# PREPARATION OF NEW ORGANIC LUMINOPHORES BASED ON 3,5-DIACETYLPYRIDINES

Pavel LHOTÁK and †Antonín KURFÜRST

*Department of Organic Chemistry,*
*Prague Institute of Chemical Technology, 166 28 Prague 6*

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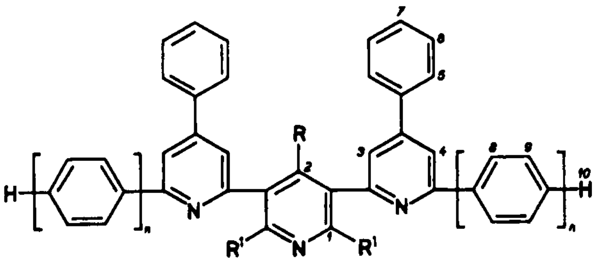
The reaction of acetylacetone or sodium salt of oxymethyleneacetone with corresponding aldehydes has been used to prepare 3,5-diacetyl-1,4-dihydropyridines *III* which have been oxidized to diacetylpyridines *VII*. These compounds have been transformed by an acid-catalyzed reaction with benzaldehyde into the chalcones *VIII* which have been utilized for the Kröhnke synthesis of luminophoric terpyridines *I* and *II*.

2,4,6-Triarylpyridines and polyphenylpyridines are known to exhibit a significant luminescence activity[1]. In the context of our studies of new organic luminophors based on similar systems we have dealt with the synthesis and investigation of properties of the arylpyridines of the types *I* and/or *II*.

The starting 3,5-diacetyl-1,4-dihydropyridines *IIIa* – *IIIf* were obtained by the reaction of 2,5-pentanedione[2 – 4] or sodium salt of hydroxymethyleneacetone[5,6] with the corresponding aldehyde in the presence of $(NH_4)_2CO_3$. The attempts at preparation of dihydropyridines type *IV* from benzoylacetone gave only reaction mixures from which derivatives *V* were isolated. With regard to the fact that in all the cases compound *VI* was found as a coproduct, it is obvious that the reaction pathway is determined by greater reactivity of the corresponding carbonyl group, leading only to dihydropyridines *V*. The structure of these compounds, which have already been prepared in another way[7 – 9], was confirmed by means of MS in which the most intensive peak is that of $Ph\text{-}CO^+$ ($m/z$ = 105), which excludes the isomeric structure *IV*.

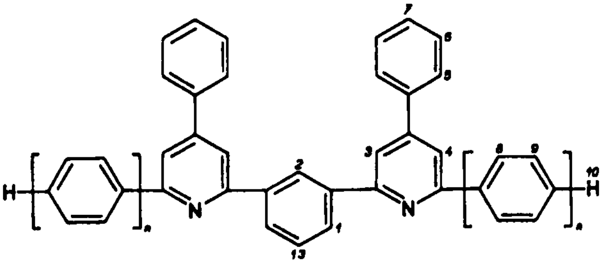
The dihydropyridines *IIIa* – *IIIf* and *Vc* were transformed into the 3,5-diacylpyridine derivatives *VII* by oxidation with nitrous gases[10,11].

The base-catalyzed reaction of the derivatives *VII* with benzaldehyde gave beside the derivatives *VIII* a large amount of polymeric products. On the other hand, satisfactory results were achieved with application of acid catalysis ($H_2SO_4$, see Table I). The attempt at preparation of compound *VIIIa* in the presence of basic alumina led to a reaction mixture from which also monochalcone *IX* was isolated. All the chalcones thus prepared are *E*-isomers ($J_{H,H} \approx 16$ Hz).

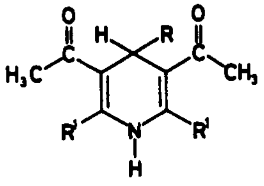


*I*

|  | *a* | *b* | *c* | *d* | *e* | *f* | *g* | *h* |
|---|---|---|---|---|---|---|---|---|
| R | H | H | $CH_3$ | $CH_3$ | Ph | Ph | H | H |
| $R^1$ | H | H | H | H | H | H | $CH_3$ | $CH_3$ |
| *n* | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |

