STERICALLY CROWDED HETEROCYCLES. III. A GENERAL APPROACH TO IMIDAZO[1,2-*a*]PYRIDINES BY FERRICYANIDE OXIDATION OF QUATERNARY PYRIDINIUM SALTS

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Substituted 1-(pyridin-2-yl)-2,4,6-triphenylpyridinium perchlorates **1b–1e** were converted with potassium ferricyanide and potassium hydroxide to sterically crowded 2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridines **2b–2e** accompanied by minor isomeric 2-benzoyl-3,5-diphenyl-1-(pyridin-2-yl)pyrroles **3c**–**3e**. 4-Phenyl-2,6-di(4-substituted phenyl)-1-(pyridin-2-yl)pyridinium salts **4a**, **4b** gave exclusively corresponding imidazo[1,2-*a*]pyridines **5a**, **5b** while the ferricyanide oxidation of 1-(5-iodo- and 5-cyanopyridin-2-yl)-2,4,6-triphenylpyridinium perchlorates **6a**, **6b** led to mixtures of major imidazo[1,2-*a*]pyridines **7a–7c** and minor pyrroles **8a–8c**. Some mechanistic aspects of the oxidation procedure are discussed in connection with a resistance of 2,6-diphenyl-1,3,5-trimethylpyridinium perchlorate (**9c**) towards the oxidizing agents.
Key words: Imidazo[1,2-*a*]pyridines; Ferricyanide oxidation.

Ferricyanide oxidation of quaternary 2,4,6-triphenylpyridinium salts possessing pyridin-2-yl-like substituents at the position 1 have been observed to undergo a ring opening-ring closure process giving 3-chain substituted imidazo[1,2-*a*]pyridines[1]. Chirality of the products has been shown to be conditioned by restricted rotation in their sterically crowded molecules[2]. Hence, the mentioned oxidation procedure might offer a versatile route to the stereochemically interesting imidazo[1,2-*a*]pyridine derivatives provided that structural variations of the starting pyridinium cations will not interfere with the general course of the oxidation.

In this communication, effects of other substitution patterns in the 1-(pyridin-2-yl) group as well as in 2- and 6-phenyl groups are investigated in eight representative examples (Table I). Thus, a general applicability of the oxidation method for the mentioned purposes is demonstrated.

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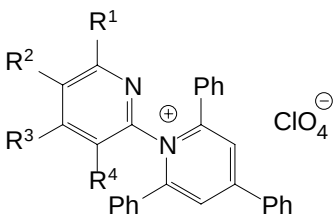
The recently reported[2] ferricyanide oxidation of 1-(4-methylpyridin-2-yl)-2,4,6-triphenylpyridinium perchlorate (**1a**) yielding 77% of expected 7-methyl-2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridine (**2a**) thus exhibited the same behaviour as parent non-methylated species[1]. Now, the 5-, 6- and 8-position isomers **2b**–**2d** have been prepared in high yields (Table II) by heating of corresponding pyridinium salts **1b**–**1d** with aqueous ethanolic potassium ferricyanide–potassium hydroxide solutions. The transformations are very selective except of the formation of the 6-methyl derivative **2c** which is accompanied by approximately 2% of the minor isomer **3a**. In the same way, 1-(6-phenylpyridin-2-yl)-2,4,6-pyridinium perchlorate (**1e**) gave a mixture of major 2,5-diphenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenylimidazo[1,2-*a*]pyridine (**2e**) and minor 2-(2-benzoyl-3,5-diphenylpyrrol-1-yl)-3-phenylpyridine (**3b**). A computer model of the molecule **2e** shows a considerable steric hindrance between the 5-phenyl group and the 3-side chain.



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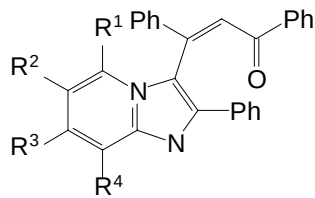

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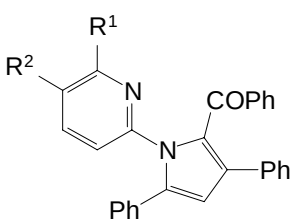
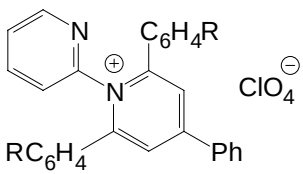


3

1-2	R^1	R^2	R^3	R^4
a	H	H	Me	H
b	Me	H	H	H
c	H	Me	H	H
d	H	H	H	Me
e	Ph	H	H	H

3	R^1	R^2
a	H	Me
b	Ph	H

The mentioned findings indicate no interference with the oxidative process caused by the additional substitution of the pyridin-2-yl group in salts **1a**–**1e**. Hence, additional attention has been focused on enlargements of the phenyl groups at the positions 2 and 6. Two quaternary pyridinium salts, namely 4-phenyl-1-(pyridin-2-yl)-2,6-di(4-*tert*-butylphenyl)pyridinium perchlorate (**4a**) and 2,6-bis(biphenyl-4-yl)-4-phenyl-1-(pyridin-2-yl)-pyridinium perchlorate (**4b**), have been oxidized with potassium ferricyanide and potassium hydroxide under the standard conditions. Both expected 2-(*tert*-butylphenyl)-3-[(*Z*)-1-phenyl-3-(*tert*-butylphenyl)-3-oxopropenyl]imidazo[1,2-*a*]pyridine (**5a**) and 2-(biphenyl-4-yl)-3-[(*Z*)-1-phenyl-3-(biphenyl-4-yl)-3-oxopropenyl]imidazo[1,2-*a*]pyridine (**5b**) were isolated in moderate yields (Table II).



