STERICALLY CROWDED HETEROCYCLES. X. A NEW MECHANISTIC APPROACH TO THE FERRICYANIDE OXIDATION OF 4,6′-DISUBSTITUTED 1-(PYRIDIN-2′-YL)-2,6-DIPHENYLPYRIDINIUM SALTS

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Received February 9, 1999
Accepted April 27, 1999

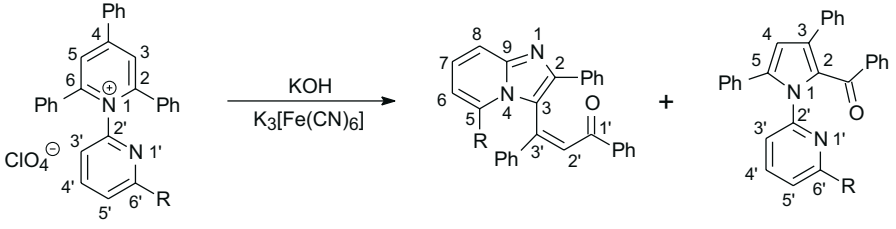
The oxidations of the title perchlorates, bearing the sterically diverse 6′-substituents (H, Me, Et, i-Pr, n-Bu, *t*-Bu and Ph) in two series with the same 4-substituents (Ph and *t*-Bu) lead to pairs of isomeric 3′,5-disubstituted (*Z*)-1′-phenyl-3′-(2-phenylimidazo[1,2-*a*]pyridin-3-yl)prop-2′-en-1′-ones and 3,6′-disubstituted [5-phenyl-1-(6′-pyridin-2′-yl)-1*H*-pyrrol-2-yl](phenyl)methanones except where the both variable substituents are *t*-Bu and then only pyrrolic product is formed. Considering steric interactions of the substituents in some intermediate and/or transition states a multistep mechanism for the oxidative transformation is proposed and supported by model PM3-PECI calculations of some radical intermediates.

Key words: Imidazo[1,2-*a*]pyridines; Pyrroles; Ferricyanide oxidation; Pyridinium salts; Pyrilium salts; Aminopyridines; PM3 calculations; Semiempirical calculations.

Systematic investigations on oxidative transformations of sterically hindered heterocyclic molecules performed in our laboratory have shown[1] that ferricyanide oxidation of quaternary 2,4,6-triarylpyridinium salts bearing a pyridin-2-yl-like substituent in the position 1 afford as a rule sterically crowded 3-imidazo[1,2-*a*]hetaryl-(*Z*)-1,3-diarylprop-2-en-1-ones sometimes accompanied by isomeric (1-hetaryl-3,5-diaryl-1*H*-pyrrol-2-yl)(aryl)-methanones[1b,2]. On the other hand, the minor pyrrole derivatives turned out to be the only products from 2,4,6-triarylpyridinium salts having in the position 1 other than pyridin-2-yl-like substituents[2]. Although the transformations seem to be very general[1b] and useful[1c,1d] only tentative mechanistic considerations have been presented[1a,3]. Since at least two competitive reaction paths leading to the both mentioned types of reaction products start from the same substrates, a possibility offers to follow those paths by systematic changing certain substituents capable of favouring or suppress-

ing the formation of the individual isomers in the final reaction mixture. Considering a multistep nature of the processes, our attention has been so far concentrated on variation of the substituents in such positions where they may sterically affect formation of alternative intermediate and/or transition states and consequently ratios of the isomeric products. The latter may be monitored by HPLC and then isolated in a preparative scale.

To acquire a deeper insight into the oxidative transformations, two reaction series have been investigated involving phenyl (P) or *tert*-butyl (TB) groups as alternative 4-substituents in the substrate molecules (P- or TB-series, respectively). The P-series corresponds to the general transformation (Scheme 1) and these conversions of the perchlorates **1a** (R = H), **1b** (R = Me) and **1g** (R = Ph) have been already published[1b,2] but now they



a, R = H b, R = Me c, R = Et d, R = iPr e, R = n-Bu f, R = *t*-Bu g, R = Ph

SCHEME 1

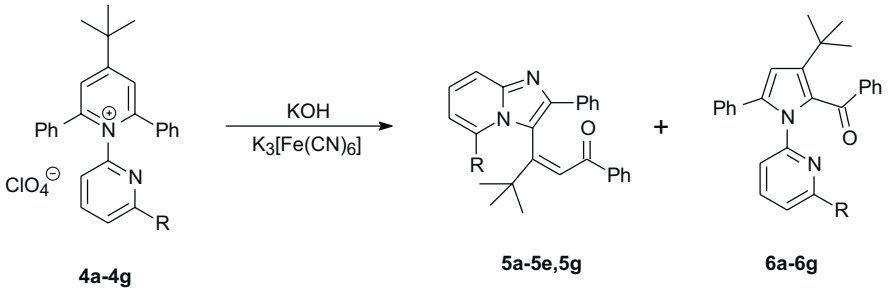
have been repeated under mild conditions and completed by HPLC monitoring. The remaining salts **1c**–**1f** (R = Et, i-Pr, n-Bu and *t*-Bu) are new compounds (Table I) and their preparation is discussed below. All the substrates **1a**–**1g** have been observed to be very reactive towards the potassium hexacyanoferrate(III)–potassium hydroxide reagent, their oxidations being already completed after 30 min at room temperature. An exceptional example was the starting perchlorate **1f** (R = *t*-Bu) affording the predominant pyrrole **3f** in addition to the minor isomeric (*Z*)-enone **2f**. In all other cases the imidazo[1,2-*a*]pyridinoic (*Z*)-enones **2a**–**2e** and **2g** were found to be major products (Table II) but the minor isomers **3a**–**3e** and **3g** were detected, too. Compounds **3d** and **3f** were the only pyrroles isolated (Table III).

The TB-series started from all new quaternary salts **4a**–**4g** (Table I) the syntheses of which are also described below. The reactivity of these perchlorates possessing TB groups towards the potassium hexacyanoferrate(III)–potassium hydroxide reagent turned out to be lower in comparison with that of the P-series, the conversions shown in Scheme 2

being completed after 90 min only in refluxing ethanol. Except for the strongly sterically hindered (*Z*)-enone **5f** (R = *t*-Bu) all other imidazo-[1,2-*a*]pyridines **5a**–**5e** and **5g** as well as isomeric pyrroles **6a**–**6g** were detected and isolated (Tables II and III). This transformation can be regarded as a further generalization of the extended Decker oxidation[1a] to quaternary pyridinium salts possessing TB group in the position 4. It may be noted that an oxidative elimination of the alkyl group from the position 2 has been observed under similar conditions[3b].

TABLE I
Yields and physical properties of perchlorates **1c**–**1f** and **4a**–**4g**

Compound	Yield %	M.p., °C solvent	Formula M.w.	Calculated/Found			
				% C	% H	% N	% Cl
1c	84	213–216 ethanol	$C_{30}H_{25}ClN_2O_4$ 513.0	70.24 70.29	4.91 4.88	5.46 5.57	6.91 6.95
1d	85	261–263 ethanol	$C_{31}H_{27}ClN_2O_4$ 527.0	70.65 70.63	5.16 5.44	5.32 5.29	6.73 6.76
1e	60	262–263 ethanol	$C_{32}H_{29}ClN_2O_4$ 541.1	71.04 70.77	5.40 5.59	5.18 5.07	6.55 6.53
1f	86	252–254 ethanol	$C_{32}H_{29}ClN_2O_4$ 541.1	71.04 71.29	5.40 5.59	5.18 5.07	6.55 6.53
4a	85	231–232 ethanol	$C_{26}H_{25}ClN_2O_4$ 465.0	67.17 67.19	5.42 5.52	6.03 6.01	7.63 7.39
4b	82	170–172 ethanol–ether	$C_{27}H_{27}ClN_2O_4$ 479.0	67.71 67.87	5.68 5.86	5.85 5.86	7.40 7.47
4c	60	226–229 ethanol	$C_{30}H_{25}ClN_2O_4$ 513.0	68.22 68.02	5.93 5.71	5.68 5.73	7.19 7.34
4d	90	238–241 ethanol	$C_{30}H_{25}ClN_2O_4$ 513.0	68.70 68.49	6.16 6.40	5.52 5.40	6.99 7.15
4e	71	160–162 ether	$C_{30}H_{25}ClN_2O_4$ 513.0	69.15 69.44	6.38 6.54	5.38 5.40	6.80 6.68
4f	57	194–197 ether	$C_{30}H_{25}ClN_2O_4$ 513.0	69.15 69.48	6.38 6.69	5.38 5.30	6.80 6.59
4g	81	153–155 ethanol	$C_{30}H_{25}ClN_2O_4$ 513.0	71.04 71.17	5.40 5.67	5.18 5.02	6.55 6.49



4a-4g **5a-5e,5g** **6a-6g**

a, R = H b, R = Me c, R = Et d, R = iPr e, R = n-Bu f, R = *t*-Bu g, R = Ph

SCHEME 2

TABLE II
Yields and physical properties of enones **2a**–**2g** and **5a**–**5e**, **5g**

Compound	Yield %	M.p., °C solvent	Formula M.w.	Calculated/Found			IR ν, cm^{-1}
				% C	% H	% N	
2c	74	150–151 ethanol–water	$C_{30}H_{24}N_2O$ 428.5	84.08 83.84	5.65 5.91	6.54 6.34	1 659
2d	95	70–74[b]	$C_{31}H_{26}N_2O$ 442.6	84.13 83.93	5.92 6.29	6.33 6.39	1 660
2e	61	191–193 methanol	$C_{32}H_{28}N_2O$ 456.6	84.18 84.24	6.18 6.33	6.14 6.15	1 660
2f	9	65–69[b]	$C_{32}H_{28}N_2O$[c] 456.6				1 660
5a	36	156–158 ethanol	$C_{26}H_{24}N_2O$ 380.5	82.07 82.11	6.36 6.70	7.36 7.30	1 666
5b	61	177–179 acetone–heptane	$C_{27}H_{26}N_2O$ 394.5	82.20 82.29	6.64 6.95	7.10 7.11	1 664
5c	42	36–40[b]	$C_{28}H_{28}N_2O$[d] 408.5				1 665
5d	30	218–222 methanol	$C_{29}H_{30}N_2O$ 422.6	82.43 82.42	7.16 7.23	6.63 6.67	1 666
5e	45	107–113[b]	$C_{30}H_{32}N_2O$ 436.6	82.53 82.66	7.39 7.43	6.42 6.35	1 665
5g	13	170–172[b]	$C_{32}H_{28}N_2O$ 456.6	84.18 84.24	6.18 6.40	6.14 6.17	1 664

[a] Preparative chromatographic values. [b] Just evaporated. [c] The formula was determined by high resolution MS; for MH^+ calculated: 457.22800, found: 457.227989. [d] The formula was determined by high resolution MS; for MH^+ calculated: 409.22800, found 409.227989.

