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POLAROGRAPHY OF NITRO AND CARBONYL DERIVATIVES OF ARYLFURANS IN ANHYDROUS DIMETHYLFORMAMIDE

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It is shown that the first reversible one-electron wave in the reduction of 5-arylfurans in anhydrous dimethylformamide (DMF) corresponds to the formation of an anion radical and that the subsequent waves are associated with cleavage of the C−Hal bond in the case of halo derivatives and with reduction of the anion radical and the arylfuran fragment. The character of the reduction of 5-(p-nitrophenyl)furan derivatives is determined by the ability of the substituent in the 2 position to delocalize the negative charge. In conformity with this, the first two reversible waves of carbonyl-substituted derivatives are one-electron waves and correspond to the formation of a stable dianion, the greatest contribution to the resonance hybrid of which is made by a p-quinoid structure. The second wave of 5-(p-nitrophenyl)furan and its 2-CH_2OH derivative is irreversible and corresponds to the transfer of three electrons. Lithium ions have a substantial effect on the height and $E_{1/2}$ value of the second reduction wave, and this effect is manifested more markedly, the less the substituent in the 2 position is capable of delocalizing the negative charge. The transmission factor of the furan ring is 0.48.

It has been previously established that furfural [1] and its 5-aryl derivatives [2] in aqueous alcohol buffered media are reduced on a dropping mercury electrode in conformity with the principles characteristic for the reduction of other aromatic aldehydes. The polarographic behavior of 5-(p-R-phenyl)furfurals (I), where R=H (a), CH_3 (b), OCH_3 (c), Cl (d), Br (e), and NO_2 (f), in anhydrous dimethylformamide (DMF) was investigated

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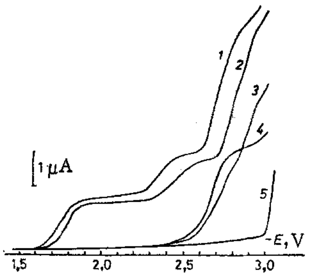

Fig. 1

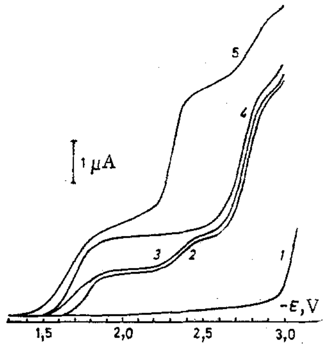

Fig. 2

Fig. 1. Polarograms of 1.0 mM solutions of 5-phenylfurfural (1), 5-(p-tolyl)furfural (2), 5-(p-tolyl)-2-hydroxymethylfuran (3) and 2-phenylfuran (4) in a 0.05 M Bu_4NClO_4 base electrolyte in DMF (5).

Fig. 2. Polarograms of a 0.78 mM solution of 5-phenylfurfural in DMF in a 0.05 M Bu_4NClO_4 base electrolyte (1) at benzoic acid concentrations of 0 (2), 0.47 (3), 1.9 (4), and 5.0 mM (5).

in the present research in order to study the electroreduction uncomplicated by protonation steps and to study the transmission of the effect of a substituent through the furan ring under these conditions.

Furfural Ia forms two waves of equal height in DMF in a tetramethylammonium iodide base electrolyte. Calculation by the Ilkovich equation and comparison of the i_{lim} values of the reduction waves of furfural Ia with the height of the first one-electron reduction wave of If in DMF make it possible to conclude that each of the waves corresponds to transfer of one electron. The $\Delta E/\Delta \log [i/(i_{lim} - i)]$ value and the cyclical voltamperometric data constitute evidence for the reversiblity of the first reduction step and the irreversibility of the second step.

Thus it is logical to suppose that, as in the reduction of aromatic aldehydes and ketones of the benzene series [3-6], the first wave of furfural Ia corresponds to the formation of ketyl anion radical and that a fast protonation reaction follows after transfer of the second electron.