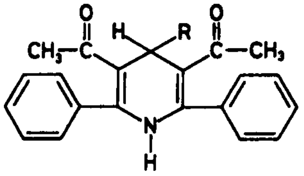


*IIa*, *n* = 1
*IIb*, *n* = 2

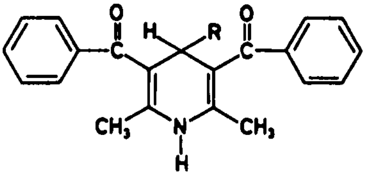


*III*

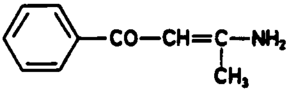
|  | *a* | *b* | *c* | *d* | *e* | *f* |
|---|---|---|---|---|---|---|
| R | H | $CH_3$ | Ph | H | $CH_3$ | Ph |
| $R^1$ | H | H | H | $CH_3$ | $CH_3$ | $CH_3$ |



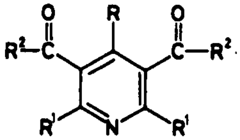
*IV*



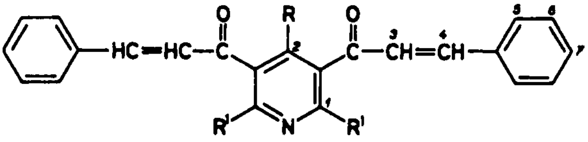
*Va*, R = H
*Vb*, R = $CH_3$
*Vc*, R = Ph



*VI*

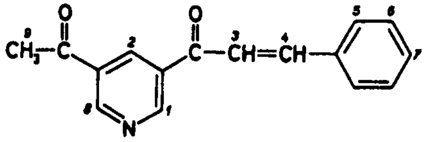


| *VII* | *a* | *b* | *c* | *d* | *e* | *f* | *g* |
|---|---|---|---|---|---|---|---|
| R | H | $CH_3$ | Ph | H | $CH_3$ | Ph | Ph |
| $R^1$ | H | H | H | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ |
| $R^2$ | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ | Ph |



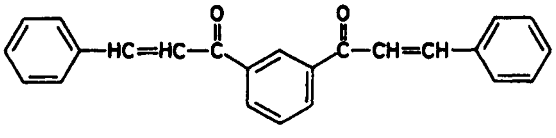
*VIII*

|  | *a* | *b* | *c* | *d* | *e* | *f* |
|---|---|---|---|---|---|---|
| R | H | $CH_3$ | Ph | H | $CH_3$ | Ph |
| $R^1$ | H | H | H | $CH_3$ | $CH_3$ | $CH_3$ |

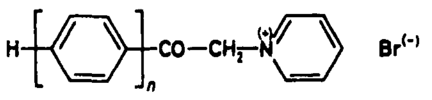


*IX*

The attempts at preparation of chalcones from dihydropyridines *III* resulted in a complex mixture of polymeric compounds. Only the acid-catalyzed reaction of *IIIa* with excess benzaldehyde gave the derivative *VIIIa* as the main product which was formed from the dihydropyridine derivative probably by oxidation to the detriment of excess benzaldehyde.



*X*



*XIa*, $n = 1$
*XIb*, $n = 2$

TABLE I
Reaction conditions of preparation of compounds *VIII*

| Compound | Yield % | Reaction time, days | Recrystallization | M.p., °C |
|---|---|---|---|---|
| *VIIIa* | 48 | 2 | $CHCl_3$–methanol | 214.5 – 215.5 |
| *VIIIb* | 48 | 3 | $C_2H_5OH$–acetone | 156.5 – 158 |
| *VIIIc* | 53 | 1 | methanol | 141 – 143 |
| *VIIId* | 59 | 3 | methanol | 96 – 98.5 |
| *VIIIe*[a] | 82 | 10 h | benzene | 127 – 129 |
| *VIIIf*[b] | 82 | 5 h | 2-propanol | 202.5 – 204 |

[a] The reaction was carried out by 10 h boiling of methanolic solution of diacetylpyridine *VIIe* with a fivefold excess of benzaldehyde in the presence of piperidine as the catalyst; [b] a mixture of 1.1 mmol *VIIf* and 11 mmol benzaldehyde was stirred at room temperature with 10 ml saturated methanolic solution of NaOH.

The derivatives *I* and *II* were prepared by the Kröhnke reaction[1,12] consisting in heating the chalcones *VIIIa*, *VIIIb*, *VIIIc*, *VIIId*, or *X* with the pyridinium salt *XIa* and *XIb* in a mixture of acetic acid and DMF in the presence of ammonium acetate. The reaction conditions are summarized in Table II. The compounds *IIa* and *IIb* probably exhibit the properties of liquid crystals manifested by very indistinct (*IIa*) or double melting temperature (*IIb*). The luminescence properties of compounds *I* and *II* will be discussed in the next communication.