While the (*Z*)-configuration of the **2**-like ketones follows from earlier structural studies[1e,2], the analogous (*Z*)-stereospecifity of the conversions **4a**–**4e**, **4g** → **5a**–**5e**, **5g** (Scheme 2) has been now supported by the ^{1}H NMR investigations on the 5-methyl derivative **5b** indicating a strong NOE effect between the methine signal of the proton in the position 2′ (δ 7.65 ppm) and the methyl signal of the TB group (δ 0.92 ppm) in the position 3′.

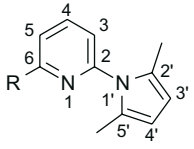
The product ratios are compared in Table IV. It is evident that the higher reactivity in the P-series with respect to that in the TB-series is in accord with the general reactivity–selectivity principle and the selectivity in the P-series is much more pronounced. On the other hand, the relative substituent effects preferring the formation of the (*Z*)-enones H > Me > Et = n-Bu > i-Pr > Ph > *t*-Bu are the same in the both series and follow the values of various steric constants[4].

TABLE III
Yields and physical properties of pyrroles **3d**, **3f** and **6a**–**6g**

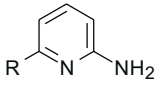
Compound	Yield %	M.p., °C solvent	Formula M.w.	Calculated/Found % C	% H	% N	IR ν, cm^{-1}
3d	5	133–136 heptane	$C_{31}H_{26}N_2O$ 442.6	84.13 84.07	5.92 6.22	6.33 6.32	1 628
3f	71	113–117 ethanol	$C_{32}H_{28}N_2O$ 456.6	84.18 84.04	6.18 6.34	6.14 6.15	1 638
6a	49	166–168 heptane	$C_{26}H_{24}N_2O$[c] 380.5	82.07 81.96	6.36 6.24	7.36 7.48	1 656
6b	30	138–140 heptane	$C_{27}H_{26}N_2O$ 3945	82.20 82.19	6.64 6.92	7.10 7.21	1 655
6c	47	92–94 heptane	$C_{28}H_{28}N_2O$ 408.5	82.32 82.36	6.91 6.94	8.86 6.89	1 657
6d	49	119.5–120.5 heptane	$C_{29}H_{30}N_2O$[d] 422.6	82.43 82.55	7.16 7.31	6.63 6.65	1 658
6e	45	89–92 methanol	$C_{30}H_{32}N_2O$ 436.6	82.53 82.70	7.39 7.57	6.42 6.68	1 657
6f	88	90–95[b]	$C_{30}H_{32}N_2O$ 436.6	82.53 82.57	7.39 7.36	6.42 6.13	1 657
6g	80	134–135 heptane	$C_{32}H_{28}N_2O$ 456.6	84.18 84.14	6.18 6.11	6.14 6.20	1 656

[a] Preparative chromatographic values. [b] Just evaporated.

The starting salts **1a**–**1g** and **4a**–**4g** were prepared from 6-substituted (pyridin-2-yl)amines **7a**–**7g** and 2,4,6-triphenylpyrylium or 4-*tert*-butyl-2,6-diphenylpyrylium perchlorates by standard procedure for the preparation of pyridinium perchlorates[5], respectively. To prepare commercially not available amines **7c**–**7f** (R = Et, i-Pr, n-Bu and *t*-Bu), an improved procedure[6] going out from 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine **8a** was applied. Thus, the compound **8a** was reacted with appropriate organolithium reagents RLi and converted *via* labile 1,6-dihydropyridine intermediates to 6-alkylated products **8c**–**8f**. The latter were then hydrolyzed[7] to the required amines **7c**–**7f** in good yields.



8a-8f



7a-7g

a, R = H b, R = Me c, R = Et d, R = iPr e, R = n-Bu f, R = *t*-Bu g, R = Ph

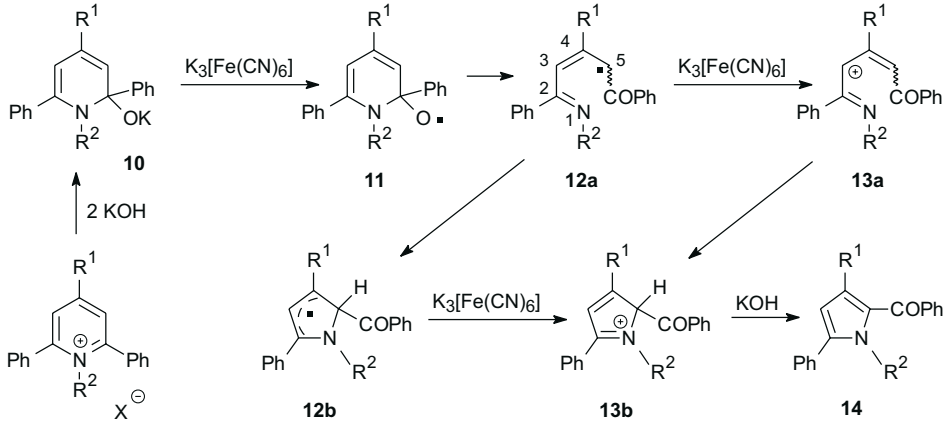
To understand the parallelism of substituent effects in the both P- and TB-series it is desirable to outline possible multistep reaction paths explaining the oxidative transformations. Scheme 3 shows the suggested general route to pyrrole products. Although some speculative mechanistic sugges-

TABLE IV
Relative product ratios in Schemes 1 and 2 detected by HPLC in the crude reaction mixtures

R	Substituent (E_s), ref.[4a]	Pyrole (Ω_s), ref.[4b]	(*Z*)-Enone	
			P-series[a]	TB-series[b]
H	(0.00)	(0.00)	35	0.7
Me	(–1.24)	(0.21)	30	2.0
Et	(–1.31)	(0.26)	26	1.2
i–Pr	(–1.71)	(0.30)	25	0.4
n–Bu	(–1.63)	(0.27)	26	1.1
t–Bu	(–2.17)	(0.35)	0.05	0.0
Ph	(–1.01 to –3.82)[c]	–	6	0.1

[a] After 30 min at room temperature. [b] After 90 min in refluxing ethanol. [c] Different E_s values are reported[4] depending on model compounds considered.

tions regarding the problem have been proposed[1a], this is a new version based on the recent experimental progress in the area[1b–1d]. The first step is the same as that resulting from the kinetic investigations[8] of the standard Decker synthesis of pyridones from quaternary pyridinium salts. Since the hexacyanoferrate(III) ion is a typical one-electron acceptor, the resulting potassium 1,2-dihydropyridine-2-olate **10** is evidently oxidized in the second step to the primary *O*-radical **11** which undergoes the ring-opening



SCHEME 3

and ring-closure isomerizations *via* radical **12a** to the five-membered heterocyclic radical **12b**. The secondary **12**-like radicals may be key intermediates and therefore quantum chemical open-shell calculations using the PM3-PECI method[9] were performed on their simple MO models (R^1 = Ph, R^2 = Me). It has been found that the former radical may exist in two stereoisomeric conformers *a*-**12a** and *s*-**12a**, differing by only 0.9 kcal/mol in favour of the *s*-**12a** form while the heterocyclic radical **12b** is significantly preferred by 18.8 kcal/mol with respect to the isomer *s*-**12a**. Hence, the heterocyclic ring closure **12a** → **12b** should be accompanied by an energy release. As follows from Table V, the spin densities in the radicals *a*,*s*-**12a** in positions 1 and 5, between which the new C–N bond is formed, are quite different; at the *C*-centre considerably high (0.79 and 0.24) while at the *N*-centre virtually zero. It may be therefore expected that the conversion will be forced by spin density currents from the carbon to the nitrogen in agreement with the final spin density distribution in the heterocyclic radical **12b**. The optimized molecular geometries of the radicals *a*,*s*-**12a** and **12b** are shown in Figs 1–3. In the former cases the 4-phenyl group is almost

coplanar with the π-systems while the 2- and 6-phenyl groups are virtually perpendicular to them. Hence, it is more probable that the nature of the 4-substituent would influence stabilities of the radical structures (Fig. 4) by electronic effects in the "radical" reaction path **12a** → **12b** → **13b** → **14**,

TABLE V
Selected spin densities in some radicals and net charges in some cationic intermediates

Species (R^1 = Ph)	ΔH_f kcal/mol	Position[a]				
		1	2	3	4	5
Radicals						
***a*-12a**	101.75	+0.01	+0.02	+0.12	–0.04	+0.79
***s*-12a**	100.88	0.00	–0.01	–0.06	–0.01	+0.24
12b[b]	82.08	+0.37	–0.85	–0.14	+0.78	+0.04
12b[c]	119.16	+0.21	–0.13	–0.02	+0.12	–0.14
15a	137.52	–0.10	+0.02	–0.05	–0.02	–0.26
15b	137.10	+0.25	–0.01	–0.05	–0.02	+0.07
Cations						
***a*,*s*-16a**[d]	313.59	+0.18	–0.10	+0.33	–0.11	+0.02
***s*,*s*-16a**[d]	318.29	+0.21	–0.14	+0.31	–0.15	+0.14
16b	315.90	+0.19	–0.10	+0.26	–0.01	+0.01
16c	263.28	+0.39	+0.10	–0.21	+0.10	–0.19

[a] The numbering, see Scheme 1. [b] R^2 = Me. [c] R^2 = 6-R-pyridin-2-yl. [d] The first *a* and *s* symbols denote conformations of the pyridin-2-yl group.