More negative potentials (a rise in the base electrolyte current is observed only at −3.0 V) become accessible when tetrabutylammonium perchlorate is used as the base electrolyte. In this case, in addition to the two one-electron waves on the polarograms of furfural Ia, one observes another two poorly resolved waves at potentials more negative than −2.6 V. A comparison of the total current of these waves with the limiting current of the first two reduction waves of Ia provides evidence that they correspond to the transfer of three to four electrons.*

A new wave at more negative potentials, the height of which depends linearly on the benzoic acid concentration, develops on the polarograms of furfural Ia when proton donors (phenol, benzoic acid) are present. Since the first reduction wave of derivative Ia is reversible, it is impossible to conclude whether this is associated with a prior or subsequent protonation step. However, in excess benzoic acid the resulting wave exceeds the height of the first wave of Ia by a factor of two and becomes irreversible, i.e., it corresponds to the transfer of two electrons. In this case it may be assumed that the shift to positive potentials of the lower portion of the curve as the benzoic acid concentration is further increased (Fig. 2) is associated with the prior formation of a protonated complex.

The p-CH_3 and p-OCH_3 derivatives (Ib and Ic) are reduced in the same way as furfural Ia (Fig. 1).

The reduction of the p-Cl and p-Br derivatives of Ia presents a more complicated pattern. Additional waves, which are associated with processes involving the C−Hal bond, are present on the polarograms of these

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*The nature of these polarographic waves was not studied in the present research, but it may be assumed that they are associated both with reduction of the alcohol group formed in the first two steps of the reduction of furfural Ia and with reduction of the arylfuran fragment, which apparently proceeds in the same way as the reduction of diphenyl. This conclusion can be drawn from a comparison of the reduction waves of Ia and its derivatives in the negative-potential region with the polarograms of model compounds − 2-phenylfuran and 5-(p-tolyl)-2-hydroxymethylfuran (Fig. 1).

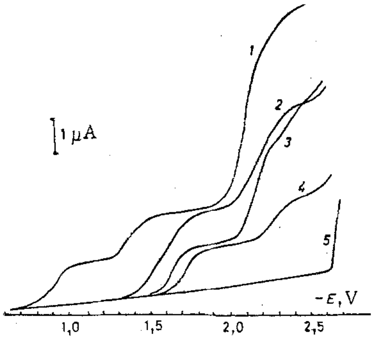


Fig. 3

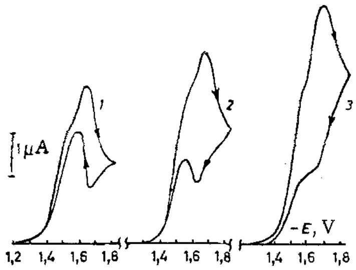


Fig. 4

Fig. 3. Polarograms of 1.0 mM solutions of 5-(p-nitrophenylfurfural (1), 5-(p-bromophenyl)furfural (2), 5-(p-chlorophenyl)furfural (3), and 5-phenylfurfural (4) in a 0.05 M Me_4Ni base electrolyte in DMF (5).

Fig. 4. Cyclical voltamperograms of a 1.0 mM solution of 5-(p-bromophenyl)furfural in the presence of 0.95 mM phenol in a 0.05 M solution of Bu_4NClO_4 base electrolyte in DMF at a potential-scanning rate of 20 (1), 50 (2), and 100 mV/sec (3).

compounds, in addition to the reduction wave indicated above. An irreversible two-electron wave follows the first reversible one-electron wave of reduction of Id in a tetramethylammonium iodide base electrolyte (Fig. 3). In conformity with the electron-acceptor properties of the Cl substituent, the first wave of furfural Id is found at more positive potentials and the first wave of Ia, and the $E_{1/2}$ values of the first reduction waves of furfurals Ia-d are linked by a correlation relationship with the σ_p substituent constants ($\rho = 0.315$, $R = 0.983$, and $s_0 = 0.016$). The third wave of Id coincides with respect to the potentials with the second wave of Ia. Thus, whereas the first reduction wave of furfural Id is due to electron transfer to the aldehyde group, at the potentials of the second wave cleavage of the C−Cl bond in the ketyl anion radical of derivative Id probably occurs with rapid proton transfer, i.e., the anion radical of Ia is formed. In a tetrabutylammonium perchlorate base electrolyte the second two-electron reduction wave of Id is observed at more negative potentials and merges with the third reduction wave, and a one-electron wave and, at more negative potentials, an elongated wave, the height of which corresponds to three electrons, are therefore observed on the polarograms. When proton donors (benzoic acid) are present, the anion radical of Id is protonated rapidly, and transfer of a second electron becomes possible at the potentials of the first wave; as in the case of furfural Ia, this wave therefore is doubled and shifted to the positive-potential region, whereas the wave of furfural Id decreases to the level corresponding to the transfer of two electrons.