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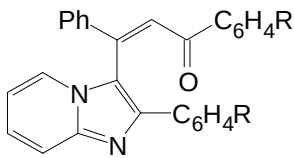


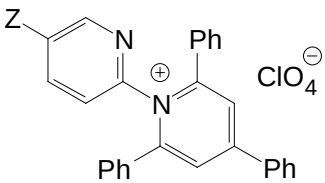
5

4, 5	R
a	*t*-Bu
b	Ph

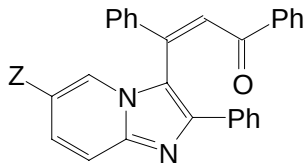
Finally, attempts have been made to examine a behaviour of two exchangeable or transferable substituents Z in the pyridin-2-yl group, namely the iodo and cyano groups, towards the oxidizing agent. As evident from Table II, the oxidation of 1-(3-iodopyridin-2-yl)-2,4,6-triphenylpyridinium perchlorate (**6a**) proceeded without nucleophilic substitution of iodine and two products, i.e. major 6-iodo-2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridine (**7a**) and minor 2-(2-benzoyl-3,5-diphenylpyrrol-1-yl)-5-iodopyridine (**8a**), were isolated. On the other hand, partial hydrolysis of the cyano group (Z = CN) to the carboxamide fundtion (Z = $CONH_2$) has been observed in analogous major and minor products arised from 1-(5-cyanopyridin-2-yl)-2,4,6-triphenylpyridinium perchlorate (**6b**). Thus, in addition to expected 6-cyano-2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridine (**7b**) and 2-(2-benzoyl-3,5-diphenylpyrrol-1-yl)-5-pyridinecarbonitrile (**8b**) also corresponding carboxamides **7c** and **8c** were isolated in comparable yields (Table II).

The above mentioned findings suggest a general potency of the extended Decker oxidation[3] for the preparation of sterically crowded imidazo[1,2-*a*]pyridine derivatives. Any use of the procedure for preparative purposes is undoubtedly limited by accessi-

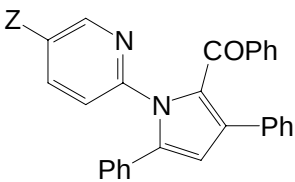
bility of corresponding pyrylium salts, from which the starting quaternary pyridinium salts are to be prepared[4–6]. We have found that e.g. the heterocyclization of benzaldehyde with two equivalents of 4-*tert*-butylacetophenone belongs to unfavourable cases yielding only 13% of 2,6-di(4-*tert*-butylphenyl)pyrylium perchlorate (**9a**). Another example is represented by the preparation of 3,5-dimethyl-2,4,6-triphenylpyrylium perchlorate (**9b**) resulting only in ca 9% yield of the substance. On the other hand, conversion of the salt **9b** with methylamine to 1,3,5-trimethyl-2,4,6-triphenylpyridinium perchlorate (**9c**) gave a high yield of the product (Table I).



6a, 6b

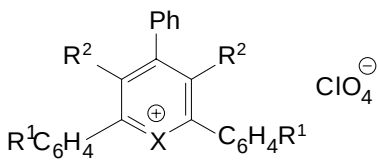


7



8

6-8	Z
a	I
b	CN
c	$CONH_2$



9	R^1	R^2	X
a	*t*-Bu	H	O
b	H	H	O
c	H	Me	NMe

Surprisingly, the quaternary salt **9c** was found to be very resistant towards the potassium ferricyanide–potassium hydroxide reagent under the standard conditions used in all other cases. This finding let us to the assumption that the extended Decker oxidation[3] proceeds exclusively via an open chain intermediate rather than via a cyclic one as considered previously[7]. In the case of the salt **9c**, its pseudobase is probably incapable of a ring opening from steric reasons. The fact, that the 3,5-phenyl groups (unlike the 3,5-methyl substituents) do not interfere with the oxidation[8], suggests a less steric requirement of the aryl substituents, at least in open form intermediates.

The molecular structure determination of all prepared compounds is based on their assigned characteristics in corresponding ^{1}H NMR, ^{13}C NMR and IR spectra. The recent analyses of spectral data[1,2] of similar quaternary pyridinium salts, imidazo[1,2-*a*]-pyridine and pyrrole derivatives have been employed.

EXPERIMENTAL

The temperature data are uncorrected. Melting points were determined on a Boetius block. NMR spectra (δ, ppm; *J*, Hz) were taken on Gemini 300 HC or Varian VXR-400 instruments in $(CD_3)_2SO$ unless stated otherwise with TMS as internal standard at 297 K. The working frequency was 300 or 400 MHz for ^{1}H and 75 or 100 MHz for ^{13}C, respectively. IR spectra ($\tilde{\nu}$, cm^{-1}, KBr technique) were measured on a FTIR spectrometer Nicolet 740.

The starting substituted 2-aminopyridines were purchased from Aldrich (2-amino-5-methylpyridine) or prepared according to refs[9–12].

Preparation of the Quaternary Pyridinium Salts **1b**–**1e**, **4a**, **6a** and **4b**

A mixture of 2,4,6-triphenylpyrylium perchlorate[13] (8 g, 19.6 mmol), corresponding substituted 2-aminopyridine (25 mmol), and ethanol (350 ml) was stirred under reflux for 9 h. The crystals precipitated on cooling were collected by suction, washed with ethanol and ether and recrystallized from an appropriate solvent. Yields, melting points and elemental analyses of the products are given in Table I.

Salt **1b**: ^{1}H NMR spectrum: 2.27 s, 3 H (CH_3); 7.19 d, 1 H, *J* = 7.7; 7.35–7.76 m, 11 H; 7.59–7.76 m, 4 H; 8.38 d, 2 H, *J* = 6.4; 8.71 s, 2 H (H-3 and H-5). ^{13}C NMR spectrum: 23.07 CH_3, 121.34 CH, 124.80 CH, 125.29 CH, 128.10 CH, 128.95 CH, 129.59 CH, 129.65 CH, 130.19 CH, 132.38 C, 132.57 CH, 133.39 C, 138.93 CH, 150.15 C, 155.37 C, 156.37 C, 157.95 C.

