

PREPARATION OF PYRIDINIUM SALTS OF 2-FURANE DERIVATIVES*

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Received December 9th, 1983

Pyridinium salts have been prepared by nucleophilic substitution reaction of 5-halogeno-2-furane derivatives with pyridine and its 3- and 4-substituted derivatives, where R = 3-methyl, 3-ethyl, 3-amino, 3-methoxycarbonyl, 3-ethoxycarbonyl, 3-aminocarbonyl, 4-amino, 4-aminocarbonyl, 4-phenoxy, and 3,4-dimethyl, and structure of the derivatives prepared has been confirmed by their ¹H NMR and ¹³C NMR spectra.

Nucleophilic substitution reactions of furane derivatives become increasingly significant for preparation of furane compounds. In the previous papers¹⁻³ we studied the nucleophilic substitutions of halogen or other suitable leaving groups in 2-furane derivatives with primary and secondary amines, thiolate anions, rhodanide anion, *etc.*

The present paper deals with a study of the nucleophilic substitution reaction of 5-halogeno-2-furane derivatives as *e.g.* 5-halogeno-2-furfurylidene malononitrile, methyl 3-(5-halogeno-2-furyl)-2-propenoate, and 3-(5-halogeno-2-furyl)-2-propenamide with tertiary amines of pyridine type. Pyridinium salts of five- and six-membered heterocycles are little known in literature. Pyridinium salts of tetrahydro- and dihydrofurane⁴, pyridine, pyrimidine, 1,3,5-triazine, benzimidazole, benzotriazole, benzoxazole⁵⁻⁷ have been prepared so far.

The quaternization was carried out in a series of solvents: benzene, toluene, ethyl acetate, methyl acetate, 1,2-dimethoxyethane, dioxane, acetone, methanol, ethanol. Ethyl acetate was found to be the most suitable, the reaction being fast enough in it (the quaternization is finished within several hours to several days at room temperature), and the pyridinium salt produced being not contaminated by any products of subsequent reactions. In polar solvents, as *e.g.* ethanol, methanol, N,N-dimethylformamide, and sulfolane, the quaternization time is shortened, but the pyridinium salt formed is contaminated probably with products of subsequent pyridine ring opening. Similarly impure pyridinium salts are formed by the quaternization at en-

* Part CLXXXI in the series Furane Derivatives; Part CLXXX: This Journal 49, 2141 (1984).

hanced temperatures as well as by the reactions in sealed tubes. In non-polar solvents, as *e.g.* benzene, toluene, hexane, heptane, *etc.*, the obtained pyridinium salts do not contain side products, but the quaternization is very slow (several days) especially with pyridines containing electron-acceptor substituents (several weeks). Pyridines with electron-donor substituents give the respective pyridinium salts at room temperature already, whereas those with electron-acceptor substituents give very low yields of the pyridinium salts at room temperature. At enhanced temperatures the quaternization time is shortened, and the deactivated pyridines give 75–80% yields of the pyridinium salts. With the activated pyridines the corresponding yields are 90–95% (Table I).

The respective 5-chloro- and 5-iodo-2-furane derivatives were used in the nucleophilic substitution reactions. The quaternization rate was higher with the 5-chloro-derivative than with the 5-bromo-derivative, whereas the 5-iodo-derivative reacted slowly and gave low yields. 2-, 3-, and 4-Cyanopyridines, 2-bromo- and 2-chloropyridines did not react in the nucleophilic substitution reaction. Low reactivity of these pyridines is due probably to their low basicity and (in case of the 2-substituted pyridines) sterical effects.