The structure of the substances newly prepared was determined by means of NMR spectroscopy (Tables III and IV) and elemental analysis (Table V). The $^1$H NMR spectra of compounds *I* exhibit signals of pyridine protons H1, H2 with downfield shifts as compared with the rest of the molecule. The biphenyl skeleton is characterized by the subspectra of AA'XX' or AA'BB' type (the derivatives *Ib*, *Id*, *If*, *Ih*, and *IIb*), the chemical shift of the individual protons H8–H13 being inverse proportional to the distance from the pyridine nucleus (Table IV). The chemical shift of the protons H3 and H4 depends very much on the substitution of the central pyridine nucleus ($R^1$). With the compounds *Ie*, *If* the H3 signal is markedly shifted upfield due to magnetic anisotropy of phenyl nucleus at 4 position ( $\delta \approx 7.10$ ppm as compared with 8.62 ppm for the derivative *Ia*). The precise assignment of signals was carried out with the help of the 2D COSY experiments.

TABLE II
Reaction conditions of preparation of compounds *I* and *II*

| Compound | Starting compounds | | Reaction time, h | Yield, % | M.p., °C |
|---|---|---|---|---|---|
| | Chalcone | Pyr. salt | | | |
| *Ia* | *VIIIa* | *XIa* | 7 | 48 | 267 – 268[a] |
| *Ib* | *VIIIa* | *XIb* | 7 | 39 | 297 – 298[a] |
| *Ic* | *VIIIb* | *XIa* | 8 | 36 | 283 – 285[b] |
| *Id* | *VIIIb* | *XIb* | 5 | 38 | 285 – 287[a] |
| *Ie* | *VIIIc* | *XIa* | 10 | 45 | 216 – 218.5[c] |
| *If* | *VIIIc* | *XIb* | 9 | 27 | 162 – 165[c] |
| *Ig* | *VIIId* | *XIa* | 20 | 24 | 174 – 176[d] |
| *Ih* | *VIIId* | *XIb* | 20 | 37 | 163 – 165[c] |
| *IIa* | *X* | *XIa* | 10 | 34 | 162 – 173[a] |
| *IIb* | *X* | *XIb* | 10 | 27 | 139 – 141/244 – 247[e] |

[a] Chloroform–methanol; [b] dioxane; [c] acetone–ethanol; [d] methanol; [e] acetone–methanol.

## EXPERIMENTAL

The melting points were estimated with the use of a Boetius apparatus and are not corrected. The IR spectra were measured with a Perkin–Elmer 325 spectrometer. The $^1$H NMR spectra were measured with a Bruker AM 400 apparatus (400 MHz) with tetramethylsilane as the internal standard ($\delta$ = 0.00 ppm). The mass spectra were measured by the method of field desorption and method of chemical ionization using a JEOL DX 303/DA 5000 apparatus.

The purity of the substances synthetized and the course of reactions were monitored by TLC using the Silufol and Alufol plates (Kavalier, Sázava). The detection was carried out by means of $I_2$ vapours or UV light.

### General Procedure of Preparation of Dihydropyridines *Va* – *Vc*

A solution of 6 mmol benzoylacetone and 3 g ammonium carbonate in 100 ml aqueous ethanol (1:1) was treated with 3 mmol respective aldehyde, and the mixture was stirred at room temperature 20 – 27 h. The separated solid was collected by suction and recrystallized from aqueous ethanol.

Compound, yield, m.p. (literature): *Va*, 27%, 193 – 194 °C ( ref.[9] 195 – 200 °C); *Vb*, 9%, 251 – 253 °C (ref.[7] 238 – 239 °C); *Vc*, 27%, 229 – 231 °C (ref.[8] 222 °C). The mother liquors of *Vc* were concentrated to give white crystalline *VI*, m.p. 144 – 144.5 °C (ref.[8] 143 °C).

