SYNTHESIS AND SPECTRAL PROPERTIES OF FURYL-SUBSTITUTED PYRIDINES AND PYRYLIUM AND PYRIDINIUM SALTS

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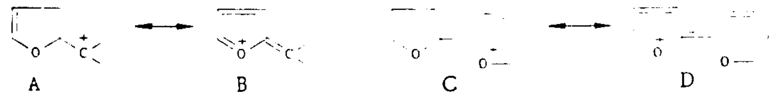
2,6-Diphenyl-4-(5-R-2-furyl)pyrylium and 2,4-diphenyl-6-(5-bromo-2-furyl)pyrylium perchlorates and the corresponding pyridines and 1-methylpyridinium perchlorates were synthesized. On the basis of the UV and PMR spectra it was concluded that there is significant electronic interaction of the furylium substituent with the pyrylium and pyridinium cations.

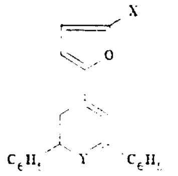
The clearly expressed ability of the furan ring to transmit its electron density to any electron-deficient centers — both intermolecularly and intramolecularly — is manifested in many reactions of furan derivatives and, in particular, in the special properties of furyl-substituted carbonium ions. Stabilized by one or several furan (as well as arene) groupings, such ions can exist in the form of crystalline perchlorates [1], but they are more often proposed as active intermediate particles in the reactions of furan compounds with nucleophiles [2]. Divald and co-workers [2] explain the relative stabilities of such salts by means of their partially "furylium" state, i.e., by resonance stabilization of carbonium cation A in conformity with canonical structure B.

2-Methylfurylium cation B is isomeric with respect to the pyrylium cation. The question as to the "contribution" of structures of the C and D type to the overall charge distribution in the system in which the furan ring is located in the 2 or 4 position of the pyrylium cation is therefore of great interest.

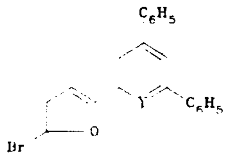


A method for obtaining furyl-containing pyrylium salts by the action of acetyl perchlorate on 5-X-substituted furfurylidenediacetophenones (FDA) was proposed in [3]; the first representative of this series, viz., pyrylium salt Ic, which was converted to the corresponding pyridine derivative IIc, was synthesized.

In the present research we studied the cyclization of a more extensive series of FDA under the same conditions. For the first time we were able to obtain pyrylium salts Ia, b, d in pure form. Compound IV, which contains a furan substituent in the 2 position of the pyrylium cation, was obtained in the reaction of equimolar amounts of benzylideneacetophenone and 5-bromo-2-acetyl-furan with perchloric acid in acetic anhydride.



I–III a–d



IV–VI

I, IV Y=$\overline{O}$; II, V Y=N; III, IV Y=$\overline{N}$—CH$_3$; I–III a X=Cl; b X=Br; c X=I; d X=CH$_3$

Pyrylium salts Ia-d and IV were converted to the corresponding pyridines IIa-d and V and N-methylpyridinium salts IIIa-d and VI by the action of ammonia and methylamine.

Data on the properties of I-VI are presented in Tables 1-3.

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TABLE 1. Properties of Pyrylium Salts Ia-d and Pyridinium Salts IIIa-d

Compound	mp, °C (from AcOH)	PMP spectrum, δ, ppm				Yield, %
		3(5)-H	3'-H	4'-H	N–CH	
Ia	198...199 (dec.)	7.83	7,64	6.30	—	32
Ib	219...220 (dec.)	7.85	7,58	6.43	—	40
Ic	216...218 (dec.)	7.84	7,46	6.64	—	44
Id*	165...168 (dec.)	7.73	7.59	6.20	—	36
IIIa	195...198	7.54	7.01	6,09	3.43	68
IIIb	215...217	7.51	6.95	6.19	3.41	67
IIIc	231...232	7.51	6.86	6.40	3.40	72
IIId*	106...110 (dec.)	7.53	7,01	5,59	3,39	70

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*In the PMR spectra of Id and IIId the signal of the 5'-CH_3 group has values of 2.16 and 2.02 ppm, respectively.

TABLE 2. Properties of Pyridines IIa-d

Compound	mp, °C (from hexane	PMR spectrum, δ, ppm			Found, %			Empirical formula	Calc., %			Yield, %
		3(5)-H	3'-H	4'-H	C	H	N		C	H	N	
IIa	192...193	7,75	7,14	6.15	75,9	4.3	4,4	$C_{21}H_{14}ClNO$	76.0	4.2	4,2	45
IIb	172...173	7,73	7,09	6.25	67,1	3.7	3,8	$C_{21}H_{14}BrNO$	67,0	3.7	3,7	48
IIc	128...129	7,73	7,00	6,49	59,8	3,4	3,2	$C_{21}H_{14}INO$	59,6	3.3	3.3	52
IId*	163...164	7,73	7,13	6,03	84,8	5,6	4.4	$C_{22}H_{17}NO$	84,9	5.5	4,5	56

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*In the PMR spectrum of IId the signal of the 5'CH_3 group has a δ value of 2.08 ppm.