The ^1H NMR spectra of the pyridinium salts prepared (Table II) show 6 or 7 main resonance signals. In the region 8.56–7.89 δ there is a singlet signal which was assigned to the $\text{H}_{\alpha 1}$ proton. Typical furane doublet signals in the regions 7.21–7.84 δ and 7.97–7.79 δ with the coupling constant $^3J = 4.0$ Hz indicate the presence of a 2,5-substituted furane nucleus, which confirms the substitution of the halogen at 5-position of the furane ring. The pyridinium protons H_α , H_β , H_γ of the pyridinium salts *I*, *XII*, *XV*; $\text{H}_{\alpha 1}$, $\text{H}_{\alpha 2}$, $\text{H}_{\beta 2}$, H_γ of the 3-substituted pyridinium salts *II*, *III*, *IV*, *VI*, *VII*, *XIII*, *XIV*; and H_α , H_β of the 4-substituted pyridinium salts *VIII*, *X*, *IX* were ascribed to the values of the chemical shifts given in Table II. The pyridinium salts *I*, *XII*, *XV* show three types of the pyridinium protons in their spectra. From their multiplicity and values of chemical shifts followed the assignments: $\text{H}_\alpha = 9.46\text{--}9.47\delta$ (d), $\text{H}_\beta = 8.42\text{--}8.44\delta$ (d, d), and $\text{H}_\gamma = 8.87\text{--}8.84\delta$ (t). In case of the 3-substituted pyridinium salts *II*, *IV*, *V*, *VI*, *VII*, *XII*, and *XIV* the chemical shifts and multiplicities enabled the assignment of the chemical shift of the $\text{H}_{\alpha 1}$ proton whose singlet signal is found in the region 8.51–9.52 δ (for the electron-donor substituents) or 9.63 to 9.83 δ (electron-acceptor substituents). The $\text{H}_{\alpha 2}$ proton gives a doublet-doublet signal with the coupling constants $^3J = 8.0$ Hz, $^4J = 1.5$ Hz in the region 9.29 to 9.83 δ . The doublet signal of the H_γ proton lies in the region of 8.02–8.72 δ (electron-donor substituents) or 9.16–9.20 δ (electron-acceptor substituents). The typical doublet-doublet signal with the coupling constants $^3J = 8.0$ Hz, $^3J = 7.0$ Hz which lies in the region of 7.88–8.56 δ was assigned to the $\text{H}_{\beta 2}$ proton. The spectra of 4-substituted pyridinium derivatives exhibit two types of the pyridinium protons, *viz* in the regions of 8.44–9.56 δ and 7.05–8.68 δ . The protons found in the former region were ascribed to the H_α protons, those in the latter to the H_β protons. The

TABLE I
Physico-chemical data about the pyridinium salts synthesized

R ^a Salt	Formula (mol.wt.)	Calculated/Found				M.p., °C yield, %
		% C	% H	% N	% Br	
I H	C ₁₃ H ₈ BrN ₃ O (302.1)	51.58	2.67	13.91	26.45	255–260 ^b
		51.46	2.59	13.41	26.05	88.5
II 3-CH ₃	C ₁₄ H ₁₀ BrN ₃ O (316.2)	53.19	3.19	13.24	25.29	245–247 ^b
		53.27	3.24	13.32	25.46	89.0
III 3-C ₂ H ₅	C ₁₅ H ₁₂ BrN ₃ O (330.2)	54.57	3.66	12.73	24.20	224–228
		54.41	3.51	12.81	24.09	91.4
IV 3-COOCH ₃	C ₁₄ H ₁₀ BrN ₃ O ₃ (348.2)	49.74	3.34	11.60	22.06	201–204
		49.61	3.28	11.42	22.03	74.1
V 3-COOC ₂ H ₅	C ₁₅ H ₁₂ NrN ₃ O ₃ (362.2)	48.30	2.90	12.07	22.95	212–215
		48.21	2.83	11.83	22.91	7.40
VI 3-NH ₂	C ₁₃ H ₉ BrN ₄ O (317.1)	49.23	2.86	17.67	25.20	191–195 ^b
		48.60	3.00	17.34	25.13	94.5
VII 3-CONH ₂	C ₁₄ H ₉ BrN ₄ O ₂ (345.2)	48.72	2.63	16.23	23.15	210–210 ^b
		48.66	2.59	16.16	23.48	7.41
VIII 4-NH ₂	C ₁₃ H ₉ BrN ₄ O (317.1)	49.23	2.86	17.67	25.20	235–240 ^b
		49.26	2.90	17.47	25.11	98.5
IX 4-C ₆ H ₅ O	C ₁₉ H ₁₂ BrN ₃ O ₂ (394.2)	57.89	3.07	10.66	20.27	^c
		57.72	3.11	10.67	20.34	79.4
X 4-CONH ₂	C ₁₄ H ₉ BrN ₄ O ₂ (345.2)	48.72	2.63	16.23	23.15	^c
		48.93	2.60	16.87	23.23	77.8
XI 3,5-(CH ₃) ₂	C ₁₅ H ₁₂ BrN ₃ O (330.2)	54.57	3.66	12.73	24.20	^c
		53.95	3.79	12.85	23.39	92.3
XII H	C ₁₄ H ₁₁ BrN ₂ O ₃ (321.2)	50.17	3.31	8.36	23.84	217–219
		50.01	3.15	8.12	23.67	77.9
XIII 3-CH ₃	C ₁₅ H ₁₃ BrN ₂ O ₃ (335.2)	51.60	3.75	8.02	22.88	^c
		51.46	3.68	8.11	22.93	91.2
XIV 3-CONH ₂	C ₁₅ H ₁₂ BrN ₃ O ₄ (364.2)	49.47	3.32	7.69	21.94	^c
		49.41	3.28	7.82	22.03	71.3
XV	C ₁₃ H ₁₀ BrN ₃ O ₂ (320.1)	48.77	3.15	13.13	24.96	^c
		48.64	3.18	13.79	25.10	75.3