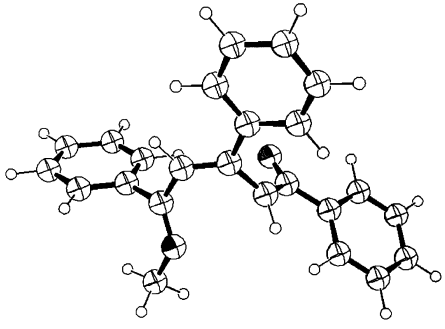
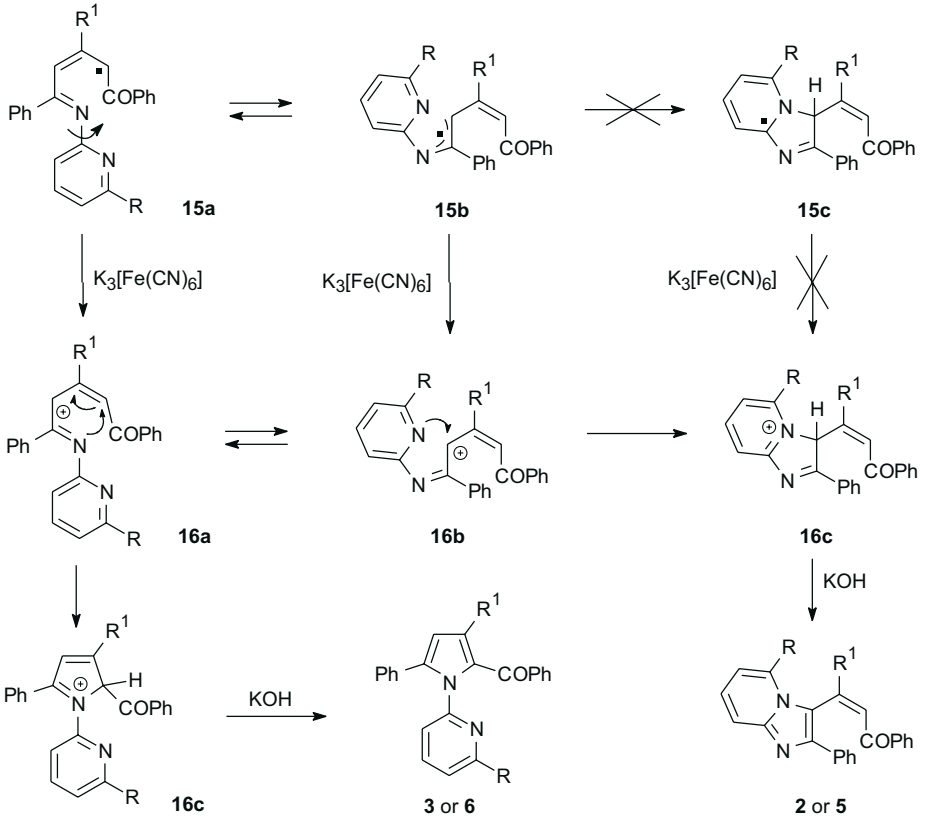


FIG. 1
The molecular skeleton of the radical ***a*-12a** (R^1 = Ph, R^2 = Me) optimized by PM3-PECI method

where the heterocyclic ring closure takes place prior to the one-electron abstraction. The final deprotonization with potassium hydroxide to pyrrole products **14** is evidently favoured by aromatization and can hardly affect the rate of the whole process in Scheme 3. However, here comes into consideration an alternative "cationic" reaction path **12a** → **13a** → **13b** → **14**, where the radical **12a** is oxidized to the cationic open form **13a** prior to the heterocyclization. Bellow it will be argued against the general validity of the sequence at least for the formation of **3**- and **6**-like pyrroles.

Scheme 4 shows reaction paths modified for cases, where R^2 denotes an R-substituted pyridin-2-yl group in Scheme 3, and leading to the mixtures



SCHEME 4

of two isomeric products **2** and **3** or **5** and **6**, respectively. Considering formation of the pyrroles **3** or **6**, the intermediate radical **15a**, as a special case of **12a** mentioned in Scheme 3, might also take part in the transformation

involving the second one-electron abstraction **15a** → **16a** prior to the heterocyclization **16a** → **16c**. However, charge distribution in the PM3 optimized model of the cationic moiety in **16a** (R = H, R^1 = Ph), especially the net charges +0.18 and +0.02 *e* (Table V), suggests that the closure between the positions 1 and 5, though exothermic (–50 kcal/mol), should not be fast enough to compete with the analogous exothermic step **16b** → **16c** (–55 kcal/mol) *via* the conformationally changed intermediate **16b** exhibiting a net charge +0.26 *e* in the position 3, favourable for eletrophilic attack at the pyridine nitrogen (Fig. 5). It may be noted that the calculated net charge –0.08 *e* at the nitrogen does not fully involve the real electron pair density mainly localized outside the nitrogen. Thus, the formation of imidazo[1,2-*a*]pyridine derivatives **2** or **5** can be better explained by the reaction steps **15a** → **16a** → **16b** → **16c** → **2** or **5**. On the other hand, the second possibility involving the sequence **15a** → **15b** → **15c** → **16c** → **2** or **5** seems to be hardly realistic because of the spin density distribution in the intermediate radical **15b** (Fig. 5) quite unfavourable for cyclization to its heterocyclic isomer **15c**.

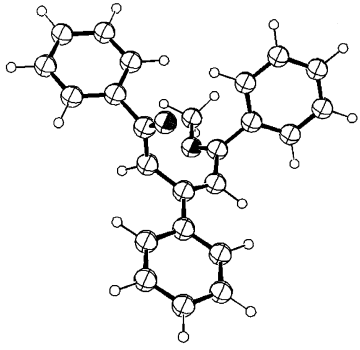


FIG. 2
The molecular skeleton of the radical *s*-**12a** (R^1 = Ph, R^2 = Me) optimized by PM3-PECI method

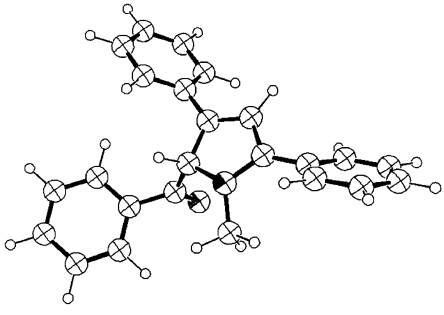
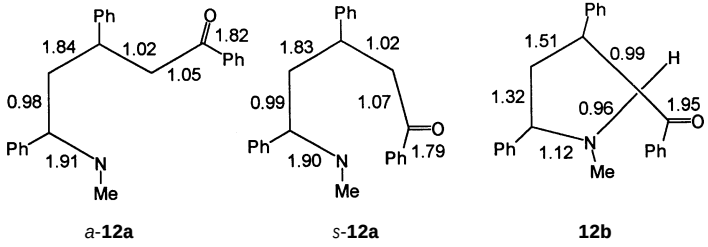


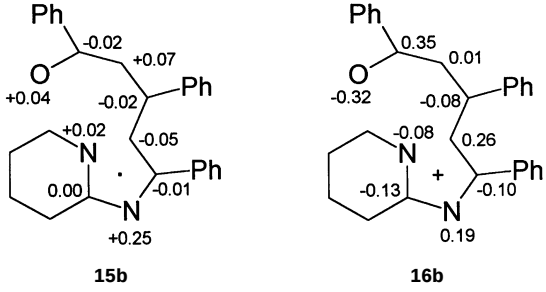
FIG. 3
The molecular skeleton of the radical **12b** (R^1 = Ph, R^2 = Me) optimized by PM3-PECI method

As follows from the molecular geometry of the cation in **16b** (Fig. 6) any substituent R in the corresponding formula shown in Scheme 4 should come into a steric interaction with the side chain of the species. Hence, the bulkier the substituent R is, the more the rate of the ring closure **16b** → **16c**



a-**12a** *s*-**12a** **12b**

FIG. 4
Selected PM3-PECI bond orders for the radicals *a*-**12a**, *s*-**12a** and **12b** (R^1 = Ph, R^2 = Me)



15b **16b**

FIG. 5
Selected PM3-PECI spin densities for the radicals **15b** (R = H, R^1 = Ph) and corresponding PM3 net charges for the cation **16b** (R = H, R^1 = Ph)

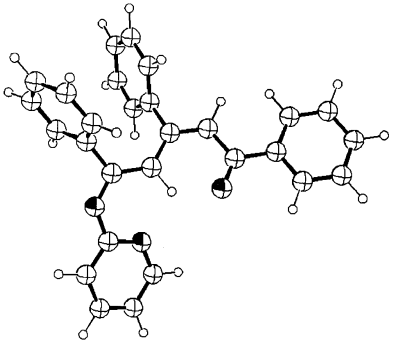


FIG. 6
The molecular skeleton of the coiled cation **16b** (R = H, R^1 = Ph) optimized by PM3 method

decreases. Consequently, the population of the **2**- or **5**-like products will tend to be lower with respect to that of the pyrrole isomers **3** or **6**. Kinetic stabilities of the radicals **15a** seem to be a critical point. If the life-time of one of the intermediates is longer, the second one-electron oxidation **15a** → **16a** should be faster than the competitive cyclization to the **12b**-like secondary radicals and *vice versa*. In agreement with the PM3 optimized molecular geometry, optimization of the radical **15a** (R = H), similarly to that *a*,*s*-**12a** (Figs 1 and 2), resulted in the almost coplanar 4-phenyl group (R^1 = Ph) which extends π-electron delocalization and enhances kinetic stability of the species. In fact, the imidazo[1,2-*a*]pyridines **2** are entirely predominating in the P-series contrary to their counterparts **5** in the TB-series (R^1 = *t*-Bu) where the stabilizing effect is evidently absent (Table IV).