Salt **1c**: ^{1}H NMR spectrum: 2.17 s, 3 H (CH_3); 7.35 d, 1 H, *J* = 8.0; 7.35–7.49 m, 10 H; 7.60 dd, 1 H, *J* = 8.0 and ≈1.5; 7.61–7.76 m, 3 H; 8.19 d, 1 H, *J* = ≈1.5; 8.38 d, 2 H, *J* = 7.3; 8.71 s, 2 H (H-3 and H-5). ^{13}C NMR spectrum: 17.29 CH_3, 123.85 CH, 125.36 CH, 128.20 CH, 128.96 CH, 129.59 CH, 129.62 CH, 130.22 CH, 132.43 C, 132.60 CH, 133.34 C, 135.58 C, 138.88 CH, 148.54 CH, 148.80 C, 155.57 C, 156.34 C.

Salt **1d**: ^{1}H NMR spectrum: 1.91 s, 3 H (CH_3); 7.33–7.54 m, 11 H; 7.62 dd, 1 H, *J* = 7.8 and ≈1.3; 7.63–7.77 m, 3 H; 8.34 dd, 1 H, *J* = 4.6 and ≈1.5; 8.41 dd, 2 H, *J* = 8.3 and ≈1.5; 8.77 s, 2 H (H-3 and H-5). ^{13}C NMR spectrum: 16.08 CH_3, 125.97 CH, 126.59 CH, 128.21 CH, 129.13 CH, 129.53 CH, 129.66 CH, 130.17 C, 130.65 CH, 131.57 C, 132.78 CH, 133.23 C, 141.12 CH, 145.41 CH, 149.76 C, 155.12 C, 156.91 C.

Salt **1e**: ^{1}H NMR spectrum: 7.34–7.43 m, 6 H; 7.44–7.59 m, 8 H; 7.66–7.77 m, 3 H; 7.79–7.92 m, 4 H; 8.41 dd, 2 H, *J* = 8.1 and ≈1.6; 8.77 s, 2 H (H-3 and H-5). ^{13}C NMR spectrum: 121.67 CH, 122.79 CH, 125.44 CH, 126.63 CH, 128.22 CH, 128.84 CH, 129.00 CH, 129.61 CH, 130.02 CH, 130.24 CH,

TABLE I
Yields and physical properties of perchlorates **1b**–**1e**, **4a**, **4b**, **6a**, **6b** and **9a**–**9c**

Compound	Yield, %	M.p., °C (solvent)	Formula (M.w.)	Calculated/Found		
				% C	% H	% N
1b	96	264–266	$C_{29}H_{23}ClN_2O_4$	69.81	4.65	5.61
		(ethanol)	(499.0)	69.81	4.69	5.34
1c	89	221–222	$C_{29}H_{23}ClN_2O_4$	69.81	4.65	5.61
		(ethanol–ether)	(499.0)	69.62	4.74	5.31
1d	71	129–132	$C_{29}H_{23}ClN_2O_4$	69.81	4.65	5.61
		(ethanol–ether)	(499.0)	69.84	4.87	5.47
1e	98	234–235	$C_{34}H_{25}ClN_2O_4$	72.79	4.49	4.99
		(ethanol)	(561.0)	72.56	4.67	4.72
4a	66	271–272	$C_{36}H_{37}ClN_2O_4$[a]	72.41	6.25	4.69
		(ethanol)	(597.2)	72.20	6.44	4.55
4b	83	>330[b]	$C_{40}H_{29}ClN_2O_4$[c]	75.41	4.59	4.40
		(ether[d])	(637.1)	75.31	4.81	4.14
6a	74	227–229	$C_{28}H_{20}ClIN_2O_4$[e]	55.06	3.30	4.59
		(ethanol)	(610.8)	54.80	3.41	4.46
6b	82	273–275	$C_{29}H_{20}ClN_3O_4$	68.30	3.95	8.24
		(ethanol)	(510.0)	68.06	3.97	8.02
9a	13	295–297	$C_{31}H_{33}ClO_5$	71.46	6.38	6.81[f]
		(ether–DCE[g])	(521.1)	71.74	6.64	6.81[f]
9b	8.6	303–304[h]	$C_{25}H_{21}ClO_5$	68.73	4.84	8.12[f]
		(ethanol)	(436.9)	68.47	4.98	8.51[f]
9c	97	>330[b]	$C_{26}H_{24}ClNO_4$[i]	69.41	5.38	3.11
		(ethanol)	(449.9)	69.18	5.49	2.92

[a] % Cl; calculated: 5.94, found: 5.97. [b] M.p. was not determined. [c] % Cl; calculated: 5.56, found: 5.87. [d] Washed with solvent only. [e] % I; calculated: 20.78, found: 20.73. [f] % Cl. [g] DCE; 1,2-dichloroethane. [h] Ref.[16]: 298–299 °C. [i] % Cl; calculated: 7.88, found: 7.99.