^a R is the substituent in the pyridine ring, ^b decomposition, ^c the compound does not melt below 300°C.

pyridinium salt *XI* exhibits two singlet signals in its spectrum: at 9.23 δ and 8.601 which were ascribed to the H $_{\alpha}$ and H $_{\gamma}$ protons, respectively.

In the ^{13}C NMR spectra (Table III) of the pyridinium salts prepared there are 13 signals in each basic spectrum. All the signals were assigned on the basis of the off resonance spectrum and NOE spectrum. The ^{13}C NMR spectra of the starting 5-halogeno-2-furane derivatives are given in ref.⁸

EXPERIMENTAL

The melting points were determined with a Kofler apparatus and were not corrected. The IR spectra were measured by the KBr technique using a UR 20 Zeiss Jena apparatus with the accuracy of $\pm 1\text{ cm}^{-1}$. The UV spectra were measured in water with a Specord UV VIS (Zeiss, Jena) apparatus with the accuracy $\pm 1\text{ nm}$. The ^1H NMR spectra were measured with an 80 MHz apparatus Tesla BS 487 C in hexadeuteriodimethyl sulphoxide at 25°C, using tetramethylsilane as internal standard. The ^{13}C NMR spectra were measured with a FT-NMR JEOL 100 MHz apparatus at the frequency of 25.05 MHz.

TABLE II
 ^1H NMR spectra of the pyridinium salts *I*–*XV*

Salt ^a	δ	H $_{01}$ (s)	H $_3$ (d)	H $_4$ (d)	H $_{\alpha_1}$ (s)	H $_{\alpha_2}$ (d)	H $_{\beta_2}$ (dd)	H $_{\gamma}$ (t)	Other protons
<i>I</i> ^b	8.51	7.80	7.84		9.46(d)		8.42	8.87	—
<i>II</i>	8.49	7.78	7.81		9.40	9.23	8.30	8.71	$\delta\text{CH}_3 = 2.62(\text{s})$
<i>III</i>	8.56	7.79	7.89		9.39	9.31	8.47	8.78	$\delta\text{CH}_3 = 1.34(\text{q})$ $\delta\text{CH}_2 = 2.98(\text{t})$
<i>IV</i>	8.52	7.79	7.93		9.66	9.75	8.53	9.21	$\delta\text{CH}_2 = 4.52(\text{q})$ $\delta\text{CH}_3 = 1.42(\text{t})$
<i>V</i>	8.55	7.79	7.97		9.63—9.83(m)		8.56	9.18	$\delta\text{CH}_3 = 4.04(\text{s})$
<i>VI</i>	7.89	7.52	7.75		8.51	8.51	7.88	8.02	—
<i>VII</i>	8.52	7.81	7.95		9.80	9.60	8.50	9.20	—
<i>VIII</i>	8.22	7.21	7.61		8.44(d)		7.05	—	—
<i>IX</i>	8.48	7.64	7.75		9.24(d)		7.84	—	$\delta\text{C}_6\text{H}_5 =$ $= 7.50—7.29(\text{m})$
<i>X</i>	8.54	7.80	7.88		9.56(d)		8.68(d)	—	—
<i>XI</i>	8.55	7.78	7.85		9.23(s)		—	8.60 s	$\delta\text{CH}_3 = 2.58(\text{s})$
<i>XII</i> ^b	8.37		7.83(s)		9.47(d)		8.44	8.86	$\delta\text{OCH}_3 = 3.94(\text{s})$
<i>XIII</i>	8.36	7.81	7.88		9.51	9.29	8.34	8.72	$\delta\text{OCH}_3 = 3.89(\text{s})$ $\delta\text{CH}_3 = 2.63(\text{s})$
<i>XIV</i>	8.37	7.84	7.96		9.81	9.54	8.55	9.16	$\delta\text{OCH}_3 = 3.89(\text{s})$
<i>XV</i>	8.18	7.66	7.79		9.46		8.42	8.84	—