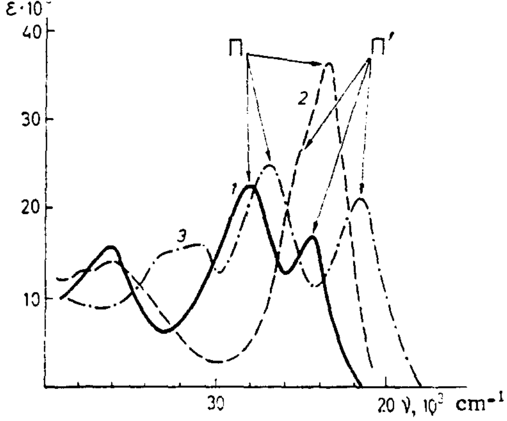

Fig. 1. Electronic absorption spectra of the 2,4,6-triphenylpyrylium salt (1) and IV (3) in acetonitrile.

It is apparent from Figs. 1 and 2 that a successive bathochromic shift of the long-wave absorption bands is observed for 2- and 4-furyl-substituted compounds on passing from pyridines to the corresponding pyridinium salts and then to the corresponding pyrylium salts. To explain the differences in the absorption spectra of the 2- and 4-furyl-substituted compounds we used model systems — 2,4,6-triphenylpyrylium (Fig. 1) and 1-methyl-2,4,6-triphenylpyridinium (Fig. 2) salts.

It is known that the long-wave transitions in 2,4,6-phenyl-substituted pyrylium and pyridinium salts are local transitions of intramolecular charge transfer (ICT) from phenyl rings in different positions (2, 6, or 4) to the heteroring [4, 5]. The $S_0 \rightarrow S_1$ (Π' in Fig. 1) transition, which is associated with the 2- and 6-phenyl substituents, and the $S_0 \rightarrow S_2$ (Π) transition, which is associated with the 4-phenyl substituent, show up separately only in the case of 2,4,6-triphenylpyrylium perchlorate.

The increase in the electron-donor capacity of the substituent upon replacement of the phenyl ring by the 5-bromo-2-furyl ring affects the form of the absorption spectra of the

TABLE 3. Properties of 2-(5-Bromo-2-furyl)-Substituted Pyridines and Pyrylium and Pyridinium Salts

Compound	mp, °C (from AcOH)	PMR spectrum, δ, ppm, J, Hz					Yield, %
		3'-H	4'-H	3-H	5-H	J_{35}	
IV	253...256 (dec.)	7.38	6.38	7.91	7.81	1.3	15
V	91...92**	—***	6.35	7.91	7.75	1.5	76
VI*	218...220 (dec.)	6.94	6.26	7.91	7.49	2.0	42

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*In the PMR spectrum of VI the signal of the N–CH_3 group has a δ value of 3.71 ppm

**From hexane.

***Superimposition on the signal of the aromatic protons.

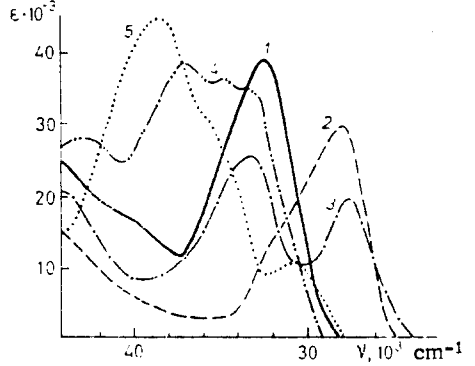

Fig. 2. Electronic absorption spectra of the 2,4,6-triphenylpyridinium salt (1) and IIIb (2) VI (3), IIb (4), and V (5) in acetonitrile.

isomeric 2- and 4-furyl-substituted pyrylium and pyridinium perchlorates differently. For the 2-furyl-substituted compounds one observes a bathochromic shift of the Π' band associated with the substituents in the 2 position; this leads to an increase in the splitting between the Π and Π' bands (Figs. 1 and 2). In the case of 4-furyl-substituted cations a long-wave shift is observed for the Π absorption band, which corresponds to intramolecular charge transfer (ICT) from the substituent in the 4 position; this draws the two transitions together and leads to the formation of a common absorption band with a distinct inflection on the short-wave wing.