TABLE II
Yields and physical properties of ferricyanide oxidation products **2b**–**2e**, **3c**, **3e**, **5a**, **5b**, **7a**–**7c** and **8a**–**8c**

Compound	Yield, %	M.p., °C (solvent)	Formula (M.w.)	Calculated/Found		
				% C	% H	% N
2b	76	191–192 (ethanol)	$C_{29}H_{22}N_2O$ (414.5)	84.03 84.22	5.35 5.43	6.76 6.70
2c	93	172–173 (ether)	$C_{29}H_{22}N_2O$ (414.5)	84.03 84.24	5.35 5.47	6.76 6.57
2d	84	129–130[a] (ether)	$C_{29}H_{22}N_2O$ (414.5)	84.03 84.24	5.35 5.42	6.76 6.51
2e	70	168–169 (ether)	$C_{34}H_{26}N_2O$ (478.6)	85.33 85.26	5.48 5.35	5.85 5.64
3c	2	179–181 (ether)	$C_{29}H_{22}N_2O$ (414.5)	84.03 83.77	5.35 5.48	6.76 6.49
3e	18	137–138 (ether)	$C_{34}H_{26}N_2O$ (478.6)	85.33 85.05	5.48 5.16	5.85 5.64
5a	58	112–113 (ether)	$C_{36}H_{36}N_2O$ (512.7)	84.34 84.15	7.08 7.24	5.46 5.28
5b	58	194–196 (ether)	$C_{40}H_{28}N_2O$ (552.7)	86.93 86.71	5.11 5.24	5.07 4.92
7a	68	183–185 (ethanol)	$C_{28}H_{19}IN_2O$ (526.4)	63.89 63.62	3.64 3.67	5.32 5.18
7b	12	215–217 (ether)	$C_{29}H_{19}N_3O$ (425.5)	81.86 81.77	4.50 4.65	9.88 9.63
7c	13	250–252 (ether)	$C_{29}H_{21}N_3O_2$ (443.5)	78.54 78.32	4.77 4.84	9.47 9.29
8a	8	198–199 (ethanol)	$C_{28}H_{19}IN_2O$[c] (526.4)	63.89 63.81	3.64 3.89	5.32 5.28
8b	10	194–196 (ether)	$C_{29}H_{19}N_3O$ (425.5)	81.86 81.78	4.50 4.62	9.88 9.61
8c	17	247–249 (ether)	$C_{29}H_{21}N_3O_2$ (443.5)	78.54 78.37	4.77 4.93	9.47 9.25

[a] Ref.[17]: 68–70 °C (4% MeOH in benzene). [b] % I; calculated: 24.11, found: 23.83. [c] % I; calculated: 24.11, found: 24.08.

132.50 C, 132.62 CH, 133.44 C, 136.27 C, 139.92 CH, 150.78 C, 155.78 C, 155.39 C, 155.61 C, 156.56 C (one CH signal was overlapped).

Salt **4a**: A mixture of pyrylium salt **9a** (0.4 g, 0.8 mmol), 2-aminopyridine (0.1 g, 1 mmol) and ethanol (16 ml) gave colourless crystals (0.3 g) of pyridinium salt **4a**. ^{1}H NMR spectrum: 1.45 s, 18 H ($2 \times$ *tert*-C_4H_9); 7.30–7.43 m, 9 H; 7.61–7.83 m, 5 H; 8.35–8.41 m, 3 H; 8.69 s, 2 H (H-3 and H-5). ^{13}C NMR spectrum: 30.72 CH_3, 34.50 C, 124.60 CH, 125.01 CH, 125.21 CH, 125.66 CH, 128.95 CH, 129.51 CH, 129.63 C, 132.56 CH, 133.41 C, 138.85 CH, 148.68 CH, 151.12 C, 153.02 C, 155.55 C, 156.22 C.

Salt **6a**: ^{1}H NMR spectrum: 7.39–7.49 m, 10 H; 7.50 d, 1 H, J = 8.4; 7.64–7.75 m, 3 H; 8.22 dd, 1 H, J = 8.4 and 2.1; 8.36–8.41 m, 2 H; 8.63 d, 1 H, J = 2.1; 8.73 s, 2 H (H-3 and H-5). ^{13}C NMR spectrum: 96.16 C, 125.35 CH, 126.18 CH, 128.32 CH, 128.99 CH, 129.59 CH, 129.65 CH, 130.39 CH, 132.15 C, 132.70 CH, 133.26 C, 146.95 CH, 150.32 C, 154.38 CH, 155.28 C, 156.66 C.

Salt **6b**: A mixture of 2,4,6-triphenylpyrylium perchlorate[13] (4.9 mmol), 2-aminopyridine-5-carbonitrile[10] (5.2 mmol) and dry dimethylformamide (10 ml) was refluxed for 1 h. After cooling the crude salt **6b** was precipitated with water (100 ml), sucked off and crystallized from ethanol. ^{1}H NMR spectrum: 7.39–7.51 m, 10 H; 7.66–7.77 m, 3 H; 7.92 d, 1 H, J = 8.4; 8.37–8.44 m, 3 H; 8.79 s, 2 H (H-3 and H-5); 8.92 d, 1 H, J = 2.0. ^{13}C NMR spectrum: 110.58 C, 115.22 C, 125.19 CH, 125.43 CH, 128.48 CH, 129.10 CH, 129.64 CH, 129.74 CH, 130.57 CH, 131.83 C, 132.86 CH, 133.22 C, 143.03 CH, 152.08 CH, 153.39 C, 155.17 C, 157.08 C.

5-Methyl-2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl)]imidazo[1,2-*a*]pyridine (**2b**)

A solution of potassium ferricyanide (8 g, 24 mmol) and potassium hydroxide (2 g, 36 mmol) in water (50 ml) was added to a boiling mixture of pyridinium salt **1b** (3.5 g, 7 mmol) and ethanol (250 ml). After 15 min reflux, the reaction mixture was added to ice-water (500 ml) and extracted with chloroform (5×70 ml). The combined extracts were washed with 200 ml water, dried with magnesium sulfate and evaporated. The residue was crystallized from ethanol and gave yellow ketone **2b**. ^{1}H NMR spectrum: 2.27 s, 3 H (CH_3); 7.19 d, 1 H, J = 7.7; 7.35–7.50 m, 11 H; 7.59–7.76 m, 4 H; 8.38 d, 2 H, J = 6.4; 8.71 s, 2 H (H-3 and H-5). ^{13}C NMR spectrum: 23.07 CH_3, 121.34 CH, 124.80 CH, 125.29 CH, 128.10 CH, 128.95 CH, 129.59 CH, 129.65 CH, 130.19 CH, 132.38 C, 132.57 CH, 133.39 C, 138.93 CH, 150.15 C, 155.37 C, 156.37 C, 157.95 C. IR spectrum: 1 632 and 1 663 (C=C–C=O); for non-methylated ketone **2** (R^1 = R^2 = R^3 = R^4 = H) and for isomeric ketone **2a** found[14]: 1 637, 1 651 and 1 648, respectively. Yield, melting point and elemental analysis are given in Table II.