As follows further from Table IV, in the P-series (R^1 = Ph), the substituents R obey the usual steric order *t*-Bu > (Ph) > i-Pr > Bu > Et > Me > H indicating the above predicted repulsive interaction between the both substituents R and the side chain in the cationic intermediates. On the other hand, in the TB-series (R^1 = *t*-Bu), there is an exception for R = H which seems to be somewhat surprising because the hydrogen apparently inhibits more the formation of appropriate (*Z*)-ketone **5a** than methyl, ethyl or butyl groups (compounds **15b**–**15d**). The explanation does not seem to be trivial and may consist in the charge–charge components of repulsion between the hydrogen centre and the side chain and/or in other conformational changes.

Anyway, it can be finally concluded that the selectivity of the transformations (Schemes 1 and 2) can be mainly controlled by kinetic stability of the radicals **15a** as well as by steric effects of the substituents R in intermediates **16b** in the multistep formation of sterically crowded molecules shown in Scheme 4.

EXPERIMENTAL

The temperature data are uncorrected. Melting points were determined on a Boetius block. NMR spectra (δ, ppm; *J*, Hz) were taken on a GEMINI 300 HC instrument at 297 K. The working frequency was 300 MHz for ^{1}H and 75 MHz for ^{13}C. The one-dimensional DPFGSE-NOE experiment[10] was applied to investigate the (*Z*)-configuration of the compound **5b**, and was performed on a Bruker DRX 500 Avance instrument. IR spectra (ν, cm^{-1}; $CHCl_3$ solutions) were measured on a FTIR spectrometer Nicolet 740. HR MS FAB spectra were mesured on a ZAB-SEQ instrument. HPLC analyses were performed using an Ecom LCP 4000 chromatograph with an LCD 2082 UV/VIS detector, column was Nucleosil C-18 Macherey–Nagel column, mobile phase was CH_3OH–H_2O (8 : 2 or 7 : 3). Samples for HPLC analyses were dissolved in MeOH. Commercial Silufol plates (Kavalier Sázava, Czech Republic) were used for TLC. Merck 40 and Merck 60 PF_{254} silica gels were used for column and pre-

parative TLC chromatography, respectively. Eluent for column or TLC chromatography was CH_2Cl_2 : EtOH (98 : 2 for TLC, gradient for column chromatography).

The preparation of compounds **1a**, **1b**, **1g**; **2a**, **2b**, **2g**; and **3g** was reported earlier[1b,2]. Pyridin-2-yl amine (**7a**) and 6-methylpyridin-2-yl amine (**7b**) were commercial products (Sigma–Aldrich). 6-Phenylpyridin-2-yl amine (**7g**) was prepared by the described[11] procedure. 6-Ethylpyridin-2-yl amine (**7c**) was prepared by alkylation of **8b** according to literature[12] with the modification[7] that BuLi was employed as the base in place LDA.

1-(6-Substituted Pyridin-2-yl)-2,4,6-triphenylpyridinium Perchlorates **1c**–**1f**

A mixture of 2,4,6-triphenylpyrylium perchlorate[13] (5 g, 12.2 mmol), and 6-substituted 2-aminopyridine **7** (13.4 mmol) in ethanol (200 ml) was stirred under reflux for 2 h. The white crystals precipitated on cooling were collected by suction, washed with ethanol and recrystallized from the same solvent, see Table I.

1-(6-Ethylpyridin-2-yl)-2,4,6-triphenylpyridinium perchlorate (**1c**): ^{1}H NMR (DMSO-d_6): 0.87 t, 3 H, J = 7.1 (6′-$CH_2C\mathbf{H}_3$); 2.55 q, 2 H, J = 7.1 (6′-$C\mathbf{H}_2CH_3$); 7.19 d, 1 H, J = 7.7; 7.33–7.49 m, 11 H; 7.61–7.76 m, 4 H; 8.38 d, 2 H, J = 8.2; 8.72 s, 2 H (H-3 and H-5). ^{13}C NMR (DMSO-d_6): 13.43 CH_3, 29.80 CH_2, 121.65 CH, 124.01 CH, 125.39 CH, 128.25 CH, 129.03 CH, 129.71 CH, 130.24 CH, 132.53 C, 132.69 CH, 133.49 C, 139.23 CH, 150.43 C, 155.44 C, 156.48 C, 163.06 C (one CH signal was overlapped).

1-(6-Isopropylpyridin-2-yl)-2,4,6-triphenylpyridinium perchlorate (**1d**): ^{1}H NMR (DMSO-d_6): 0.97 d, 6 H, J = 7.1 (6′-CH($C\mathbf{H}_3$)$_2$); 2.87 h, 1 H, J = 6.6 (6′-$C\mathbf{H}(CH_3)_2$); 7.19 d, 1 H, J = 7.7; 7.33–7.49 m, 11 H; 7.61–7.77 m, 4 H; 8.38 d, 2 H, J = 6.6; 8.73 s, 2 H (H-3 and H-5). ^{13}C NMR (DMSO-d_6): 21.76 CH_3, 34.76 CH, 121.68 CH, 122.91 CH, 125.41 CH, 128.24 CH, 129.04 CH, 129.71 CH, 130.23 CH, 132.52 C, 132.66 CH, 133.54 C, 139.40 CH, 150.45 C, 155.42 C, 156.55 C, 166.60 C (one CH signal was overlapped).

1-(6-Butylpyridin-2-yl)-2,4,6-triphenylpyridinium perchlorate (**1e**): ^{1}H NMR (DMSO-d_6): 0.80 t, 3 H, J = 6.6 (6′-$CH_2CH_2CH_2C\mathbf{H}_3$); 0.90–1.10 m, 4 H (6′-$CH_2C\mathbf{H}_2CH_2CH_3$); 1.27 t, 2 H, J = 7.1 (6′-$C\mathbf{H}_2CH_2CH_2CH_3$); 7.19 d, 1 H, J = 7.7; 7.32–7.52 m, 11 H; 7.61–7.78 m, 4 H; 8.37 d, 2 H, J = 6.6; 8.71 s, 2 H (H-3 and H-5). ^{13}C NMR (DMSO-d_6): 13.65 CH_3, 21.05 CH_2, 30.80 CH_2, 36.05 CH_2, 121.83 CH, 124.74 CH, 125.54 CH, 128.32 CH, 129.14 CH, 129.79 CH, 130.33 CH, 132.63 C, 132.75 CH, 133.62 C, 139.10 CH, 150.57 C, 155.56 C, 156.62 C, 162.16 C (one CH signal was overlapped).

1-(6-tert-Butylpyridin-2-yl)-2,4,6-triphenylpyridinium perchlorate (**1f**): ^{1}H NMR (DMSO-d_6): 1.09 s, 9 H (6′-C($C\mathbf{H}_3$)$_3$); 7.29–7.47 m, 12 H; 7.63–7.76 m, 4 H; 8.38 d, 2 H, J = 6.6; 8.73 s, 2 H (H-3 and H-5). ^{13}C NMR (DMSO-d_6): 29.15 CH_3, 120.52 CH, 121.28 CH, 125.32 CH, 128.12 CH, 128.96 CH, 129.59 CH, 130.10 CH, 132.43 C, 132.56 CH, 133.46 C, 139.36 CH, 149.78 C, 155.33 C, 156.44 C, 168.52 C (one CH signal was overlapped, C signal of *t*-Bu was overlapped by DMSO).

1-(6-Substituted Pyridin-2-yl)-4-*tert*-butyl-2,6-diphenylpyridinium Perchlorates **4a**–**4g**

To a stirred and refluxed suspension of 4-*tert*-butyl-2,6-diphenylpyrylium perchlorate[14] (2 g, 5.1 mmol) in ethanol (10 ml) was added a solution of corresponding 6-substituted 2-aminopyridine **7** (5.7 mmol) in ethanol (5 ml). The reaction mixture was stirred under reflux for 1 h, treated with charcoal, and filtered. The white crystals precipitated on cooling were collected by suction, washed with ethanol, ether and recrystallized from an appropriate solvent, see Table I.

1-(Pyridin-2-yl)-4-tert-butyl-2,6-diphenylpyridinium perchlorate (**4a**): ^{1}H NMR (DMSO-d_6): 1.53 s, 9 H (4-C(C**H**$_3$)$_3$); 7.28–7.50 m, 11 H; 7.64 d, 1 H, *J* = 7.7; 7.76 ddd, 1 H, *J* = 7.7, 7.7 and 1.7; 8.32 d, 3 H, *J* = 6.0 (H-3, H-5 and H-6′). ^{13}C NMR (DMSO-d_6): 29.50 CH_3, 36.95 C, 124.76 CH, 125.92 CH, 126.20 CH, 128.43 CH, 129.80 CH, 130.37 CH, 132.56 C, 139.07 CH, 148.93 CH, 151.19 C, 154.97 C, 172.45 C.

1-(6-Methylpyridin-2-yl)-4-tert-butyl-2,6-diphenylpyridinium perchlorate (**4b**): After filtration the reaction mixture was evaporated and residue crystallized on treatment with ethanol–ether. ^{1}H NMR (DMSO-d_6): 1.52 s, 9 H (4-C(C**H**$_3$)$_3$); 2.23 s, 3 H (6′-C**H**$_3$); 7.18 d, 1 H, *J* = 7.7; 7.33–7.48 m, 11 H; 7.61 dd, 1 H, *J* = 7.7 and 8.2; 8.32 s, 2 H (H-3 and H-5). ^{13}C NMR (DMSO-d_6): 22.99 CH_3, 29.47 CH_3, 36.86 C, 121.47 CH, 124.94 CH, 126.09 CH, 128.29 CH, 129.77 CH, 130.29 CH, 132.58 C, 139.07 CH, 150.32 C, 154.87 C, 158.14 C, 172.25 C.

