ELECTROCHEMICAL REDUCTION OF PYRYLIUM SALTS IN AN APROTIC MEDIUM

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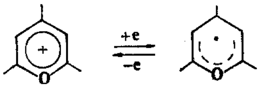
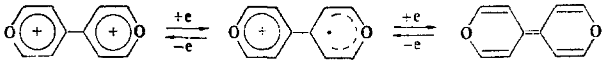
The electrochemical reduction of pyrylium salts in anhydrous acetonitrile is not complicated by adsorption and may serve as a convenient method for the evaluation of the effect of structural factors on the ability of pyrylium cations to undergo conversion to the corresponding pyranyl radicals and the ability of the latter to undergo dimerization. The stepwise two-electron reduction of conjugated dipyrylium salts leads successively to cation radicals and dipyranylidene structures.

It is known that the one-electron reduction of pyrylium cations leads to the corresponding free radicals [1, 2]:



Under the influence of reducing agents dipyrylium salts are converted to stable cation radicals, the subsequent reduction of which leads to dipyranylidenes [2, 3]:



In order to determine the direction and ease of electronic transitions of this type as a function of the nature of the pyrylium salt we undertook a study of the oscillopolarographic reduction of perchlorates of various pyrylium cations in an aprotic medium (acetonitrile). Pyrylium salts of various types* were investigated to establish the limits of applicability of the selected method and, where necessary, the degree of reversibility of electron transfer. The measurements were made with an OP-2 oscillopolarograph with a dropping mercury electrode with a lithium perchlorate base electrolyte in an argon atmosphere.

The electrochemical reduction of pyrylium salts in an aqueous ethanol medium [4, 5] is complicated by adsorption effects, and this makes it practically impossible to use the results of the measurements for the evaluation of the structural effects in the molecules of pyrylium salts. In a few of the investigated cases in which the reduction was carried out in dimethylformamide (DMF), adsorption effects could be avoided [4], but these measurements were made only for a narrow reaction series — for 2,4-diphenyl-8-arylidomethylene-5,6,7,8-tetrahydrobenzopyrylium perchlorates. In addition, the nature of the second of the two observed cathode waves remained unclear in this case.

In all the cases that we studied we observed neither adsorption nor kinetic waves; this, in conjunction with the known ESR data [1, 3], makes it possible to confidently assign the diffusion waves found in this study to the corresponding pyranyl radicals. Since the nature of the elementary electrochemical act is identical in all the cases under comparison, the

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*The investigated pyrylium salts were furnished us by co-workers of the department of heterocyclic and heteroorganic compounds of the Scientific-Research Institute of Physical and Organic Chemistry, Rostovon-Don, for which we express our thanks.

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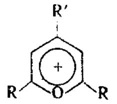
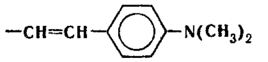
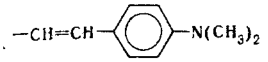
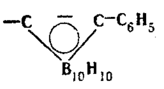
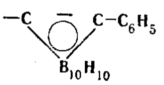
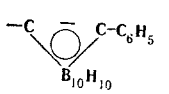
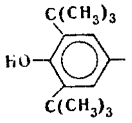
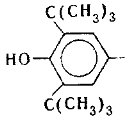
TABLE 1. Polarographic Reduction of Pyrylium Salts



Compound	R	R′	Peak potential $-E_p$, V	Coefficient of reversibility α
I	$(CH_3)_3C$	H	0,74	0,32
II	$(CH_3)_3C$	$(CH_3)_3C$	0,98	1,00
III	C_6H_5	H	0,32	—
IV	C_6H_5	C_6H_5	0,49	—
V	p-$CH_3OC_6H_4$	H	0,50	0,43
VI			0,53	1,00
VII*	$(CH_3)_3C$		0,18	0,90
VIII*	C_6H_5		0,38	0,48
IX*	p-$CH_3OC_6H_4$		0,10	0,90
XV		H	0,68	0,60
XX	$(CH_3)_3C$		0,88	0,80
XXI	CH_3	CH_3	0,98	0,98
XIV†	2,4-Diphenylpyrylium cation		1,46	1,00
XVI†	2-Phenylbenzopyrylium cation		1,29	0,20

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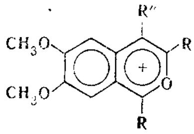
*The $SbCl_6^-$ ion.

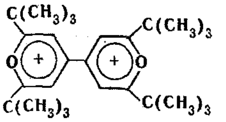
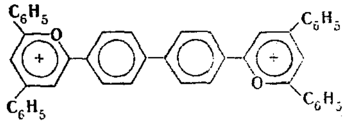
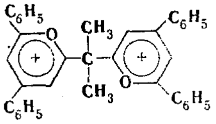
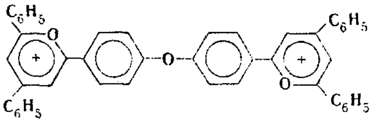
†This is the $-E_p$ value of the second wave.