6-Methyl-2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridine (**2c**) and 2-Benzoyl-1-(3-methylpyridin-2-yl)-3,5-diphenylpyrrole (**3a**)

A solution of potassium ferricyanide (20 g, 61 mmol) and potassium hydroxide (5.5 g, 98 mmol) in water (100 ml) was added to a hot mixture of pyridinium salt **1c** (10 g, 21 mmol) and ethanol (500 ml). After 10 min reflux the mixture was cooled, poured into ice-water (1 500 ml) and extracted with chloroform (3×150 ml). The collected extracts were washed with 200 ml water, dried with sodium sulfate and evaporated. The residue was treated with ether (50 ml) and let to stand at room temperature overnight. The yellow crystalline ketone **2c** was filtered off and purified by crystallization (Table II). ^{1}H NMR spectrum: 2.19 s, 3 H (CH_3); 7.03 dd, 1 H, J = 9.2 and ≈1.6; 7.10–7.24 m, 5 H; 7.31–7.42 m, 5 H; 7.46–7.53 m, 4 H; 7.58–7.62 m, 2 H; 7.63–7.68 m, 2 H. ^{13}C NMR spectrum: 18.91 CH_3, 117.33 CH, 117.88 C, 122.61 C, 122.76 CH, 128.15 CH, 128.17 CH, 128.22 CH, 128.51 CH, 128.68 CH, 128.71 CH, 129.75 CH, 130.92 CH, 132.86 CH, 134.24 C, 138.29 C, 138.48 C, 142.41 C, 145.29 C, 146.29 C, 191.64 CO (some CH signals were overlapped). IR spectrum: 1 652 (C=C–C=O). The by-product **3a** was obtained from the evaporated filtrate by column chromatography (40 g silica, $CHCl_3$) (Table II).

^{1}H NMR spectrum: 2.33 s, 3 H (CH_3); 6.60 s, 1 H (H-4); 7.04–7.14 m, 6 H; 7.17–7.30 m, 8 H; 7.45 dd, 2 H, *J* = 8.2 and ≈2.0 (H-10 and H-11); 7.68 d, 2 H, *J* = 7.7; 8.27 d, 1 H, *J* = ≈2.0 (H-8). ^{13}C NMR spectrum: 18.76 CH_3, 112.31 CH, 123.09 CH, 127.14 CH, 128.22 CH, 128.25 CH, 128.43 CH, 128.84 CH, 129.54 CH, 130.02 CH, 130.65 CH, 130.71 C, 132.38 C, 132.56 CH, 133.24 C, 133.96 C, 135.81 C, 138.78 CH, 139.06 C, 139.75 C, 149.75 CH, 150.27 C, 188.71 CO. IR spectrum: 1 623 (C=O). Yields, melting points and elemental analyses are given in Table II.

8-Methyl-2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridine (**2d**)

Ferricyanide oxidation of salt **1d** was performed in the same way as above but the reaction time was only 10 min. The residue after evaporation of the chloroform extracts was treated with ether (40 ml) and let to stand at room temperature overnight. The yellow crystals of ketone **2d** were isolated by suction. ^{1}H NMR spectrum ($CDCl_3$): 2.67 s, 3 H (CH_3); 6.17 dd, 1 H, *J* = 6.8 and 6.8; 6.98 d, 1 H, *J* = 6.9; 7.12 dd, 1 H, *J* = 7.4 and 7.4; 7.18 dd, 4 H; 7.18 dd, 4 H, *J* = 7.5 and 7.5; 7.32–7.40 m, 4 H; 7.44 s, 1 H; 7.47 m, 3 H; 7.57 d, 2 H, *J* = 7.6; 7.62 d, 2 H, *J* = 6.4. ^{13}C NMR spectrum ($CDCl_3$): 17.07 CH_3, 112.35 CH, 119.12 C, 122.42 CH, 123.75 CH, 127.54 CH, 127.68 2 × CH; 127.70 2 × CH, 127.90 2 × CH, 127.94 CH, 128.11 2 × CH, 128.23 2 × CH; 129.15 2 × CH, 130.27 CH, 132.16 CH, 134.02 C, 137.94 2 × C, 142.00 2 × C, 145.82 2 × C, 146.15 C, 191.05 CO. IR spectrum: 1 652 (C=C–C=O). Yield, melting point and elemental analysis are given in Table II.

