimidine ring); 6.47 dd, 1 H (A, J = 7.9 and 1.3); 6.91 ddd, 1 H (B, J = 7.9, 7.7 and 1.5); 6.96 ddd, 1 H (C, J = 7.7, 7.7 and 1.3); 7.18 – 7.29 m, 6 H (D, *m*-Ph1, *m*- and *p*-Ph2); 7.32 tt, 1 H (*p*-Ph3, J = 7.4 and 1.3); 7.38 – 7.45 m, 3 H (*p*-Ph1 and *m*-Ph3); 7.51 – 7.55 m, 2 H (*o*-Ph2); 7.62 – 7.66 m, 2 H (*o*-Ph3); 7.72 – 7.76 m, 2 H (*o*-Ph1).

^{13}C NMR ($CDCl_3$): 43.23, CH_2; 65.77, C (pyrimidine ring); 105.64, CH (pyrimidine ring); 113.67, CH (A); 122.14, CH (*p*-Ph3); 122.78, CH (C); 123.65, C; 125.53, CH (B); 125.75, 2 CH (*o*-Ph2); 126.23, 2 CH (*o*-Ph3); 127.96, CH; 128.03, 2 CH (*m*-Ph2); 128.05, CH; 128.15, 2 CH (*o*-Ph1); 128.41, 2 CH (*m*-Ph1); 129.25, 2 CH (*m*-Ph3); 132.90, CH (*p*-Ph1); 137.71, C; 137.77, C; 138.34, C; 139.45, C; 144.71, C; 161.32, C; 197.76, CO.

Alkalysis of Salt *VId*

Reaction was as with salt *V*. Substance *XII* was purified by crystallization from an acetone–chloroform mixture rather than by precipitation.

^{1}H NMR ($CDCl_3$): 3.46 s, 3 H (CH_3); 4.01 d, 1 H (CH_2, J = 13.9); 4.29 d, 1 H (CH_2, J = 13.9); 5.18 s, 1 H (pyrimidine ring); 6.48 d, 1 H (J = 7.8); 6.80 ddd, 1 H (J = 7.8, 7.8 and 0.9); 6.88 dd, 1 H (J = 7.4 and 0.9); 7.02 ddd, 1 H (J = 7.8, 7.8 and 0.9); 7.20 – 7.35m, 7 H (3 × 2 *m* and 1 *p*); 7.35 – 7.45 m, 2 H (2 × 1 *p*); 7.65 – 7.73 m, 6 H (3 × 2 *o*).

^{13}C NMR ($CDCl_3$): 27.46, CH_3; 43.94, CH_2; 64.37, C; 101.42, CH; 107.08, CH; 110.46, CH; 120.61, CH; 121.77, CH; 125.79, 2 CH; 126.63, 2 CH; 127.58, CH; 127.74, CH; 127.86, 2 CH; 128.05, 4 CH; 128.71, 2 CH; 128.90, C; 132.37, CH; 132.55, C; 138.00, C; 139.27, C; 142.16, C; 144.75, C; 150.15, C; 198.15, C.

Cold Alkalysis of Salt *VIc*

To a suspension of salt *VIc* (1 g, 1.91 mmol) in ethanol (50 ml) was added a solution of potassium hydroxide (0.15 g, 2.67 mmol) in water (5 ml), and the whole was stirred vigorously for 1 h at room temperature. After filtering off the precipitated potassium perchlorate, the red filtrate was diluted with 400 ml of water and extracted with 4 × 50 ml of chloroform. The combined chloroform extracts were washed with 100 ml of water, dried with sodium sulfate and evaporated to dryness. The residue was crystallized from absolute benzene. Red crystals of 1-(2-benzimidazolyl)-2,4,6-triphenylpyridinium betaine (*X*) were obtained.

Hot Alkalysis of Salt *VIc*

To a boiling suspension of salt *VIc* (1 g, 1.91 mmol) in ethanol (50 ml) was added a solution of KOH (0.4 g, 7.13 mmol) in water (7 ml), and the whole was refluxed for 15 min. The red colour of the solution vanished gradually and a yellow precipitate separated. The mixture was diluted with 250 ml of water and extracted with 5 × 100 ml of chloroform. The combined extracts were washed with 100 ml of water, dried and evaporated, and the evaporation residue was crystallized from an ethanol–chloroform mixture to obtain yellow crystals of 2,4-diphenylbenzimidazo[1,2-*a*]pyrimidine (*XI*).

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