^a $^3J_{\text{H}_3, \text{H}_4} = 4.0\text{ Hz}$, $^3J_{\text{H}_{\alpha_2}, \text{H}_{\beta}} = 7.0—8.0\text{ Hz}$, $^3J_{\text{H}_{\beta}, \text{H}_{\gamma}} = 7.0—8.0\text{ Hz}$; $^4J_{\text{H}_{\alpha_2}, \text{H}_{\gamma}} = 1.5\text{ Hz}$;

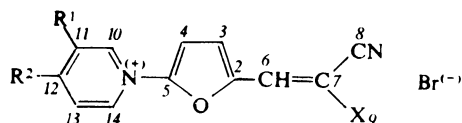
^b $^3J_{\text{H}_{\alpha}, \text{H}_{\beta}} = 6.5\text{ Hz}$, $^3J_{\text{H}_{\beta}, \text{H}_{\gamma}} = 8.0\text{ Hz}$, $^4J_{\text{H}_{\alpha}, \text{H}_{\gamma}} = 1.5\text{ Hz}$

1-(5-(2,2-Dicyanovinyl)-2-furyl)-3- or -4-X-pyridinium Bromides

Solution of 10 g (44.8 mmol) 5-bromofurfurylidene malononitrile in 200 ml ethyl acetate (benzene) was treated with 44.8 mmol pyridine or 3-, 4-substituted pyridine. The mixture was refluxed

TABLE III

^{13}C NMR spectra of the pyridinium salts



Salt ^a	R ¹	R ²	X	C ₂	C ₃	C ₄	C ₅	C ₆
<i>I</i>	H	H	CN	146.58	127.35	106.82	149.31	144.11
<i>II</i>	CH ₃	H	CN	146.58	127.35	106.69	149.31	144.11
<i>IV</i>	COOC ₂ H ₅	H	CN	147.32	126.49	107.30	148.20	143.11
<i>VI</i>	NH ₂	H	CN	146.15	123.68	106.08	149.25	143.75
<i>VII</i>	CONH ₂	H	CN	146.58	126.59	107.39	148.77	143.75
<i>VIII</i>	H	NH ₂	CN	143.45	128.59	101.51	150.71	144.51
<i>X</i>	H	CONH ₂	CN	148.31	126.20	107.30	149.95	143.40
<i>XII</i>	H	H	COOCH ₃	146.79	125.50	106.25	148.26	138.16
<i>XIII</i>	CH ₃	H	COOCH ₃	146.73	126.08	116.19	148.48	138.49
<i>XIV</i>	CONH ₂	H	COOCH ₃	147.14	126.02	106.95	148.37	138.43
<i>XV</i>	H	H	CONH ₂	147.90	122.57	105.96	147.90	134.45

Salt	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄
<i>I</i>	78.49	113.83	113.18	141.92	129.24	148.62	—	—
<i>II</i>	78.62	112.96	113.44	143.22	138.24	148.22	128.44	139.62
<i>IV</i>	78.80	113.10	112.63	142.62	129.74	147.82	126.94	143.92
<i>VI</i>	78.11	113.45	113.45	130.02	150.49	134.42	130.14	131.12
<i>VII</i>	78.98	113.80	113.20	133.72	134.64	149.42	129.94	143.32
<i>VIII</i>	74.77	114.36	113.62	142.82	115.44	168.22	—	—
<i>X</i>	79.05	113.10	112.57	142.54	126.39	153.77	—	—
<i>XII</i>	100.17	114.91	161.70	141.92	129.24	148.62	—	—
<i>XIII</i>	99.99	115.38	161.94	143.22	138.24	148.22	128.44	139.62
<i>XIV</i>	100.34	115.26	161.94	144.72	134.64	149.42	129.94	143.32
<i>XV</i>	104.91	115.73	161.54	141.92	129.24	148.62	—	—