TABLE III
$^1$H NMR spectra of chalcones *VIIIa* – *VIIIf* and *IX* in $CDCl_3$ with TMS as the internal standard

| Compound | δ, ppm/*J*, Hz | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6,7 | $R^1$ | R |
| *VIIIa* | 9.41 d<br>2.14 | 8.84 t<br>2.16 | 7.55 d<br>15.67 | 7.91 d<br>15.67 | 7.70 m | 7.47 m | – | – |
| *VIIIa*[a] | 9.55 d<br>1.94 | 9.02 t<br>1.77 | 7.87 d<br>15.64 | 8.05 d<br>15.62 | 7.96 m | 7.50 m | – | – |
| *VIIIb* | 8.47 s | – | 7.12 d<br>16.12 | 7.47 m | 7.58 m | 7.44 m | – | 2.46 s ($CH_3$) |
| *VIIIc* | 8.91 s | – | 6.49 d<br>16.03 | 7.22 – 7.34 m | | | – | 7.22 – 7.34 m (Ph) |
| *VIIId* | – | 7.91 s | 7.13 d<br>16.05 | 7.51 d<br>16.08 | 7.57 m | 7.41 m | 2.72 s | |
| *VIIIe* | – | – | 6.98 d | 7.25 d<br>16.34 | 7.55 m | 7.43 m | 2.50 s | 2.13 s ($CH_3$) |
| *VIIIf* | – | – | 6.51 d<br>16.24 | 7.08 d<br>16.25 | 7.32 m | 7.32 m | 2.59 s | 7.17 m (Ph) |

[a] Measured in $(CD_3)_2SO$.

TABLE IV

$^1$H NMR spectra of terpyridines *Ia* – *Ih* and bipyridines *IIa*, *IIb* in $CDCl_3$ with TMS as the internal standard

| Compound | δ, ppm/*J*, Hz | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6,7 | 8 | 9 (10) | 11[a] | 12[a] | 13[a] |
| *IIa*[b] | 8.30 d (d) | 9.01 t | 8.01 d | 7.93 d | 7.79 d | 7.51 m | 8.26 d | 7.51 m | – | – | – |
| | 7.71 | | | | | | | | | | |
| | 1.78 | 1.80 | 1.36 | 1.37 | 7.02 | | 7.11 | | | | |
| *IIb*[c] | 8.29 d (d) | 9.08 s | 8.00 d | 7.96 d | 7.78 d | 7.53 m | 8.35 d | 7.76 d | 7.67 m | 7.45 t | 7.37 t |
| | 7.74 | | | | | | | | | | |
| | 1.65 | | 0.96 | 1.01 | 8.13 | | 8.33 | 8.50 | | 7.78 | 7.26 |
| *Ia*[d] | 9.74 d | 9.68 d | 8.62 s | 8.42 s | 8.18 d | 7.59 m | 8.52 d | 7.59 m | – | – | – |
| | 1.98 | 1.98 | | | 7.06 | | 7.26 | | | | |
| *Ib*[e] | 9.57 s | 9.57 s | 8.50 s | 8.37 s | 8.11 d | 7.60 m | 8.55 d | 7.90 d | 7.78 d | 7.49 m | 7.40 m |
| | | | | | 6.53 | | 7.62 | 7.39 | 7.36 | | |
| *Ic*[f] | 8.87 d | – | 8.00 d | 7.53 s | 7.84 d | 7.51 m | 8.23 d | 7.51 m | – | – | – |
| | 1.20 | | 1.20 | | 7.23 | | 7.35 | | | | |
| *Id*[e,g] | 8.82 s | – | 8.03 d | 7.69 d | 7.79 d | 7.55 m | 8.23 d | 7.75 d | 7.67 d | 7.47 m | 7.38 t |
| | | | 1.48 | 1.53 | 6.93 | | 8.42 | 8.41 | 7.04 | | 7.35 |
| *Ie*[h] | 9.19 s | – | 7.10 d | 7.80 d | 7.31 d | 7.41 m | 8.00 d | 7.47 m | – | – | – |
| | | | 1.45 | 1.45 | 7.75 | | 6.81 | | | | |
| *If*[i] | 9.20 s | – | 7.11 d | 7.83 d | 7.33 d | 7.40 m | 8.07 d | 7.73 d | 7.67 d | 7.46 m | 7.37 m |
| | | | 1.38 | 1.38 | 7.78 | | 8.45 | 8.45 | 8.44 | | |
| *Ig*[j] | – | 8.08 s | 7.93 d | 7.64 d | 7.72 d | 7.48 m | 8.15 d | 7.48 m | – | – | – |
| | | | 1.30 | 1.30 | 7.65 | | 7.79 | | | | |
| *Ih*[k] | – | 8.21 s | 8.08 d | 7.75 s | 7.84 d | 7.58 m | 8.34 d | 7.83 d | 7.75 d | 7.58 m | 7.31 t |
| | | | 0.84 | | 7.02 | | 8.31 | 8.25 | 7.20 | | 7.31 |