1-(6-Ethylpyridin-2-yl)-4-tert-butyl-2,6-diphenylpyridinium perchlorate (**4c**): ^{1}H NMR (DMSO-d_6): 0.88 t, 3 H, *J* = 7.1 (6′-CH_2C**H**$_3$); 1.54 s, 9 H (4-C(C**H**$_3$)$_3$); 2.53 overlapped by DMSO, 2 H (6′-C**H**$_2$$CH_3$); 7.18 d, 1 H, *J* = 7.7; 7.33–7.48 m, 11 H; 7.64 dd, 1 H, *J* = 7.7 and 7.7; 8.32 s, 2 H (H-3 and H-5). ^{13}C NMR (DMSO-d_6): 13.32 CH_3, 29.50 CH_3, 29.70 CH_2, 36.91 C, 121.72 CH, 124.07 CH, 126.14 CH, 128.36 CH, 129.77 CH, 130.26 CH, 132.69 C, 139.31 CH, 150.56 C, 154.88 C, 163.18 C, 172.26 C.

1-(6-Isopropylpyridin-2-yl)-4-tert-butyl-2,6-diphenylpyridinium perchlorate (**4d**): ^{1}H NMR (DMSO-d_6): 0.91 d, 6 H, *J* = 6.6 (6′-CH(C**H**$_3$)$_2$); 1.54 s, 9 H (4-C(C**H**$_3$)$_3$); 2.85 h, 1 H, *J* = 7.1 (6′-C**H**$(CH_3)_2$); 7.18 d, 1 H, *J* = 7.7; 7.30–7.46 m, 11 H; 7.63 dd, 1 H, *J* = 7.7 and 8.2; 8.33 s, 2 H (H-3 and H-5). ^{13}C NMR (DMSO-d_6): 21.63 CH_3, 29.51 CH_3, 34.65 CH, 36.92 C, 121.77 CH, 122.95 CH, 126.13 CH, 128.33 CH, 129.75 CH, 130.23 CH, 132.66 C, 139.46 CH, 150.55 C, 154.86 C, 166.72 C, 172.27 C.

1-(6-Butylpyridin-2-yl)-4-tert-butyl-2,6-diphenylpyridinium perchlorate (**4e**): After filtration the reaction mixture was evaporated and residue crystallized on treatment with ether. ^{1}H NMR (DMSO-d_6): 0.79 t, 3 H, *J* = 7.1 (6′-$CH_2CH_2CH_2$C**H**$_3$); 0.93 tq, 2 H, *J* = 7.1 and 7.7 (6′-CH_2CH_2C**H**$_2CH_3$); 1.25 tt, 2 H, *J* = 7.1 and 7.1 (6′-CH_2C**H**$_2CH_2CH_3$); 1.53 s, 9 H (4-C(C**H**$_3$)$_3$); 2.53 overlapped by DMSO, 2 H (6′-C**H**$_2CH_2CH_2CH_3$); 7.17 d, 1 H, *J* = 7.7; 7.33–7.48 m, 11 H; 7.63 dd, 1 H, *J* = 7.7 and 7.7; 8.31 s, 2 H (H-3 and H-5). ^{13}C NMR (DMSO-d_6): 13.66 CH_3, 21.05 CH_2, 29.51 CH_3, 30.84 CH_2, 36.04 CH_2, 36.91 C, 121.83 CH, 124.75 CH, 126.18 CH, 128.36 CH, 129.76 CH, 130.29 CH, 132.68 C, 139.29 CH, 150.56 C, 154.87 C, 162.14 C, 172.24 C.

1-(6-tert-Butylpyridin-2-yl)-4-tert-butyl-2,6-diphenylpyridinium perchlorate (**4f**): After filtration the reaction mixture was evaporated and residue crystallized on treatment with ether. ^{1}H NMR (DMSO-d_6): 1.06 s, 9 H (6′-C(C**H**$_3$)$_3$); 1.53 s, 9 H (4-C(C**H**$_3$)$_3$); 7.26–7.46 m, 12 H; 7.65 dd, 1 H, *J* = 7.7 and 7.7; 8.33 s, 2 H (H-3 and H-5). ^{13}C NMR (DMSO-d_6): 29.14 CH_3, 29.52 CH_3, 36.93 C, 36.98 C, 120.68 CH, 121.45 CH, 126.11 CH, 128.33 CH, 129.72 CH, 130.23 CH, 132.65 C, 139.54 CH, 150.00 C, 154.84 C, 168.74 C, 172.25 C.

1-(6-Phenylpyridin-2-yl)-4-tert-butyl-2,6-diphenylpyridinium perchlorate (**4g**): ^{1}H NMR (DMSO-d_6): 1.55 s, 9 H (4-C(C**H**$_3$)$_3$); 7.17 d, 1 H, *J* = 7.7; 7.30–7.50 m, 12 H; 7.54 d, 1 H, *J* = 7.7; 7.74–7.92 m, 4 H; 8.37 s, 2 H (H-3 and H-5). ^{13}C NMR (DMSO-d_6): 29.53 CH_3, 36.98 C, 121.88 CH, 122.96 CH, 126.27 CH, 126.84 CH, 128.45 CH, 129.03 CH, 129.75 CH, 130.22 CH, 130.39 CH, 132.72 C, 136.45 C, 140.11 CH, 150.99 C, 154.92 C, 155.83 C, 172.44 C.

Ferricyanide Oxidation of Perchlorates **1c**–**1f**. General Procedure

A solution of potassium ferricyanide (1.93 g, 5.85 mmol) and potassium hydroxide (438 mg, 7.8 mmol) in water (20 ml) was added to a stirred suspension of perchlorate **1c**–**1f** (1.95 mmol) in ethanol (50 ml). After 30 min the reaction mixture was poured into cold water (150 ml), extracted with 4 × 20 ml of dichloromethane and the collected organic extracts were dried with sodium sulfate and evaporated. The residue was crystallized from appropriate solvent or chromatographed on a column.

(Z)-3-(5-Ethyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-1,3-diphenylprop-2-en-1-one (**2c**): The residue was crystallized from ethanol affording yellow crystals of enone **2c**. ^{1}H NMR ($CDCl_3$): 1.34 t, 3 H, *J* = 7.1 (5-$CH_2C\mathbf{H}_3$); 2.56 dq, 1 H, *J* = 7.1 and 8.2 (5-$C\mathbf{H}_2CH_3$); 3.22 dq, 1 H, *J* = 7.1 and 7.7 (5-$C\mathbf{H}_2CH_3$); 6.56 d, 1 H, *J* = 7.1; 7.08–7.22 m, 6 H; 7.33–7.62 m, 12 H. ^{13}C NMR ($CDCl_3$): 12.57 CH_3, 25.39 CH_2, 110.83 CH, 116.21 CH, 118.65 C, 125.72 CH, 128.08 CH, 128.22 CH, 128.63 CH, 128.71 CH, 128.82 CH, 128.99 CH, 129.85 CH, 130.12 CH, 130.78 CH, 133.11 CH, 134.95 C, 138.40 C, 140.92 C, 143.08 C, 144.87 C, 145.53 C, 147.85 C, 192.09 CO. Yield and other characteristics of compound **2c** are given in Table II.

(Z)-3-(5-Isopropyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-1,3-diphenylprop-2-en-1-one (**2d**) *and [1-(6-isopropylpyridin-2-yl)-3,5-diphenyl-1H-pyrrol-2-yl](phenyl)methanone (***3d**): The reaction was started from perchlorate **1d** (4 g, 7.59 mmol). The crude reaction mixture was chromatographed on a column (80 g silica gel, dichloromethane–ethanol as an eluent, concentration gradient was 1% of ethanol per 100 ml of eluent). The less polar fractions contained pyrrole derivative **3d** which was recrystallized from heptane to yield light yellow crystals. ^{1}H NMR ($CDCl_3$): 1.10 d, 6 H, *J* = 6.6 (6′-$CH(C\mathbf{H}_3)_2$); 2.92 h, 1 H, *J* = 6.6 (6′-$C\mathbf{H}(CH_3)_2$); 6.63 s, 1 H (H-4); 6.91 d, 1 H, *J* = 7.7; 7.03 d, 1 H, *J* = 7.7; 7.08–7.20 m, 4 H; 7.20–7.39 m, 9 H; 7.49 dd, 1 H, *J* = 7.7 and 7.7; 7.75 d, 2 H, *J* = 7.1. ^{13}C NMR ($CDCl_3$): 22.55 CH_3, 36.34 CH, 112.30 CH, 120.06 CH, 120.21 CH, 127.24 CH, 128.18 CH, 128.35 CH, 128.61 CH, 128.83 CH, 129.60 C, 129.69 CH, 129.88 CH, 130.63 CH, 132.75 CH, 132.81 C, 132.87 C, 135.78 C, 138.53 CH, 138.97 C, 139.19 C, 150.65 C, 166.84 C, 188.64 CO. The fractions containing enone **2d** were evaporated to dryness to afford an orange solid foam. ^{1}H NMR ($CDCl_3$): 0.72 d, 3 H, *J* = 6.6 (5-$CH(C\mathbf{H}_3)_2$); 1.29 d, 3 H, *J* = 6.6 (5-$CH(C\mathbf{H}_3)_2$); 3.58 h, 1 H, *J* = 6.1 (5-$C\mathbf{H}(CH_3)_2$); 6.62 d, 1 H, *J* = 7.1; 7.07–7.29 m, 6 H; 7.30–7.60 m, 12 H. ^{13}C NMR ($CDCl_3$): 23.38 CH_3, 24.66 CH_3, 30.05 CH, 110.11 CH, 116.04 CH, 118.46 C, 125.86 CH, 128.01 CH, 128.28 CH, 128.60 CH, 128.72 CH, 129.16 CH, 129.45 CH, 130.08 CH, 130.79 CH, 132.99 CH, 135.00 C, 138.36 C, 140.08 C, 144.67 C, 146.00 C, 148.29 C, 148.97 C, 191.74 CO. Yields and other characteristics of compounds **2d** and **3d** are given in Tables II and III.