^a Other chemical shifts: *II* $\delta_{\text{CH}_3} = 18.06$ (q); *IV* $\delta_{\text{OCH}_2} = 62.61$ (t); $\delta_{\text{CH}_3} = 13.41$ (q), $\delta_{\text{COOC}_2\text{H}_5} = 160.54$ (s); *VII* $\delta_{\text{CONH}_2} = 161.88$ (s); *X* $\delta_{\text{CONH}_2} = 162.30$ (s); *XII* $\delta_{\text{OCH}_3} = 53.25$ (q); *XIII* $\delta_{\text{CH}_3} = 17.91$ (q); $\delta_{\text{OCH}_3} = 53.53$ (q); *XIV* $\delta_{\text{CONH}_2} = 162.12$ (s), $\delta_{\text{OCH}_3} = 53.60$ (q).

several hours or days (depending on the nature of the substituted pyridine). The separated pyridinium salt was filtered off, washed several times with ether, and dried. The raw product was recrystallized from a methanol-ether mixture. By the procedure described the compounds I–XI were prepared.

1-(5-(2,2-Dicyanovinyl)-2-furyl)pyridinium bromide (I), 10 h. UV spectrum, λ_{\max} (nm) $\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$): 370 (3·30). IR spectrum (cm^{-1}): 960, 981, 1 020, 1 040, 1 052, 1 108, 1 217, 1 285, 1 371, 1 479, 1 575, 1 614, 2 232, 2 984, 2 998, 3 061.

1-(5-(2,2-Dicyanovinyl)-2-furyl)-3-methylpyridinium bromide (II), 8 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 369 (3·31). IR spectrum (cm^{-1}): 943, 957, 1 025, 1 058, 1 121, 1 275, 1 478, 1 555, 1 575, 1 606, 1 618, 2 224, 2 233, 3 038, 3 051, 3 109, 3 044, 3 101, 3 118.

1-(5-(2,2-Dicyanovinyl)-2-furyl)-3-ethylpyridinium bromide (III), 8 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 370 (3·37). IR spectrum (cm^{-1}): 947, 969, 1 025, 1 058, 1 123, 1 271, 1 281, 1 317, 1 452, 1 492, 1 549, 1 571, 1 602, 2 227, 2 229.

1-(5-(2,2-Dicyanovinyl)-2-furyl)-3-ethoxycarbonylpyridinium bromide (IV), 30 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 475 (2·76), 379 (3·15), 346 i (3·02), 252 (3·02). IR spectrum (cm^{-1}): 969, 1 020, 1 106, 1 151, 1 263, 1 312, 1 446, 1 494, 1 553, 1 609, 1 731, 2 231, 2 876, 2 939, 2 964.

1-(5-(2,2-Dicyanovinyl)-2-furyl)-3-methoxycarbonylpyridinium bromide (V), 35 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 468 (2·76), 377 (3·16), 345 i (3·04), 251 (3·00). IR spectrum (cm^{-1}): 931, 975, 1 025, 1 049, 1 133, 1 231, 1 267, 1 306, 1 333, 1 429, 1 454, 1 614, 1 634, 1 739, 2 233, 2 873, 2 908, 2 964, 3 043, 3 061, 3 085, 3 124.

1-(5-(2,2-Dicyanovinyl)-2-furyl)-3-aminopyridinium bromide (VI), 6 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 372 (3·36), 257 (3·13), 231 (3·30). IR spectrum (cm^{-1}): 933, 969, 982, 1 019, 1 043, 1 271, 1 322, 1 354, 1 462, 1 507, 1 557, 1 579, 1 606, 1 634, 2 232, 2 996, 3 029, 3 044, 3 069, 3 145, 3 273, 3 424.

1-(5-(2,2-Dicyanovinyl)-2-furyl)-3-aminocarbonylpyridinium bromide (VII), 24 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 375 (3·22), 341 i (3·05), 324 i (2·98), 249 (3·03). IR spectrum (cm^{-1}): 955, 979, 1 022, 1 045, 1 116, 1 273, 1 388, 1 476, 1 550, 1 603, 1 673, 1 689, 2 230, 3 013, 3 063, 3 123.