The first step in the reduction of Ie is probably associated with cleavage of the C−Br bond. The first wave on the polarograms of this compound (Fig. 3) is observed at considerably more positive potentials than the first wave of Id. This wave is irreversible, and an anode peak is absent on the cyclical voltamperograms at the potentials of the cathode peak, but an anode peak due to the formation of the Br^- anion appears in the positive-potential region. A Br^- anode wave also appears in the polarograms after electrolysis at the potentials of the first wave. It is difficult to conceive of a mechanism for the reduction of this compound from the polarographic data. As in the case of Id, the total current of Ie in a tetramethylammonium iodide base electrolyte corresponds to the transfer of four electrons, and the first wave corresponds to the stepwise transfer of two electrons. Equimolar amounts of benzoic acid have practically no effect on the magnitude of the limiting current of this wave. The steepness of the wave increases in excess benzoic acid such that the break on the wave becomes imperceptible and the wave is shifted to positive potentials.

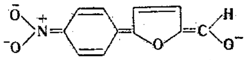
Examples of the cleavage of the C−Br bond in anion radicals after transfer of one electron in the electroreduction in DMF of 4-(p-bromostyryl)pyridine [7], p-bromobenzophenone [5], p-bromonitrobenzene [8], etc., have been described in the literature. In these studies it was established that a chemical step involving cleavage of the C−Br bond, which in itself is reversible, follows transfer of one electron, but this step is followed by irreversible detachment of a proton from the solvent. Electrolysis at the potentials of the limiting current of the first wave of p-bromobenzophenone leads to the formation of benzophenones [5]. This reduction scheme cannot be adopted for furfural Ie, since, as we have already noted above, the reduction wave of Ie is found at more positive potentials than the first reduction wave of Id, whereas the electron-acceptor properties of the

Br and Cl substituents are practically identical, and transfer of a second electron (the upper portion of the curve), although it does coincide in potential with the first reduction wave of 5-phenylfurfural, is irreversible. In addition, three one-electron steps are observed in the reduction of p-bromobenzophenone [5], whereas four electrons are consumed in the reduction of 5-(p-bromophenyl)furfural. It is interesting to note that the anionic products arising at the potentials of the first wave are capable of reacting with a component of the medium at a relatively low rate, as a result of which particles that are capable of undergoing reduction at the potentials of the first wave are formed, and an equimolar amount of benzoic acid does not affect the rate of this process. This is responsible for the unusual form of the cyclical curves with increasing cathode currents upon application of a potential in the anode direction at a low rate (Fig. 4).

It was established in [9] that the reduction of the nitro group in p-nitrobenzaldehyde and 5-(p-nitrophenyl)-furfural If in DMF in a lithium chloride base electrolyte proceeds in two successive steps with transfer of one electron in the first step and three electrons in the second. In addition, according to the data in [3, 10], only two one-electron waves are observed in the reduction of p-nitrobenzaldehyde in DMF in a tetraethylammonium iodide base electrolyte up to the discharge potentials of the base electrolyte, and the product of two-electron reduction is stabilized by the formation of a quinoid structure:

The first two waves are also reversible in the reduction of If in DMF in quaternary ammonium salt base electrolytes, and each corresponds to the transfer of one electron.

In comparison with other electron-acceptor substituents, the nitro and carbonyl groups have the maximum capacity for delocalization of the negative charge in the carbanion [11]. Thus, as in the case of p-nitrobenzaldehyde, a dianion, the maximum contribution to the resonance hybrid of which is made by a p-quinoid structure with localization of the anionic centers on the oxygen atoms of the carbonyl and nitro groups, is formed by transfer of two electrons to the furfural If molecule:



The possibility of the formation of a p-quinoid structure and the large distance between the charges, which substantially decreases the coulombic interaction, determine the energic advantageousness and adequate stability of dianion If. As a result, it is incapable of detaching a proton from the solvent, and the subsequent reduction of this dianion is possible only at extremely negative potentials (more negative than −2.6 V in a tetrabutylammonium perchlorate base electrolyte and at somewhat more positive potentials in a tetramethylammonium iodide base electrolyte) (Fig. 3).