(Z)-3-(5-Butyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-1,3-diphenylprop-2-en-1-one (**2e**): The reaction was started from perchlorate **1e** (680 mg, 1.26 mmol). Crystallization of the crude product from methanol afforded yellow crystals of enone **2e**. ^{1}H NMR ($CDCl_3$): 0.76 t, 3 H, *J* = 7.1 (5-$CH_2CH_2CH_2C\mathbf{H}_3$); 1.10–1.34 m, 2 H (5-$CH_2CH_2C\mathbf{H}_2CH_3$); 1.34–1.52 m, 1 H (5-$CH_2C\mathbf{H}_2CH_2CH_3$); 1.52–1.72 m, 1 H (5-$CH_2C\mathbf{H}_2CH_2CH_3$); 2.56 dt, 1 H, *J* = 4.9 and 5.5 (5-$C\mathbf{H}_2CH_2CH_2CH_3$); 3.10 dt, 1 H, *J* = 5.3 and 5.5 (5-$C\mathbf{H}_2CH_2CH_2CH_3$); 6.54 d, 1 H, *J* = 6.6; 7.07–7.28 m, 6 H; 7.30–7.59 m, 12 H. ^{13}C NMR ($CDCl_3$): 14.37 CH_3, 22.96 CH_2, 32.24 CH_2, 32.67 CH_2, 111.64 CH, 116.15 CH, 118.59 C, 125.67 CH, 128.09 CH, 128.26 CH, 128.57 CH, 128.71 CH, 128.78 CH, 129.02 CH, 129.92 CH, 130.11 CH, 130.78 CH, 133.01 CH, 134.97 C, 138.47 C, 140.88 C, 142.01 C, 144.84 C, 148.00 C, 191.96 CO (one C signal was overlapped). Yield and other characteristics of compound **2e** are given in Table II.

(Z)-3-(5-tert-Butyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-1,3-diphenylprop-2-en-1-one (**2f**) *and [1-(6-tert-butylpyridin-2-yl)-3,5-diphenyl-1H-pyrrol-2-yl](phenyl)methanone* (**3f**): The reaction was started from perchlorate **1f** (3 g, 5.54 mmol). The crude reaction mixture was chromatographed on a column (silica gel 80 g, dichloromethane–ethanol as an eluent, concentration gradient was 1% of ethanol per 100 ml of eluent). Less polar fractions contained pyrrole derivative **3f** which was recrystallized from ethanol affording light yellow crystals. ^{1}H NMR ($CDCl_3$): 1.15 s, 9 H (6′-C(C**H**$_3$)$_3$); 6.59 s, 1 H (H-4); 6.85 d, 1 H, *J* = 7.9; 7.05–7.33 m, 14 H; 7.49 dd, 1 H, *J* = 7.7 and 7.7; 7.73 d, 2 H, *J* = 7.3. ^{13}C NMR ($CDCl_3$): 29.63 CH_3, 37.33 C, 111.34 CH, 117.46 CH, 118.89 CH, 126.41 CH, 127.30 CH, 127.56 CH, 127.81 CH, 128.01 CH, 128.88 CH, 129.03 CH, 129.90 CH, 131.64 C, 132.00 CH, 132.17 C, 134.92 C, 137.52 CH, 137.86 C, 138.33 C, 149.93 C, 168.87 C, 188.73 CO (one C signal was overlapped). More polar fractions were evaporated to dryness affording 95% (HPLC) pure orange compound **2f** (because of its photoisomerization the pure **2f** could not be isolated). ^{1}H NMR ($CDCl_3$): 1.28 s, 9 H (5-C(C**H**$_3$)$_3$); 6.91 dd, 1 H, *J* = 7.7 and 1.1; 6.98–7.09 m, 3 H; 7.10–7.54 m, 14 H; 7.64 dd, 1 H, *J* = 8.8 and 1.1. ^{13}C NMR ($CDCl_3$): 31.31 CH_3, 36.81 C, 112.70 CH, 116.92 CH, 120.94 C, 124.52 CH, 127.22 CH, 127.78 CH, 128.04 CH, 128.77 CH, 129.09 CH, 130.02 CH, 132.23 CH, 135.37 C, 138.40 C, 140.56 C, 146.45 C, 146.65 C, 149.87 C, 149.99 C, 189.09 CO (three CH signals were overlapped). Yields and other characteristics of compounds **2f** and **3f** are given in Tables II and III.

Ferricyanide Oxidation of Perchlorates **4a**–**4g**. General Procedure

A solution of potassium ferricyanide (4.25 g, 12.9 mmol) and potassium hydroxide (965 mg, 17.2 mmol) in water (20 ml) was added to a boiling solution of perchlorate **4a**–**4g** (2.15 mmol) in ethanol (50 ml). After 1 h reflux, the reaction mixture was poured into cold water (200 ml) and extracted with 4 × 30 ml of dichloromethane. The collected organic extracts were dried with sodium sulfate and evaporated. The crude reaction mixture was chromatographed on a column.

(Z)-4,4-Dimethyl-1-phenyl-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)-pent-2-en-1-one (**5a**) *and [3-tert-butyl-1-(pyridin-2-yl)-5-phenyl-1H-pyrrol-2-yl](phenyl)methanone* (**6a**): The crude reaction mixture was chromatographed on a column (silica gel 40 g, dichloromethane as an eluent). Less polar fractions contained pyrrole derivative **6a** which was recrystallized from heptane affording yellow crystals. ^{1}H NMR ($CDCl_3$): 1.37 s, 9 H (3-C(C**H**$_3$)$_3$); 6.46 s, 1 H (H-4); 6.71 d, 1 H, *J* = 7.7; 6.82 dd, 1 H, *J* = 7.1 and 2.2; 7.06–7.32 m, 9 H; 7.52 d, 2 H, *J* = 7.1; 8.13 dd, 1 H, *J* = 5.0 and 1.7. ^{13}C NMR ($CDCl_3$): 31.61 C, 31.66 CH_3, 110.70 CH, 121.55 CH, 121.95 CH, 126.97 CH, 128.17 CH, 128.47 CH, 129.03 CH, 129.37 C, 132.02 CH, 132.50 C, 133.65 C, 137.04 CH, 139.03 C, 140.02 C, 148.53 CH, 151.13 C, 193.13 C (one CH signal was overlapped). More polar fractions were evaporated and the residue was crystallized from ethanol affording yellow crystals of enone **5a**. ^{1}H NMR ($CDCl_3$): 1.07 s, 9 H (3′-C(C**H**$_3$)$_3$); 6.74 dd, 1 H, *J* = 6.6 and 6.6; 7.12–7.36 m, 4 H; 7.39–7.57 m, 3 H; 7.63 d, 2 H, *J* = 8.8; 7.72 d, 2 H, *J* = 8.2; 7.82 d, 1 H, *J* = 6.6; 7.88 d, 2 H, *J* = 8.2. ^{13}C NMR ($CDCl_3$): 29.50 CH_3, 40.49 C, 111.70 CH, 117.32 CH, 117.74 C, 124.68 CH, 127.48 CH, 128.14 CH, 128.24 CH, 128.67 CH, 129.71 CH, 133.11 CH, 135.58 C, 137.70 C, 142.08 C, 144.98 C, 154.00 C, 190.35 CO (one CH signal was overlapped). Yields and other characteristics of compounds **5a** and **6a**, see Tables II and III.

(Z)-4,4-Dimethyl-3-(5-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-1-phenylpent-2-en-1-one (**5b**) *and [3-tert-butyl-1-(6-methylpyridin-2-yl)-5-phenyl-1H-pyrrol-2-yl](phenyl)methanone* (**6b**): The

crude reaction mixture was chromatographed on a column (silica gel 40 g, dichloromethane–ethanol as an eluent, concentration gradient was 1% of ethanol per 100 ml of eluent). Less polar fractions contained pyrrole derivative **6b** which was recrystallized from heptane affording yellow crystals. ^{1}H NMR ($CDCl_3$): 1.37 s, 9 H (3-C(C**H**$_3$)$_3$); 2.23 s, 3 H (6′-C**H**$_3$); 6.46 d, 2 H, *J* = 6.0; 6.63 d, 1 H, *J* = 7.7; 7.07–7.30 m, 9 H; 7.54 d, 2 H, *J* = 7.1. ^{13}C NMR ($CDCl_3$): 23.50 CH_3, 31.85 C, 31.94 CH_3, 111.13 CH, 118.62 CH, 120.88 CH, 127.15 CH, 127.88 CH, 128.37 CH, 128.81 CH, 128.98 CH, 129.43 C, 132.05 CH, 132.98 C, 133.38 C, 137.50 CH, 139.00 C, 140.40 C, 150.43 C, 157.88 C, 193.31 CO. More polar fractions were evaporated and residue was crystallized from acetone–heptane affording yellow crystals of enone **5b**. ^{1}H NMR ($CDCl_3$): 0.92 s, 9 H (3′-C(C**H**$_3$)$_3$); 2.67 s, 3 H (5-C**H**$_3$); 6.53 d, 1 H, *J* = 7.1; 7.10 dd, 1 H, *J* = 7.1 and 6.6; 7.17–7.27 m, 3 H; 7.46–7.63 m, 6 H; 7.65 s, 1 H (H-2′); 7.98 d, 2 H, *J* = 7.1. ^{13}C NMR ($CDCl_3$): 20.86 CH_3, 30.15 CH_3, 40.92 C, 113.85 CH, 115.91 CH, 119.04 C, 124.60 CH, 127.54 CH, 128.12 CH, 128.65 CH, 129.05 CH, 129.39 CH, 130.11 CH, 133.46 CH, 136.23 C, 136.67 C, 138.31 C, 141.58 C, 146.65 C, 158.25 C, 190.71 CO. Yields and other characteristics of compounds **5b** and **6b** are given in Tables II and III.