[a] The signals of terminal nucleus of the biphenyl skeleton; [b] 7.68 t, (H14), *J* = 7.78; [c] 7.67 m (H14); [d] measured in $(CD_3)_2NCOD$; [e] measured in $(CD_3)_2SO$; [f] 3.72 s ($R^1$ = $CH_3$); [g] 2.67 s ($R^1$ = $CH_3$); [h] 7.21 m ($R^1$ = Ph, H-*ortho*); 7.29 m ($R^1$ = Ph, H-*meta, para*); [i] 7.23 m ($R^1$ = Ph, H-*ortho*); 7.31 m ($R^1$ = Ph, H-*meta, para*); [j] 2.83 s (R = $CH_3$); [k] 2.94 s (R = $CH_3$).

TABLE V
Elemental analyses and IR characteristics of the compounds prepared

| Compound | Formula (M. w.) | IR ν, cm$^{-1}$ | Calculated/Found | | |
|---|---|---|---|---|---|
| | | | % C | % H | % N |
| *Ia* | $C_{39}H_{27}N_3$ | 1 595 s, 1 540 s | 87.11 | 5.07 | 7.82 |
| | (537.7) | 1 495 s, 1 385 s | 87.15 | 5.11 | 7.59 |
| *Ib* | $C_{51}H_{35}N_3$ | 1 595 s, 1 540 s | 88.78 | 5.12 | 6.09 |
| | (689.9) | 1 485 s, 1 380 s | 88.44 | 5.27 | 5.96 |
| *Ic* | $C_{40}H_{29}N_3$ | 1 590 s, 1 456 s | | 536 $(M-CH_3)^+$ | |
| | (551.7) | 1 488 s, 1 380 s | | 459 $(M-CH_3, Ph)^+$ | |
| *Id* | $C_{52}H_{37}N_3$ | 1 595 s, 1 548 s | | 703 $(M^+)$ | |
| | (703.9) | 1 484 s, 1 386 s | | | |
| *Ie* | $C_{45}H_{31}N_3$ | 1 595 s, 1 540 s | 88.05 | 5.10 | 6.85 |
| | (613.8) | 1 494 s, 1 388 s | 87.89 | 5.34 | 6.89 |
| *If* | $C_{57}H_{39}N_3$ | 1 595 s, 1 540 s | 89.37 | 5.14 | 5.49 |
| | (766.0) | 1 486 s, 1 386 s | 89.14 | 5.39 | 5.38 |
| *Ig* | $C_{41}H_{31}N_3$ | 1 595 s, 1 545 s | 87.04 | 5.53 | 7.43 |
| | (565.7) | 1 495 s, 1 387 s | 86.72 | 5.78 | 6.93 |
| *Ih* | $C_{53}H_{39}N_3$ | 1 595 s, 1 543 s | 88.66 | 5.49 | 5.83 |
| | (717.9) | 1 487 s, 1 384 s | 88.40 | 5.78 | 5.74 |
| *IIa* | $C_{40}H_{28}N_2$ | 1 595 s, 1 544 s | | 536 $(M^+)$ | |
| | (536.7) | 1 484 s, 1 395 s | | | |
| *IIb* | $C_{52}H_{36}N_2$ | 1 590 s, 1 540 s | | 688 $(M^+)$ | |
| | (688.9) | 1 482 s, 1 445 s | | | |
| *Vb* | $C_{22}H_{21}NO_2$ | 3 300 s, 1 670 s | 79.73 | 6.39 | 4.23 |
| | (331.4) | 1 630 s, 1 565 s | 79.97 | 6.35 | 4.53 |
| *Vc* | $C_{27}H_{23}NO_2$ | 3 310 s, 1 670 s | 82.42 | 5.89 | 3.56 |
| | (393.5) | 1 630 s, 1 565 s | 82.12 | 6.08 | 3.29 |
| *VIIIa* | $C_{23}H_{17}NO_2$ | 1 661 s, 1 596 s | 81.40 | 5.05 | 4.13 |
| | (339.4) | 1 434 m, 1 165 s | 81.26 | 5.15 | 3.94 |
| *VIIIb* | $C_{24}H_{19}NO_2$ | 1 636 s, 1 590 s | 81.55 | 5.43 | 3.96 |
| | (353.4) | 1 572 s, 1 444 s | 81.24 | 5.56 | 3.79 |
| *VIIIc* | $C_{29}H_{21}NO_2$ | 1 640 s, 1 600 s | 83.82 | 5.10 | 3.37 |
| | (415.5) | 1 576 s, 1 450 s | 83.50 | 5.35 | 3.67 |
| *VIIId* | $C_{25}H_{20}NO_2$ | 1 640 s, 1 600 s | 81.93 | 5.51 | 3.82 |
| | (366.5) | 1 577 s, 1 448 s | 81.57 | 5.87 | 3.61 |
| *VIIIe* | $C_{26}H_{23}NO_2$ | 1 636 s, 1 592 m | 81.85 | 6.09 | 3.67 |
| | (381.5) | 1 572 m, 1 446 s | 81.36 | 5.93 | 3.62 |
| *VIIIf* | $C_{31}H_{25}NO_2$ | 1 640 s, 1 600 s | 83.93 | 5.69 | 3.16 |
| | (443.6) | 1 548 s, 1 448 s | 83.77 | 5.90 | 3.04 |
| *X* | $C_{16}H_{13}NO_2$ | 1 694 s, 1 667 s | 76.46 | 5.22 | 5.58 |
| | (251.3) | 1 607 s, 1 451 m | 76.64 | 5.22 | 5.60 |