Since both of the primary reduction waves of furfural If are reversible, the difference in the half-wave potentials should characterize the change in the free energy during the formation of the dianion. For p-nitrobenzaldehyde, $\Delta E_{1/2}$ is 0.58 V [10], whereas $\Delta E_{1/2}$ for If is 0.45 V, i.e., an increase in the conjugation chain and the distances between the charges determine the relative facilitation of the formation of the dianion of If as compared with the dianion of p-nitrobenzaldehyde.

The i_{lim} and $E_{1/2}$ values of the first two waves of the reduction of 2-R-5-(p-nitrophenyl)furans II and furfural If are presented in Table 1. If IIa-c are reduced in the same way as furfural If, the second wave of IIe, f, as one usually observes in the reduction of the nitro group in nonaqueous media, corresponds to the transfer of three electrons. In the latter case, as in the reduction of similar substituted nitrobenzenes [10], the

TABLE 1. Limiting Currents and $E_{1/2}$ Values of the First Two Reduction Waves of 2-R-5-(p-Nitrophenyl)furans at a Depolarizer Concentration of 0.5 mM in DMF in a 0.05 M Bu_4NClO_4 and 0.5 M Bu_4NClO_4 Base Electrolyte in the Presence of 5 mM LiCl

Compound	R	0.05 M Bu_4NClO_4 base electrolyte				0.05 M Bu_4NClO_4 base electrolyte in the presence of LiCl			
		i'_{lim}, μA	i''_{lim}, μA	$-E'_{1/2}$, V	$-E''_{1/2}$, V	i'_{lim}, μA	i''_{lim}, μA	$-E'_{1/2}$, V	$-E''_{1/2}$, V
IIa	COPh	0,52	0,6	1,020	1,455	0,52	1,23	1,010	1,355
IIb	COEt	0,59	0,86	1,050	1,590	0,59	1,65	1,040	1,400
IIc	COMe	0,54	0,73	1,020	1,560	0,55	1,48	1,015	1,380
IId	COOEt	0,60	1,44	1,035	1,650	0,60	1,67	1,025	1,375
IIe	H	0,60	1,61	1,120	1,860	0,60	1,74	1,115	1,545
IIf	CH_2OH	0,49	1,34	1,125	1,890	0,50	1,67	1,115	1,545
If	CHO	0,58	0,56	1,030	1,475	0,58	1,01	1,020	1,365

product of two-electron reduction evidently is stabilized by cleavage of the N—O bonds to give the corresponding nitroso derivatives, which is capable of taking on two electrons at the potentials of the second wave. Compound IId occupies an intermediate position. Since the COOEt group is less capable of delocalizing a negative charge than the carbonyl group [11], the second reduction wave is appreciably higher than the first but, nevertheless, lower than the level corresponding to the transfer of the three electrons. One's attention is drawn to the substantial dependence of the $E_{1/2}$ value of the second reduction wave of II on the nature of the substituent. Thus, whereas the $E_{1/2}$ value of the first reduction wave is shifted by 110 mV to positive potentials on passing from derivative IId to derivative IIf, the $\Delta E_{1/2}$ value of the second reduction wave is 385 mV, i.e., the resonance hybrid with localization of the unpaired electron on the second carbon atom of the furan ring evidently makes a substantial contribution in the anion radicals of IIe and IIf, and transfer of the second electron in IIa-c and If depends substantially on the degree of direct polar conjugation with the electron-acceptor substituent in the 2 position of the furan ring.

Protonation of the anion radicals becomes possible in the presence of weak proton donors (phenol) after transfer of the first electron to the furfural If molecule. This gives rise to a shift to positive potentials of the first reduction wave of If. The second wave is shifted to an even greater degree to positive potentials, during which its limiting current increases to the level corresponding to the transfer of three electrons, and the anode oxidation peak of dianions of If vanishes on the cyclical voltamperograms. Stronger proton donors (benzoic acid) cause an increase in the first reduction wave, such that in a fivefold excess of benzoic acid the first wave is almost tripled, whereas the overall current of the first two waves approaches a level corresponding to the transfer of four electrons. The subsequent reduction of furfural If is also facilitated substantially.