(Z)-3-(5-Ethyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-4,4-dimethyl-1-phenylpent-2-en-1-one (**5c**) *and [3-tert-butyl-1-(6-ethylpyridin-2-yl)-5-phenyl-1H-pyrrol-2-yl](phenyl)methanone* (**6c**): The reaction was started from perchlorate **4c** (900 mg, 1.83 mmol). The crude reaction mixture was chromatographed on a column (silica gel 60 g, dichloromethane–ethanol as an eluent, concentration gradient was 1% of ethanol per 100 ml of eluent). Less polar fractions contained pyrrole derivative **6c** which was recrystallized from heptane affording light yellow crystals. ^{1}H NMR ($CDCl_3$): 1.01 t, 3 H, *J* = 7.7 (6′-CH_2C**H**$_3$); 1.35 s, 9 H (3-C(C**H**$_3$)$_3$); 2.51 q, 2 H, *J* = 7.7 (6′-C**H**$_2$$CH_3$); 6.44 s, 1 H (H-4); 6.51 d, 1 H, *J* = 8.2; 6.67 d, 1 H, *J* = 7.7; 7.06–7.32 m, 9 H; 7.56 d, 2 H, *J* = 7.7. ^{13}C NMR ($CDCl_3$): 12.76 CH_3, 30.38 CH_2, 31.62 C, 31.76 CH_3, 110.75 CH, 118.77 CH, 119.60 CH, 126.84 CH, 127.67 CH, 128.11 CH, 128.56 CH, 129.15 CH, 131.85 CH, 132.81 C, 133.34 C, 137.40 CH, 138.43 C, 139.85 C, 150.32 C, 162.74 C, 193.08 CO (one C signal was overlapped). More polar fractions were evaporated affording yellow powder of enone **5c**. ^{1}H NMR ($CDCl_3$): 0.95 s, 9 H (3′-C(C**H**$_3$)$_3$); 1.37 t, 3 H (5-CH_2C**H**$_3$); 2.91 dq, 1 H, *J* = 7.2 and 9.9 (5-C**H**$_2$$CH_3$); 3.27 dq, 1 H, *J* = 7.7 and 9.9 (5-C**H**$_2$$CH_3$); 6.63 d, 1 H, *J* = 6.6; 7.06–7.24 m, 4 H; 7.40–7.66 m, 7 H; 7.97 d, 2 H *J* = 7.7. ^{13}C NMR ($CDCl_3$): 11.28 CH_3, 24.55 CH_2, 29.89 CH_3, 40.79 C, 109.66 CH, 115.49 CH, 119.24 C, 124.32 CH, 127.83 CH, 128.38 CH, 128.78 CH, 129.23 CH, 129.40 CH, 129.88 CH, 133.16 CH, 135.87 C, 136.43 C, 138.16 C, 142.12 C, 146.34 C, 158.62 C, 190.38 CO. Yields and other characteristics of compounds **5c** and **6c** are given in Tables II and III.

(Z)-3-(5-Isopropyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-4,4-dimethyl-1-phenylpent-2-en-1-one (**5d**) *and [3-tert-butyl-1-(6-isopropylpyridin-2-yl)-5-phenyl-1H-pyrrol-2-yl](phenyl)methanone* (**6d**): The crude reaction mixture was chromatographed on a column (silica gel 60 g, dichloromethane–ethanol as an eluent, concentration gradient was 1% of ethanol per 100 ml of eluent). The less polar fractions contained pyrrole derivative **6d** which was recrystallized from heptane affording light yellow crystals. ^{1}H NMR ($CDCl_3$): 0.98 d, 2 H, *J* = 7.1 (6′-CH(C**H**$_3$)$_2$); 1.34 s, 9 H (3-C(C**H**$_3$)$_3$); 2.74 h, 1 H, *J* = 6.6 (6′-C**H**$(CH_3)_2$); 6.45 s, 1 H (H-4); 6.57 d, 1 H, *J* = 7.7; 6.71 d, 1 H, *J* = 7.7; 7.09–7.33 m, 9 H; 7.60 d, 2 H, *J* = 7.1. ^{13}C NMR ($CDCl_3$): 21.72 CH_3, 31.65 C, 31.79 CH_3, 35.59 CH, 110.56 CH, 118.39 CH, 119.02 CH, 126.76 CH, 127.72 CH, 128.08 CH, 128.57 CH, 129.22 C, 129.52 CH, 132.15 CH, 132.94 C, 133.65 C, 137.48 CH, 138.19 C, 139.73 C, 150.32 C, 166.69 C, 193.12 CO. The more polar fractions were evaporated and the residue was crystallized from methanol affording orange

crystals of enone **5d**. ^{1}H NMR ($CDCl_3$): 0.95 s, 9 H (3′-C(C**H**$_3$)$_3$); 1.17 d, 3 H, *J* = 6.6 (5-CH(C**H**$_3$)$_2$); 1.38 d, 3 H, *J* = 6.6 (5-CH(C**H**$_3$)$_2$); 3.74 qq, 1 H, *J* = 7.1 and 6.6 (5-C**H**(CH$_3$)$_2$); 6.69 d, 1 H, *J* = 7.1; 7.14–7.30 m, 4 H; 7.46–7.66 m, 7 H; 7.95 d, 2 H, *J* = 7.1. ^{13}C NMR ($CDCl_3$): 22.94 CH_3, 24.65 CH_3, 29.31 CH, 30.27 CH_3, 41.01 C, 109.41 CH, 115.57 CH, 119.09 C, 124.41 CH, 127.47 CH, 127.90 CH, 128.22 CH, 128.34 CH, 128.83 CH, 129.37 CH, 133.01 CH, 135.95 C, 138.78 C, 141.18 C, 146.77 C, 148.03 C, 159.27 C, 189.55 CO. Yields and other characteristics of compounds **5d** and **6d**, see Tables II and III.

(Z)-3-(5-Butyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-4,4-dimethyl-1-phenylpent-2-en-1-one (**5e**) *and [1-(6-butylpyridin-2-yl)-3-tert-butyl-5-phenyl-1H-pyrrol-2-yl](phenyl)methanone* (**6e**): The crude reaction mixture was chromatographed on column (silica gel 60 g, dichloromethane–ethanol as an eluent, concentration gradient was 1% of ethanol per 100 ml of eluent). Less polar fractions contained pyrrole derivative **6e** which was recrystallized from methanol affording yellow crystals. ^{1}H NMR ($CDCl_3$): 0.85 t, 3 H, *J* = 7.1 (6′-$CH_2CH_2CH_2C$**H**$_3$); 1.16 tq, 2 H, *J* = 7.7 and 7.7 (6′-CH_2CH_2C**H**$_2CH_3$); 1.30–1.44 m, 11 H (6′-$CH_2CH_2CH_2C$**H**$_3$ and 3-C(CH$_3$)$_3$); 2.46 t, 2 H, *J* = 7.7 (6′-C**H**$_2CH_2CH_2CH_3$); 6.44 s, 1 H (H-4); 6.55 d, 1 H, *J* = 7.7; 6.67 d, 1 H, *J* = 7.7; 7.07–7.24 m, 8 H; 7.29 dd, 1 H, *J* = 7.7 and 7.1; 7.59 d, 2 H, *J* = 7.1. ^{13}C NMR ($CDCl_3$): 13.71 CH_3, 22.21 CH_2, 30.92 CH_2, 31.64 C, 31.78 CH_3, 37.18 CH_2, 110.68 CH, 118.87 CH, 120.36 CH, 126.81 CH, 127.72 CH, 128.11 CH, 128.55 CH, 129.21 C, 129.32 CH, 132.11 CH, 132.85 C, 133.52 C, 137.29 CH, 138.26 C, 139.85 C, 150.48 C, 161.90 C, 193.19 CO. More polar fractions were evaporated to dryness affording yellow crystals of enone **5e**. ^{1}H NMR ($CDCl_3$): 0.80–0.96 m, 9 H (3′-C(C**H**$_3$)$_3$ and 5-$CH_2CH_2CH_2C$**H**$_3$); 1.24–1.48 m, 2 H (5-CH_2CH_2C**H**$_2CH_3$); 1.64–1.84 m, 2 H (5-CH_2C**H**$_2CH_2CH_3$); 2.85 dt, 1 H, *J* = 5.5 and 4.9 (5-C**H**$_2CH_2CH_2CH_3$); 3.25 dt, 1 H, *J* = 5.5 and 4.9 (5-C**H**$_2CH_2CH_2CH_3$); 6.62 d, 1 H, *J* = 7.1; 7.10–7.28 m, 4 H; 7.46–7.66 m, 7 H; 7.97 d, 2 H, *J* = 7.1. ^{13}C NMR ($CDCl_3$): 13.76 CH_3, 22.36 CH_2, 29.31 CH_2, 30.01 CH_3, 31.46 CH_2, 40.86 C, 110.29 CH, 115.44 CH, 119.18 C, 124.27 CH, 127.40 CH, 127.83 CH, 128.35 CH, 128.79 CH, 129.16 CH, 129.24 CH, 133.14 CH, 135.88 C, 138.28 C, 141.05 C, 141.14 C, 146.41 C, 158.80 C, 190.21 CO. Yields and other characteristics of compounds **5e** and **6e** are given in Tables II and III.