TABLE 2. Reduction of 2-Benzopyrylium Salts



Compound	R	R′	R″	$-E_p$, V	Coefficient of reversibility, α
X	CH_3	CH_3	H	0,98	0,28
XI	CH_3	p-$CH_3OC_6H_4$	H	0,68	0,48
XII	CH_3	C_6H_5	C_6H_5	0,73	0,90
XIII	H	CH_3	H	0,58	0,48

TABLE 3. Reduction of Dipyrylium Salts and Other Cations

Compound	Formula	First wave, $-E_p$, V; α	Second wave, $-E_p$, V
XVII		0,48; 0,70	0,79
XVIII		1,57; 1,00	1,85
XXI		0,49	—
XXII		0,49	—

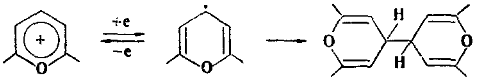
polarographic data obtained can be used for comparison of the electrochemical behavior of different pyrylium salts.

A number of general conclusions can be drawn from the experimental data (Tables 1-3). First, the presence of electron-donor substituents in the 2, 6, or 4 position facilitates the reduction of the pyrylium cation: 2,4-disubstituted pyrylium salts (I and II) are reduced more readily than the corresponding 2,4,6-trisubstituted derivatives (III and IV). The introduction of methoxy (V) and dimethylamino (VI) groups in the para position of the phenyl rings raises the reduction potentials of phenyl-substituted pyrylium salts (III and IV).

4-Phenylcarboranylpyrylium salts (VII, VIII, and IX), for which unexpectedly low half-wave potentials were found, constitute an exception to this. This circumstance obliges one to have a guarded attitude toward the traditional assignment of carboranyl substituents to the category of invariably acceptor groupings. With respect to a "rigid" cation, carboranyl substituents evidently prove to be electron-donor groupings, just as the donor or acceptor of aromatic groupings is determined by the nature of the substituents bonded to them (Table 1).

Substituted 6,7-dimethoxy-2-benzopyrylium salts (X-XIII) are also reduced at relatively low potential (Table 2).

Pyrylium salts that do not contain substituents in one of the 2, 4, or 6 positions (I, III, V, XV, and XVI) are reduced with relatively low coefficients of reversibility. This is undoubtedly associated with the previously studied [1] recombination of the pyranyl radicals formed:



Bulky substituents in these positions hinder dimerization, and 2,4,6-trisubstituted salts are reduced reversibly (II, IV, VI, and XVII-XX). It is characteristic, however, that 2,4,6-trimethylpyrylium salts XXI is reduced with a rather low coefficient of reversibility.* This is in agreement with data on the reduction of the 2,4,6-trimethylpyrylium ion to 2,2,4,4,6,6-hexamethyl-4,4-dipyranyl [7, 8].

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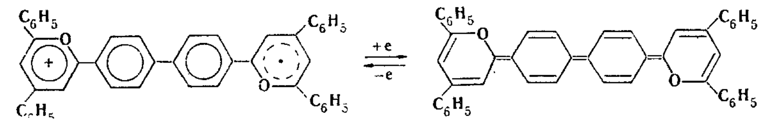
*The coefficients of reversibility of the electrode processes were determined by the Matsude–Ayabe and Hochstein methods [6].

1,3,4-Trisubstituted 2-benzopyrylium cations (XI, XIII) are reduced completely reversibly; the coefficient of reversibility drops sharply if the 4 position is unoccupied (X, XIII), and this indicates dimerization of the corresponding free radicals.

The reduction of dipyrylium salts proceeds in a peculiar manner (Table 3). In all cases in which both pyrylium rings are directly connected or are connected through a conducting chain (XVIII) the reduction process in two waves with a high degree of reversibility. It follows from this that the first step in the reduction is the formation of stable cation radicals of the previously studied [1] type of the cation radical from bis-2,6-di-tert-butylpyrylium. Subsequent reduction leads to a dipyranylidene structure, for example:



Dications with a broken conjugation chain (XX-XXII) are reduced in one two-electron wave; consequently, in this case one will hardly be able to isolate any cation radicals.

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SYNTHESIS AND SOME TRANSFORMATIONS OF 4-OXO-2-(β-ETHOXYVINYL)-4H-1,3-BENZOXAZINIUM SALTS

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A method was developed for the synthesis of 4-oxo-(β-ethoxyvinyl)-4H-1,3-benzoxazinium salts by condensation of oxo-2-alkylbenzoxazinium salts by condensation of oxo-2-alkylbenzoxazinium salts with ethyl orthoformate. During hydrolysis and aminolysis, attack of the nucleophile is directed to the β-carbon atom of the benzoxazinium salts. The previously unknown 2-formylmethylene-4-oxo-3,4-dihydro-2H-1,3-benzoxazines and their nitrogen derivatives were obtained.

In the present research it was shown the 2-alkyl-4-oxo-4H-1,3-benzoxazinium salts [1] react exceptionally readily with ethyl orthoformate to give 2-(β-ethoxyvinyl)-substituted oxobenzoxazinium salts (II, Table 1). The reaction is accomplished by brief heating of perchlorates Ia-d and ethyl orthoformate (1:2) in a mixture of acetic anhydride and nitro-

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