The polarographic behavior of the investigated compounds is determined to a considerable degree by the cation of the inert base electrolyte. As in the case of other aromatic aldehydes and ketones [4], the formation of ion pairs during electroreduction is characteristic for furfurals Ia-c. In the reduction of benzaldehydes, as a result of the formation of ion pairs with anion radicals, the $E_{1/2}$ value of the reversible wave is shifted to positive potentials as the effective radius of the cation decreases [4].

In the case of Ia-c it is impossible to form a judgment regarding the formation of ion pairs with tetraalkylammonium cations from the $E_{1/2}$ values of the first reversible reduction waves, since the $E_{1/2}$ values lie within the limits of the experimental error. However, the second waves of these compounds are irreversible, and the depolarizer is negatively charged; it is therefore completely natural that the effect of formation of ion pairs is manifested more markedly, and the $E_{1/2}$ value of the second wave depends substantially on the size of the cation. The change in the $E_{1/2}$ value because of the formation of ion pairs increases as the charge density on the reduced particle increases [4, 12], and electron-donor substituents should prevent delocalization of the negative charge in the anion radical; the change in the $E_{1/2}$ value of the second reduction wave of Ia-c as a function of the base electrolyte cation should therefore increase as the electron-donor properties of the substituents increase. In fact, the $\Delta E_{1/2}$ values of the second wave of Ia-c are, respectively, 60, 120, and 180 mV when the tetrabutylammonium base electrolyte cation is replaced by a tetramethylammonium cation. The effect of the formation of ion pairs is manifested even more markedly in the reduction of nitro derivatives If and IIa-f. Lithium ions, for example, affect the polarographic behavior of these compounds like weak proton donors. It is well known that in a series of monovalent cations lithium has the highest capacity for the formation of ion pairs with anion radicals in DMF [4, 12]. Even in equimolar amounts the lithium ion gives rise to an increase in the second reduction wave, during which both the second and first reduction waves of furfural If are shifted to positive potentials with facilitation of the subsequent reduction of the resulting reaction product (Fig. 5). The second reduction wave is doubled in a tenfold excess of lithium ion and tends to reach the level correspond-

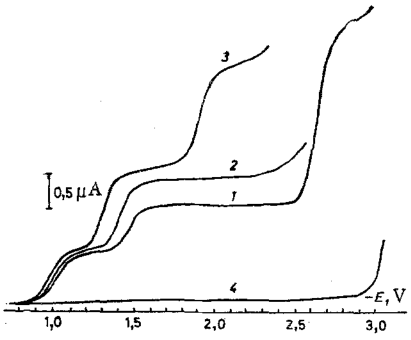


Fig. 5. Polarograms of a 0.72 mM solution of 5-(p-nitrophenyl)furfural in a 0.05 M solution of Bu_4NClO_4 base electrolyte in DMF at LiCl concentrations in solution of 0 (1), 0.83 (2), and 5.9 mM (3).

ing to the transfer of three electrons as the lithium ion concentration is further increased. As in the reduction of substituted nitrobenzenes [10], one observes the "latent current" of lithium ions, i.e., the addition of lithium ions to a DMF solution of If in 0.05 M tetrabutylammonium perchlorate does not give rise to an increase in the total reduction current, and the reduction wave of the latter appears only in a tenfold excess of lithium ions. As when weak acids are present, in addition to an increase in the second reduction wave, the anode peak of oxidation of the dianions of If vanishes on the cyclical voltamperograms of furfural If when lithium ions are added to the solution.

The change in the $E_{1/2}$ value of the second reduction wave under the influence of lithium ions may serve as a measure of the ability of anion radicals and dianions of II to form ion pairs with this cation.* As seen from Table 1, lithium ions have the smallest effect on the $E_{1/2}$ values of II that have a carbonyl substituent in the 2 position; this is in agreement with the greater ability of the carbonyl group to acquire a negative charge as compared with the COOR group [11]. In fact, the $\Delta E_{1/2}$ value of nitro derivative IId is 275 mV, whereas the $\Delta E_{1/2}$ values for IIe and IIf, which have substituents that are incapable of delocalizing the negative charge, i.e., in which the density of the negative charge on the nitro group is highest, are, respectively, 315 and 345 mV.