[3-tert-Butyl-1-(6-butylpyridin-2-yl)-5-phenyl-1H-pyrrol-2-yl](phenyl)methanone (**6f**): The reaction was started from perchlorate **4f** (100 mg, 0.19 mmol). The crude reaction mixture was chromatographed using preparative TLC (11 g of silica gel, dichloromethane as an eluent). Yellow zone was extracted with acetone–dichloromethane and afforded light yellow pyrrole derivative **6f**. ^{1}H NMR ($CDCl_3$): 1.03 s, 9 H (6′-C(C**H**$_3$)$_3$); 1.34 s, 9 H (3-C(C**H**$_3$)$_3$); 6.45 s, 1 H (H-4); 6.61 d, 1 H, *J* = 8.8; 6.88 d, 1 H, *J* = 7.1; 7.07–7.34 m, 9 H; 7.60 d, 2 H, *J* = 7.1. ^{13}C NMR ($CDCl_3$): 29.43 CH_3, 31.63 C, 31.79 CH_3, 37.25 C, 110.30 CH, 116.88 CH, 118.82 CH, 126.65 CH, 127.72 CH, 128.01 CH, 128.53 CH, 129.19 C, 129.69 CH, 132.21 CH, 133.05 C, 133.91 C, 137.38 CH, 138.07 C, 139.57 C, 149.88 C, 168.85 C, 193.04 CO. Yield and other characteristics of compound **6f** are given in Table III.

(Z)-3-(2,5-Diphenylimidazo[1,2-a]pyridin-3-yl)-4,4-dimethyl-1-phenylpent-2-en-1-one (**5g**) *and [3-tert-butyl-1-[6-phenylpyridin-2-yl]-5-phenyl-1H-pyrrol-2-yl](phenyl)methanone* (**6g**): The reaction was started from perchlorate **4g** (3 g, 5.54 mmol). The crude reaction mixture was chromatographed on a column (silica gel 140 g, dichloromethane–ethanol as an eluent, concentration gradient was 1% of ethanol per 100 ml of eluent). Less polar fractions contained pyrrole derivative **6g** which was recrystallized from heptane affording light yellow crystals. ^{1}H NMR ($CDCl_3$): 1.38 s, 9 H (3-C(C**H**$_3$)$_3$); 6.47 s, 1 H (H-4); 6.57 dt, 1 H, *J* = 2.8 and 5.5; 7.08–7.42 m, 13 H; 7.57 d, 2 H, *J* = 7.1; 7.67 dd, 2 H, *J* = 2.2 and 7.7. ^{13}C NMR ($CDCl_3$): 31.76 C, 31.91 CH_3, 110.99 CH, 117.24 CH, 119.52 CH, 126.67 CH, 126.94 CH, 127.74 CH,

128.18 CH, 128.57 CH, 128.61 CH, 128.92 C, 129.19 CH, 132.05 CH, 132.70 C, 133.07 C, 137.64 C, 137.82 CH, 138.11 C, 139.73 C, 150.48 C, 155.88 C, 193.10 CO. More polar fractions were evaporated to dryness affording yellow crystals of enone **5g**. ^{1}H NMR ($CDCl_3$): 0.51 s, 9 H (3′-C(C**H**$_3$)$_3$); 6.59 dd, 1 H, *J* = 7.1 and 1.1; 6.91 brs, 1 H; 7.10–7.65 m, 14 H; 7.71 dd, 1 H, *J* = 7.1 and 1.1; 7.87 d, 2 H, *J* = 6.6. ^{13}C NMR ($CDCl_3$): 29.84 CH_3, 40.67 C, 116.37 CH, 116.99 CH, 120.61 C, 123.84 CH, 127.40 CH, 127.72 CH, 128.16 CH, 128.25 CH, 128.65 CH, 129.20 CH, 129.23 CH, 132.81 CH, 135.02 C, 135.48 C, 139.03 C, 139.22 C, 141.68 C, 146.52 C, 177.04 C, 189.81 CO (two CH signals were overlapped). Yields and other characteristics of compounds **5g** and **6g**, see Tables II and III.

6-Substituted 2-Aminopyridines **7d**–**7f**

Compounds **7d**–**7f** were obtained using described[7] procedure and exhibited ^{1}H NMR spectra comparable with publicated data[7,12].

2-Amino-6-isopropylpyridine (**7d**): Yield 62% of colorless oil. B.p. 65–70 °C/1.7 Torr. ^{1}H NMR ($CDCl_3$): 1.22 d, 6 H, *J* = 6.6 (6-CH(C**H**$_3$)$_2$); 2.83 h, 1 H, *J* = 6.6 (6-C**H**(CH$_3$)$_2$); 4.52 brs, 2 H (2-N**H**$_2$); 6.29 d, 1 H, *J* = 8.2 (H-5); 6.51 d, 1 H, *J* = 7.1 (H-3); 7.33 dd, 1 H, *J* = 7.7 and 7.8 (H-4).

2-Amino-6-butylpyridine (**7e**): Yield 51% of colorless oil. B.p. 90 °C/1.8 Torr. ^{1}H NMR ($CDCl_3$): 0.92 t, 3 H, *J* = 7.7 (6-CH$_2$CH$_2$CH$_2$C**H**$_3$); 1.36 tq, 2 H, *J* = 7.7 and 7.2 (6-CH$_2$CH$_2$C**H**$_2$CH$_3$); 1.64 tt, 2 H, *J* = 7.7 and 7.7 (6-CH$_2$C**H**$_2$CH$_2$CH$_3$); 2.59 t, 2 H, *J* = 7.7 (6-C**H**$_2$CH$_2$CH$_2$CH$_3$); 4.52 brs, 2 H (2-N**H**$_2$); 6.30 d, 1 H, *J* = 8.2 (H-5); 6.48 d, 1 H, *J* = 7.1 (H-3); 7.33 dd, 1 H, *J* = 7.7 and 7.7 (H-4).

2-Amino-6-tert-butylpyridine (**7f**): Yield 57% of colorless oil. B.p. 67.5–68 °C/2 Torr. ^{1}H NMR ($CDCl_3$): 1.30 s, 9 H (6-C(C**H**$_3$)$_3$); 4.53 brs, 2 H (2-N**H**$_2$); 6.30 d, 1 H, *J* = 8.2 (H-5); 6.67 d, 1 H, *J* = 7.7 (H-3); 7.35 dd, 1 H, *J* = 7.7 and 8.2 (H-4).

6-Substituted 2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)pyridines **8d**–**8f**

To a stirred solution of 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine[6] (**8a**) (5 g, 29 mmol) in absolute ether (60 ml) was added at –60 °C a hexane or ethereal solution of alkyllithium (32 mmol). The mixture was allowed to slowly warm up to the ambient temperature (aproximately 5 h), stirred overnight and then dry oxygen was bubbled through for 24 h. The resulting mixture was poured into water (250 ml), extracted with 5 × 50 ml of ether and the collected organic extracts dried with sodium sulfate were evaporated. The residue was subjected to a column chromatography (200 g of silica gel, toluene–ethyl acetate as an eluent, concentration gradient was 1% of ethyl acetate per 70 ml of eluent) affording the crude products as pale yellow oils exhibiting spectra comparable with literature data[7,12].

6-Isopropyl-2-(2,5-dimethyl-1H-pyrrol-1-yl)pyridine (**8d**): Yield 56%. ^{1}H NMR ($CDCl_3$): 1.31 d, 6 H, *J* = 7.0 (6-CH(C**H**$_3$)$_2$); 2.15 s, 6 H (2′- and 5′-CH_3); 3.09 h, 1 H, *J* = 7.0 (6-C**H**(CH$_3$)$_2$); 5.89 s, 2 H (H-3′ and H-4′); 7.00 d, 1 H, *J* = 8.3 (H-5); 7.14 d, 1 H, *J* = 7.7 (H-3); 7.71 dd, 1 H, *J* = 7.7 and 7.7 (H-4).

6-Butyl-2-(2,5-dimethyl-1H-pyrrol-1-yl)pyridine (**8e**): Yield 45%. ^{1}H NMR ($CDCl_3$): 0.94 t, 3 H, *J* = 7.7 (6-CH$_2$CH$_2$CH$_2$C**H**$_3$); 1.38 tq, 2 H, *J* = 7.1 and 7.7 (6-CH$_2$CH$_2$C**H**$_2$CH$_3$); 1.74 tt, 2 H, *J* = 7.1 and 7.7 (6-CH$_2$C**H**$_2$CH$_2$CH$_3$); 2.15 s, 6 H (2′- and 5′-CH_3); 2.82 t, 2 H, *J* = 7.7 (6-C**H**$_2$CH$_2$CH$_2$CH$_3$); 5.88 s, 2 H, (H-3′ and H-4′); 7.02 d, 1 H, *J* = 7.7 (H-5); 7.15 d, 1 H, *J* = 7.7 (H-3); 7.70 dd, 1 H, *J* = 7.7 and 7.7 (H-4).

6-tert-Butyl-2-(2,5-dimethyl-1H-pyrrol-1-yl)pyridine (**8f**): Yield 55%. ^{1}H NMR ($CDCl_3$): 1.39 s, 9 H (6-C(C**H**$_3$)$_3$); 2.19 s, 6 H (2′- and 5′-CH_3); 5.93 s, 2 H (H-3′ and H-4′); 7.01 d, 1 H, *J* = 7.1 (H-5); 7.31 d, 1 H, *J* = 7.1 (H-3); 7.73 dd, 1 H, *J* = 7.7 and 7.7 (H-4).

CALCULATIONS

To express proper theoretical characteristics of the PM3 models of radical open-shell systems *a*-**12a**, *s*-**12a**, **12b**, **15b** and **16b**, the PECI-procedure[9] involving a part of correlation effects was used. On the other hand, the standard PM3 method[15] was applied for the calculation of the closed shell cation **16b**. In all cases, the molecular geometries were optimized with respect to all degrees of freedom. For those purposes, the program VAMP (ref.[16]) was used with the NLLSQ optimizer and the size of configuration interaction equal 3 for the mentioned radical species.

The work was supported by the Grant Agency of the Czech Republic (grant No. 203/96/0497). All elemental analyses were performed in the Central Laboratory of Prague Institute of Chemical Technology (Head of Analytical Division: Dr L. Helešic).

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