2,5-Diphenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridine (**2e**)
and 2-Benzoyl-1-(6-phenylpyridin-2-yl)-3,5-diphenylpyrrole (**3b**)

The reaction of salt **1e** (4 g, 7.1 mmol) in ethanol (180 ml) with potassium ferricyanide (7 g, 21 mmol) and potassium hydroxide (1.8 g, 32 mmol) in water (36 ml) was performed as mentioned above. The crude product was treated with ether (40 ml) to afford yellow crystals of ketone **2e**. ^{1}H NMR spectrum: 6.56 dd, 1 H, *J* = 7.0 and ≈1.3; 6.61 d, 1 H, *J* = 7.7; 6.74 d, 2 H, *J* = 7.8; 6.88 dd, 1 H, *J* = 7.4 and 7.4; 6.93–7.31 m, 12 H; 7.36–7.43 m, 1 H; 7.43–7.52 m, 4 H; 7.74 dd, 1 H, *J* = ≈9.0 and ≈1.3; 7.79 d, 1 H, *J* = 7.6. ^{13}C NMR spectrum: 116.22 CH, 117.26 CH, 119.44 C, 125.63 CH, 125.84 CH, 127.50 CH, 127.67 CH, 128.06 CH, 128.54 CH, 128.67 CH, 128.71 CH, 128.74 CH, 129.28 CH, 129.38 CH, 129.59 CH, 130.14 CH, 133.07 CH, 134.95 C, 135.42 C, 138.51 C, 139.20 C, 140.41 C, 144.45 C, 146.78 C, 147.98 C, 190.70 CO. IR spectrum: 1 658 (C=C–C=O). The filtrate after trituration was evaporated to dryness. The residue was purified by column chromatography (190 g silica, $CHCl_3$) and gave white crystals of compound **3b**. ^{1}H NMR spectrum: 6.67 s, 1 H (H-4); 6.97 dd, 1 H, *J* = 6.9 and ≈1.7; 7.12–7.21 m, 5 H; 7.25–7.38 m, 11 H; 7.56–7.64 m, 2 H; 7.66–7.71 m, 2 H; 7.76–7.80 m, 2 H. ^{13}C NMR spectrum: 112.44 CH, 119.28 CH, 120.89 CH, 127.25 CH, 127.50 CH, 128.27 CH, 128.42 CH, 128.61 CH, 128.88 CH, 129.19 CH, 129.74 CH, 129.75 CH, 130.46 CH, 130.60 C, 132.45 C, 132.70 C, 132.80 CH, 135.53 C, 138.33 C, 138.69 C, 138.84 CH, 139.12 C, 151.59 C, 157.13 C, 189.70 CO (one signal was overlapped). IR spectrum: 1 623 (C=O). Yields, melting points and elemental analyses are given in Table II.

3-[(*Z*)-1-Phenyl-3-(4-*tert*-butylphenyl)-3-oxopropenyl]-2-(4-*tert*-butylphenyl)imidazo[1,2-*a*]pyridine (**5a**)

A solution of potassium ferricyanide (0.8 g) and potassium hydroxide (0.2 g) was added dropwise during 1 min to a boiling solution of the salt **4a** (0.4 g, 0.67 mmol) in ethanol (40 ml). The mixture was refluxed for 10 min and then diluted with water (60 ml) and extracted with chloroform (4 × 10 ml). The combined extracts were washed with water, dried with magnesium sulfate, and evaporated to dryness. The residue was crystallized from ether to afford orange-yellow ketone **5a**. ^{1}H NMR spectrum: 1.19 s, 9 H (*tert*-C_4H_9); 6.82–6.91 m, 1 H; 7.22–7.88 m, 16 H; 8.03 s, 1 H. ^{13}C NMR spectrum:

30.70 CH_3. 30.90 CH_3, 34.14 C, 34.67 C, 112.60 CH, 116.34 CH, 117.41 C, 124.73 CH, 124.96 CH, 125.08 CH, 125.41 CH, 126.59 CH, 127.33 CH, 127.92 CH, 128.85 CH, 129.13 CH, 130.26 CH, 130.44 C, 134.98 C, 137.14 C, 140.40 C, 141.92 C, 144.14 C, 149.95 C, 155.84 C, 189.37 CO. IR spectrum: 1 601 and 1 649 (C=C–C=O). Yield, melting point and elemental analysis are given in Table II.

2,6-(Biphenyl-4-yl)-4-phenyl-1-(pyridin-2-yl)pyridinium Perchlorate (**4b**) and
3-[(*Z*)-1-Phenyl-3-(biphenyl-4-yl)-3-oxopropenyl]-2-(biphenyl-4-yl)imidazo[1,2-*a*]pyridine (**5b**)

A mixture of 2,6-(biphenyl-4-yl)-4-phenylpyrylium perchlorate[15] (1 g, 1.8 mmol), 2-aminopyridine (0.3 g, 3 mmol) and ethanol (30 ml) was refluxed for 9 h. Because only a yellow crystalline mixture of the starting perchlorate and pyridinium salt **4b** was obtained, the procedure was repeated using dimethylformamide. After 4 h of reflux, the precipitated white crystals of salt **4b** (1 g) were separated by suction and washed with ether. ^{1}H NMR spectrum: 7.37–7.57 m, 11 H; 7.63–7.89 m, 13 H; 8.38–8.44 m, 3 H; 8.78 s, 2 H (H-3 and H-5). ^{13}C NMR spectrum: 124.72 CH, 125.50 CH, 125.97 CH, 126.28 CH, 126.72 CH, 128.32 CH, 129.07 CH, 129.66 CH, 130.41 CH, 131.36 C, 132.69 CH, 133.42 C, 138.30 C, 139.16 CH, 141.62 C, 148.94 CH, 151.09 C, 155.33 C, 156.40 C, 162.25 CH. Yield, melting point and elemental analysis are given in Table I.