The observed changes in the absorption spectra are completely analogous to those that occur in the case of the successive introduction of methoxy groups into phenyl rings [5]; however, they are expressed even more clearly because of the increased electron-donor capacity of the furan substituents as compared with p-methoxyphenyl substituents. The existence of long-wave transitions of ICT from the furan substituent to the pyrylium (pyridinium) ring constitutes evidence for substantial participation of the furan ring in delocalization of the positive charge of the heterocation.

Among the peculiarities of the PMR spectra of the investigated compounds (Table 1-3) let us note the following. The 3'-H and 4'-H protons of the furan ring are observed in these spectra in the form of doublets, and the $J_{3'4'}$ value is virtually constant for all of the compounds and is equal to 4 Hz. Under the influence of various structural factors these signals may be shifted significantly to both the strong-field and weak-field sides. For all of the compounds in the order X = Cl, Br, I one observes a phenomenon that we have already previously noted in the case of 5-X-2-nitrofurans: the signals of the 3'-H and 4'-H protons draw together with an increase in the polarizability of the halogen atom, since they are shifted in the opposite direction in this order. This can be explained by the "neutralizing" effect of the halogen atom, which partially eliminates the negative mesomeric effect of the heterocation and is transmitted along the shortest pathway — through space [6].

The electronegativity of the heterocation decreases successively in the order pyrylium—pyridinium—N-methylpyridinium. The signals of the 3'-H protons for Ib, IIb, and IIIb under the influence of this effect are shifted to strong field: 7.58, 7.09, and 6.95 ppm, respectively; the same can be said regarding the 4'-H protons: 6.43, 6.25, and 6.19 ppm. The position of the signal of the heteroring protons (3- and 5-H) changes in the same order under the influence of a decrease in the degree of deshielding: 7.85, 7.73, and 7.51 ppm. Finally, the protons of the $5'-CH_3$ group in Id, IId, and IIId are also shifted to strong field under the influence of the effect of the ring: 2.16, 2.08, and 2.02 ppm, respectively.

The signals of the arene protons have an extremely complex form, and we did not analyze the pattern of spin-spin coupling (SSC) for them. Let us note here only the effect of the nature of the heteroaction. For pyrylium salts Ia-d the α-protons and the β,γ-protons are observed in the form of multiplets that are remote from one another (for salt Ib $\Delta\delta = 0.5$ ppm). In the case of the pyridinium cation these multiplets draw together (for salt IIb $\Delta\delta = 0.15$ ppm), and, finally, in the case of N-methylpyridinium salts they merge into one signal (for IIb $\delta = 7.20$ ppm). For VI only the α'-protons of the 4-phenyl ring are shifted to weaker field, and the remaining eight protons merge into one signal. We assume that the noncoplanarity of the 2-phenyl rings in the N-methylpyridinium salts plays an important role here: despite the fact that the chemical shifts of the aromatic protons are nonequivalent, because of random coincidence they give a single signal in view of the existence of the so-called "ring currents" in the aromatic system.

EXPERIMENTAL

The UV spectra of solutions in acetonitrile were recorded with a Specord M-40 spectrophotometer. The PMR spectra of solutions in trifluoroacetic acid (salts) and d_3-acetonitrile (bases) were obtained with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

2,6-Diphenyl-4-(5-X-2-furyl)pyrylium Perchlorates Ia-d. A 5-mmole sample of the corresponding furfurylideneacetophenone [7] was dissolved in 20 ml of acetic anhydride, the solution was cooled to —5°C, and a solution of 1 ml of 70% $HClO_4$ in 5 ml of acetic anhydride was added to it in small portions with cooling and stirring. The mixture was diluted with 300 ml of absolute ether, and the precipitated crystals were removed by filtration and purified by crystallization from glacial acetic acid with added $HClO_4$.

1-Methyl-2,6-diphenyl-4-(5-X-2-furyl)pyridinium perchlorates IIIa-d and 2,6-diphenyl-4-(5-X-2-furyl)pyridines IIa-d were obtained by known methods [3, 8] from pyrylium salts Ia-d.

2,4-Diphenyl-6-(5-bromo-2-furyl)pyrylium Perchlorate (IV). A mixture of 2.1 g (10 mmole) of benzylideneacetophenone and 1.9 g (10 mmole) of 5-bromo-2-acetylfuran was dissolved in 10 ml of acetic anhydride, and 2 ml of 70% $HClO_4$ was added dropwise with cooling with ice water. The precipitated crystals were removed by filtration and purified as described for Ia-d.

1-Methyl-2,4-diphenyl-6-(5-bromo-2-furyl)pyridinium perchlorate (VI) and 2,4-diphenyl-6-(5-bromo-2-furyl)pyridine (V) were obtained from salt IV by the method in [8].

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