1-(5-(2,2-Dicyanovinyl)-2-furyl)-4-aminopyridinium bromide (VIII), 2 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 400 (3·23), 230 (2·79). IR spectrum (cm^{-1}): 925, 975, 1 025, 1 043, 1 082, 1 212, 1 349, 1 496, 1 570, 1 622, 1 667, 2 231, 2 942, 2 987, 3 066, 3 107, 3 273, 3 361.

1-(5-(2,2-Dicyanovinyl)-2-furyl)-4-phenoxy pyridinium bromide (IX), 18 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 379 (3·31), 264 (2·89). IR spectrum (cm^{-1}): 930, 972, 1 025, 1 046, 1 077, 1 153, 1 179, 1 195, 1 295, 1 279, 1 329, 1 401, 1 475, 1 560, 1 605, 1 634, 2 223, 2 227, 2 963, 3 016, 3 031, 3 068, 3 121.

1-(5-(2,2-Dicyanovinyl)-2-furyl)-4-aminocarbonylpyridinium bromide (X), 24 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 388 (3·26), 347 i (3·07), 333 i (3·04), 272 (2·95), 242 (2·94).

1-(5-(2,2-Dicyanovinyl)-2-furyl)-3,5-dimethylpyridinium bromide (XI), 4 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 371 (3·30). IR spectrum (cm^{-1}): 966, 1 005, 1 039, 1 130, 1 278, 1 319, 1 386, 1 471, 1 559, 1 593, 1 605, 2 233, 2 858, 2 903, 2 954.

1-(5-(2-Methoxycarbonyl-2-cyanovinyl)-2-furyl)-2-X-pyridinium Bromides

Solution of methyl 2-cyano-3-(5-bromo-2-furyl)-2-propenoate (10 g, 39·0 mmol) in 150 ml ethyl acetate was treated with the corresponding 3-substituted pyridine (39·0 mmol). The mixture

was refluxed 8–30 h. The separated salt was recrystallized from a methanol–ether mixture. This procedure was used for the preparation of compounds *XII*–*XIV*.

1-(5-(2-Methoxycarbonyl-2-cyanovinyl)-2-furyl)pyridinium bromide (*XII*), 14 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 371 (3.28), 338i (3.11), 320i (3.00), 262 (2.85). IR spectrum (cm^{-1}): 932, 985, 1 020, 1 037, 1 099, 1 219, 1 259, 1 267, 1 285, 1 433, 1 475, 1 492, 1 572, 1 612, 1 725, 2 222, 2 990, 3 015, 3 045, 3 056, 3 079, 3 119.

1-(5-(2-Methoxycarbonyl-2-cyanovinyl)-2-furyl)-3-methylpyridinium bromide (*XIII*), 8 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 371 (3.35), 338i (3.18), 321i (3.05), 263 (2.87), 237 (2.96). IR spectrum (cm^{-1}): 953, 982, 1 021, 1 036, 1 100, 1 196, 1 217, 1 258, 1 279, 1 427, 1 473, 1 560, 1 613, 1 723, 2 219, 2 983, 3 036.

1-(5-(2-Methoxycarbonyl-2-cyanovinyl)-2-furyl)-3-aminocarbonylpyridinium bromide (*XIV*), 36 h. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 377 (3.33), 3 39i (3.15), 326i (3.13), 248 (3.19). IR spectrum (cm^{-1}): 954, 979, 1 020, 1 043, 1 098, 1 175, 1 196, 1 282, 1 390, 1 402, 1 611, 1 704, 1 725, 2 223, 3 001, 3 061, 3 228.

1-(5-(2-Aminocarbonyl-2-cyanovinyl)-2-furyl)pyridinium Bromide (*XV*)

A solution of 10 g (41.5 mmol) 2-cyano-3-(5-bromo-2-furyl)-2-propenamide in 150 ml 1,2-dimethoxyethane was treated with 3.28 g pyridine. The mixture was heated at 80°C 40 h. The separated salt was filtered off, washed with ether several times, dried, and recrystallized from a methanol–ether mixture. UV spectrum, λ_{\max} (nm) ($\log \epsilon$ ($\text{m}^2 \text{mol}^{-1}$)): 370 (4.25), 335i (4.08), 259 (3.83), 242 (3.93). IR spectrum (cm^{-1}): 930, 970, 1 017, 1 047, 1 133, 1 157, 1 229, 1 273, 1 401, 1 480, 1 575, 1 620, 1 684, 2 225, 2 998, 3 028, 3 049, 3 101.

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Translated by J. Panchartek.