A solution of potassium ferricyanide (1.2 g) and potassium hydroxide (0.3 g) in water (6 ml) was added dropwise during 1 min to a refluxing mixture of salt **4b** (0.6 g, 1.6 mmol) in ethanol (60 ml). After 10 min the reaction mixture was diluted with water (80 ml) and extracted with chloroform (3 × 15 ml). The organic extracts were washed with water, dried with magnesium sulfate, and evaporated. The crystalline residue (0.35 g) was purified by column chromatography (50 g silica, $CHCl_3$) which afforded orange crystals of ketone **5b**. ^{1}H NMR spectrum: 6.85–6.91 m, 1 H; 7.28–7.69 m, 21 H; 7.76–7.94 m, 5 H; 8.01 s, 1 H. ^{13}C NMR spectrum: 112.54 CH, 116.73 CH, 117.87 C, 124.81 CH, 125.27 CH, 126.35 CH, 126.37 CH, 126.48 CH, 126.87 CH, 127.33 CH, 127.48 CH, 127.55 CH, 128.23 CH, 128.67 CH, 128.78 CH, 128.94 CH, 129.14 CH, 130.31 CH, 132.78 C, 136.22 C, 137.20 C, 138.84 C, 139.42 C, 140.60 C, 142.60 C, 144.21 C, 144.68 C, 189.41 CO. IR spectrum: 1 602 and 1 647 (C=C–C=O). Yield, melting point and elemental analysis are given in Table II.

6-Iodo-2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridine (**7a**)
and 2-(2-Benzoyl-3,5-diphenylpyrrol-1-yl)-5-iodopyridine (**8a**)

The oxidation of salt **6a** (10 g, 16 mmol) with potassium ferricyanide (16 g, 49 mmol) and potassium hydroxide (4 g, 71 mmol) in ethanol (400 ml) and water (80 ml) was performed in the same manner as with the salt **1c**. The crude reaction mixture was separated by column chromatography (190 g silica, $CHCl_3$). Fractions containing component **8a** were collected and evaporated to dryness. The residue was treated with ethanol to give white crystals of ketone **8a**. ^{1}H NMR spectrum: 6.95 d, 1 H, J = 8.2; 7.04–7.33 m, 13 H; 7.68 d, 2 H, J = 7.9; 7.91 dd, 1 H, J = 8.2 and 2.2; 8.63 d, 1 H, J = 2.2. ^{13}C NMR spectrum: 92.38 C, 112.83 CH, 125.29 CH, 127.35 CH, 128.35 CH, 128.50 CH, 128.59 CH, 129.06 CH, 129.60 CH, 130.00 CH, 130.61 CH, 131.99 C, 132.78 CH, 134.28 C, 135.47 C, 138.81 C, 139.67 C, 146.42 CH, 151.82 C, 155.62 CH, 188.64 CO. One signal was overlapped. IR spectrum: 1 623 (CO). Fractions containing ketone **7a** were evaporated and the residue crystallized from ethanol. ^{1}H NMR spectrum of the compound **7a**: 7.11–7.50 m, 12 H; 7.62 s, 1 H; 7.64–7.72 m, 5 H; 7.87 s, 1 H. ^{13}C NMR spectrum: 75.88 C, 118.10 C, 119.00 CH, 128.04 CH, 128.30 CH, 128.46 CH, 128.50 CH, 128.71 CH, 128.77 CH, 128.87 CH, 129.83 CH, 129.97 CH, 131.15 CH, 133.12 CH, 133.41 CH, 133.59 C, 137.71 C, 138.30 C, 141.73 C, 144.63 C, 146.25 C, 191.02 CO. IR spectrum: 1 632 (C=C–C=O). Yields, melting points and elemental analyses are given in Table II.

Oxidation of Pyridinium Salt **6b** to Compounds **7b**, **7c**, **8b** and **8c**

The oxidation of salt **6b** (1 g, 1.8 mmol) with potassium ferricyanide (2.4 g, 7.3 mmol) and potassium hydroxide (0.5 g, 8.9 mmol) in boiling ethanol (50 ml) was carried out for 5 min. The reaction mixture was worked up as mentioned above and separated by column chromatography (45 g silica, eluent chloroform–ethyl acetate).

6-Cyano-2-phenyl-3-[(Z)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-a]pyridine (**7b**). ^{1}H NMR spectrum: 7.17–7.51 m, 12 H; 7.66–7.76 m, 5 H; 7.78 s, 1 H; 8.04–8.07 m, 1 H. ^{13}C NMR spectrum: 99.14 C, 117.42 C, 119.05 CH, 119.56 C, 125.43 CH, 128.13 CH, 128.65 CH, 128.67 CH, 129.09 CH, 129.18 CH, 129.29 CH, 130.18 CH, 131.30 CH, 131.67 CH, 133.16 C, 133.69 CH, 137.47 C, 138.24 C, 141.37 C, 145.37 C, 145.89 C, 190.64 CO. IR spectrum: 1 630 and 1 659 (C=C–C=O), 2 227 (C≡N).

6-Aminocarbonyl-2-phenyl-3-[(Z)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-a]pyridine (**7c**). ^{1}H NMR spectrum: 7.14–7.30 m, 3 H; 7.35–7.46 m, 5 H; 7.48–7.61 m, 4 H; 7.68–7.76 m, 3 H; 7.80 d, 1 H, J = 9.3; 7.92 d, 2 H, J = 7.8; 8.14 brs, 1 H (NH_2); 8.16 s, 1 H; 8.46 s, 1 H. ^{13}C NMR spectrum: 115.88 CH, 118.72 C, 119.67 C, 124.04 CH, 126.01 CH, 126.99 CH, 127.55 CH, 127.73 CH, 128.05 CH, 128.26 CH, 128.37 CH, 128.44 CH, 129.06 CH, 130.43 CH, 132.94 CH, 133.22 C, 137.06 C, 137.47 C, 140.49 C, 143.58 C, 144.77 C, 165.36 $CONH_2$, 189.52 COPh. IR spectrum: 1 611, 1 651 and 1 685 (CO and C=C–C=O), 3 443 (NH).