The effect of adsorption on $E_{1/2}$ is reduced in DMF as compared with aqueous media because of a shift in the reduction wave to negative potentials as an increase in the solubility. As established in [13], solvation of both the starting molecule of 2-substituted 5-nitrofuran and the corresponding anion radical is also reduced appreciably, and the lifetime of the latter increases. Thus the $E_{1/2}$ values of nitro derivatives of furan under these conditions are distorted to a lesser extent by adsorption and solvation effects, and by the effect of the formation of ion pairs when quaternary ammonium salts are used as the base electrolytes, as seen from the data presented above.

Our analysis of the $E_{1/2}$ values for the first reduction wave of substituted nitrobenzenes in DMF in a tetraethylammonium iodide base electrolyte, which were presented in [10], showed that there is a correlation relationship ($\rho = 0.422$, $r = 0.993$, $s_0 = 0.017$) between the $E_{1/2}$ values and the Hammett σ constants, whereas the analogous dependence for IIa-f and If has parameters $\rho = 0.203$, $r = 0.994$, and $s_0 = 0.005$, i.e., the transmission factor (π') for the furan ring is 0.48.

According to the data in [14-18], based on the results of both polarography and other physicochemical methods, the transmission factor of the furan ring is higher than for the benzene ring and ranges from 0.33-0.65. It may be assumed that the assumption that we made in a previous study [2] regarding the necessity of comparison of the ρ values of substituted benzaldehydes and 5-arylfurans in sufficiently alkaline media, in which the rate of protonation of the anion radicals can be disregarded, evidently are correct, since in this case the calculated π' value of the furan ring turns out to be 0.47 and practically coincides with the π' value determined by comparison of the correlation dependences for nitrobenzene derivatives and 2-substituted p-nitrophenylfurans.

EXPERIMENTAL

A capillary with a spatula for forced detachment of the drops and the following characteristics was used in this research: $m = 0.73$ mg/sec, $t = 0.30$ sec, and $m^{2/3} \cdot t^{1/6} = 0.662$. A silver wire submerged in the test solution served as the anode. The half-wave potentials of the investigated compounds were calculated relative to a saturated calomel electrode with respect to the "standard" (potassium) scale [19]. The research was carried out in a thermostatted cell at 25 ± 0.1°. The oxygen was removed from the solutions to be polarographed by means of a stream of purified nitrogen. The polarograms were recorded with a Radiometer PO-4 polarograph. The cyclical voltamperograms were recorded with a hanging mercury drop by means of a PAR-170 "electrochemical system" apparatus.

The methods for the preparation and purification of the investigated arylfuran derivatives were presented in [20-24].

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*Since the second wave is reversible when lithium ions are absent, the shift in the $E_{1/2}$ values of this wave may be due to the formation of ion pairs of lithium cations not only with the anion radicals of IIa, c, and If but also with the corresponding dianions.

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REACTION OF 2- AND 4-ALKOXY-1-BENZOPYRYLIUM SALTS WITH METHYLENE BASES OF HETEROCYCLIC CATIONS

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2-Alkoxy- and 2-alkylthio-1-benzopyrylium salts condense in the 2 position with methylene bases formed from methyl-substituted heterocyclic onium compounds. The 4-methoxy-1-benzopyrylium salt also reacts primarily in the 2 position, during which the benzopyrylium ring is cleaved. In addition, condensation also takes place in the 4 position with splitting out of the methoxy group.

We have previously shown that 4-methoxy-1-benzopyrylium salt I undergoes reaction in the 4 position with methylene bases formed from methyl-substituted heterocyclic oniom compounds to give unsymmetrical monomethylidynecyanines [1]. However, it was subsequently observed that products with a different structure are also formed in addition to the monomethylidynecyanines. The aim of the present research consisted in ascertaining the directions of the reaction of 4-methoxy-1-benzopyrylium salt I and of 2-ethoxy- and 2-ethylthio-1-benzopyrylium salts IIa, b with methylene bases of heterocyclic cations – 2-methylene-3-methylbenzothiazoline and its 3-ethyl analog. Although these compounds exist in solution primarily in the form of dimers, the latter exist in solution in equilibrium with the monomers [2], which also undergo reaction [3].

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