### General Procedure of Preparation of Pyridines *VIIa* – *VIIg*

A mixture of 100 ml ether and 24 mmol dihydropyridine *III* was treated with a solution of 130 mmol sodium nitrite in 50 ml water, whereafter 30 ml 20% $H_2SO_4$ was added dropwise at 0 – 5 °C during 1.5 h. The reaction mixture was stirred at the same temperature 4 – 15 h and then left to stand at room temperature overnight. After neutralization with NaOH solution the reaction mixture was extracted several times with small amounts of ether, the combined extracts were dried and evaporated. The residue was recrystallized from the given solvent.

Compound, yield, m.p. (solvent), (literature): *VIIa*, 71%, 68 – 69 °C (EtOH), (ref.[13] 72 °C); *VIIb*, 52%, 66 – 67 °C ($C_6H_{12}$), (ref.[13] 67 °C); *VIIc*, 48%, 141 – 142 °C (MeOH), (ref.[13] 140 °C); *VIId*, 42%, 67 – 69 °C ($C_6H_{12}$), (ref.[2] 69 – 70 °C); *VIIe*, 70%, 58 – 60 °C ($C_6H_{12}$), (ref.[10] b.p. 159 °C/1.3 kPa); *VIIf*, 76%, 192.5 – 194 °C ($C_6H_{12}$), (ref.[11] 188 °C); *VIIg*, 60%, 144 – 147 °C ($C_6H_{12}$).

### General Procedure of Preparation of Chalcones *VIIIa* – *VIIIf*

A solution of 1 g diacetylpyridine *VIIa* – *VIIf* and 2 ml benzaldehyde in 20 ml glacial acetic acid was treated with 1.5 ml concentrated sulfuric acid. When the reaction was finished, the mixture was poured into 100 ml water and extracted with chloroform. The combined extracts were washed several times with water and with saturated solution of $Na_2S_2O_5$. After drying with $CaCl_2$ and evaporation of the solvent, the solid residue was recrystallized from the given solvent (Table I).

### 3-Acetyl-5-cinnamoylpyridine (*IX*)

A solution of 0.3 g diacetylpyridine *VIIa* and 1.16 g benzaldehyde in 5 ml chloroform was treated with 5 g basic alumina and the mixture was left to stand at room temperature 2 days. After extraction with chloroform and evaporation of the solvent, the solid residue was submitted to chromatography (50 g $SiO_2$, benzene–chloroform 1:1) to give 0.04 g *VIIIa* and 0.07 g *IX*. Recrystallization from methanol gave white crystalline solid, m.p. 167.5 – 170 °C.

### General Procedure of Preparation of Terpyridines *I* and *II*

A mixture of 1 mmol *VIIIa* – *VIIId* and 3 mmol pyridinium salt *XIa*, *XIb* was boiled in 50 ml acetic acid–DMF (1:1) in the presence of 4 g ammonium acetate. After precipitation with water, the derivatives *I* and *II* were isolated chromatographically ($SiO_2$, $CHCl_3$). For the reaction conditions, melting points, and yields see Table II.

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