2-(2-Benzoyl-3,5-diphenylpyrrol-1-yl)-5-pyridinecarbonitrile (**8b**). ^{1}H NMR spectrum: 6.95 d, 1 H, J = 8.2; 7.06–7.22 m, 10 H; 7.26–7.55 m, 4 H; 7.68 d, 2 H, J = 7.8; 7.85 dd, 1 H, J = 8.3 and ≈2.0; 8.68 d, 1 H, J = ≈2.0. ^{13}C NMR spectrum: 109.19 C, 113.62 CH, 116.79 C, 123.39 CH, 127.63 CH, 128.50 CH, 128.60 CH, 128.96 CH, 129.24 CH, 129.68 CH, 129.98 CH, 130.58 CH, 130.76 C, 131.66 C, 133.09 CH, 134.60 C, 135.04 C, 138.47 C, 139.51 C, 141.18 CH, 152.61 CH, 155.20 C, 188.65 CO. IR spectrum: 1 637 (CO) and 2 228 (C≡N).

2-(2-Benzoyl-3,5-diphenylpyrrol-1-yl)-5-pyridinecarboxamide (**8c**). ^{1}H NMR spectrum: 5.81 brs, 1 H (NH_2); 6.36 brs, 1 H (NH_2); 6.61 s, 1 H; 7.05–7.20 m, 10 H; 7.22–7.31 m, 4 H; 7.66 d, 2 H, J = 7.7; 8.05 dd, 1 H, J = 8.3 and 2.2; 8.78 d, 1 H, J = 2.2. ^{13}C NMR spectrum: 113.16 CH, 123.20 CH, 127.47 CH, 128.45 CH, 128.56 CH, 128.67 C, 128.73 CH, 129.13 CH, 129.64 CH, 130.12 CH, 130.61 CH, 130.68 C, 131.88 C, 132.96 CH, 134.57 C, 135.34 C, 137.98 CH, 138.74 C, 139.80 C, 148.41 CH, 154.99 C, 167.39 $CONH_2$, 188.90 COPh. IR spectrum: 1 641 and 1 681 (CO), 3 477 (NH). Yields, melting points and elemental analyses are given in Table II.

2,6-Di(4-*tert*-butylphenyl)-4-phenylpyrylium Perchlorate (**9a**)

A mixture of 1-(4-*tert*-butyl)-3-phenylprop-2-en-1-one[16] (4 g, 15 mmol), 4-*tert*-butylacetophenone (1.35 g, 7 mmol), 70% $HClO_4$ (1.7 g) and 1,2-dichloroethane (11 ml) was refluxed for 3 h. After cooling, the reaction mixture was treated with ether (110 ml) and allowed to crystallize to form fluorescent yellow crystals of perchlorate **9a** (0.5 g). ^{1}H NMR spectrum: 1.40 s, 18 H (2 × *tert*-Bu); 7.75–7.90 m, 7 H; 8.47–8.59 m, 6 H; 9.08 s, 2 H (H-3 and H-5). ^{13}C NMR spectrum: 30.60 CH_3, 35.21 C, 114.53 CH, 126.53 C, 126.72 CH, 128.70 CH, 129.75 CH, 129.83 CH, 132.60 C, 134.87 CH, 158.62 C, 164.58 C, 169.81 C. Yield, melting point and elemental analysis are given in Table I.

3,5-Dimethyl-2,4,6-triphenylpyrylium Perchlorate (**9b**)

A mixture of benzaldehyde (2.84 g, 27 mmol), propiophenone (11.5 g, 81 mmol) and concentrated sulfuric acid (2.3 ml) was stirred at 70 °C for 15 min, cooled and diluted with ethanol (17 ml), 70% $HClO_4$ (1 ml) and ether (30 ml). After 24 h the precipitated white crystals of the compound **9b** (1 g) were separated by suction. ^{1}H NMR spectrum: 2.3 s, 6 H (2 × CH_3); 7.46–7.51 m, 9 H; 7.63–7.83 m, 9 H; 8.01–8.06 m, 4 H. ^{13}C NMR spectrum: 17.69 CH_3, 126.88 CH, 129.47 CH, 129.76 CH, 130.12 C,

130.47 CH, 130.57 CH, 131.00 C, 133.39 CH, 134.96 C, 170.32 C, 171.65 C. Yield, melting point and elemental analysis are given in Table I.

1,3,5-Trimethyl-2,4,6-triphenylpyridinium Perchlorate (**9c**)

Pyrylium salt **9b** (1 g, 2.3 mmol) was treated with a solution of methylamine (0.2 g, 6.4 mmol) in ethanol (12 ml). The reaction mixture was stirred at room temperature for 3 h and then diluted with ether (50 ml). White crystals of pyridinium salt **9c** (1 g) were separated by suction. ^{1}H NMR spectrum: 1.84 s, 6 H ($2 \times CH_3$-3,5); 3.54 s, 3 H (CH_3-1); 7.33–7.37 m, 2 H; 7.52–7.75 m, 13 H. ^{13}C NMR spectrum: 18.71 $2 \times CH_3$-3,5, 46.45 CH_3-1, 127.11 CH, 128.21 CH, 129.03 CH, 129.36 CH, 129.72 CH, 130.54 CH, 132.41 C, 134.80 C, 135.96 C, 152.41 C, 157.71 C. Yield, melting point and elemental analysis are given in Table I.

Attempts to Oxidation of Pyridinium Salt **9c**

A solution of potassium ferricyanide (2.7 g) and potassium hydroxide (1.35 g) in water (30 ml) was added to a suspension of pyridinium salt **9c** (1 g, 2.2 mmol) in boiling ethanol (70 ml). The mixture was refluxed for 6 h, cooled and extracted with chloroform (3×70 ml). Organic extracts contained only the starting perchlorate **9c** and traces of six components (according to TLC). In another experiment, ethylene glycol was used as solvent and the procedure was performed at 130 °C for 10 h. The starting salt **9c** and about six unstable components were detected in the reaction mixture.

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