column (ℓ = 10-20 cm, d = 1-2 cm) packed with 100 × 250 μ silica gel and eluted with hexane, benzene, or a mixture of benzene and ether. The yellow nitroolefins (Ia, b)-(XIXa) were collected in the first fraction which was evaporated and the residue crystallized with addition of methanol [except (IIb) and (XIb)]. For each of the compounds (I)-(XX) the condensation was carried out twice according to the method described. Samples of the reaction mixture were analyzed by chromatography-mass spectrometry and by GLC. The yields of (Ia, b)-(XXa, b) (Table 1) were determined from the results of GLC analysis of the reaction mixtures and the divergence between two determinations (from two independent experiments) did not exceed 6% (in Table 1 the average values are quoted for the yields of (Ia, b)-(XXa, b) and the residual aldehydes (I)-(XX).

B. At 10 kbar. The ratio of the reagents was the same. Portions of the mixture were placed in Teflon ampuls of 1-1.5 ml volume and heated for 3 h at 50°C and 10 kbar. Analysis was carried out as described above.

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INFLUENCE OF THE NATURE OF THE BASE ELECTROLYTE ON THE REGIOSELECTIVITY OF THE CATHODIC HYDRODIMERIZATION OF 1-ACETYLNAPHTHALENE IN AN APROTIC MEDIUM

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UDC 541.12.038:541.135:542.953:547.657

The electrolysis of 1-acetylnaphthalene at a controlled potential [DMF, $Ba\cdot(ClO_4)_2$] leads to the formation of 5-acetyl-1,2,4,5-tetrahydro-2-methyl-2-(1-naphthyl)-1,4-methano-3-benzoxepine (yield of 60%); this is explained by the stabilization of the dimeric dianion of the "head–tail" type by the Ba^{2+} cations. The formation of 2,3-dimethyl-2,3-di-(1-naphthyl)-butane-2,3-diol is observed with the acylotropic rearrangement of the intermediate anion, leading to 2-acetylnaphthalene, in the presence of lithium cations.

In one of the recent works dedicated to the electrochemical hydrodimerization of aromatic acetyl derivatives in an aprotic medium [1], it is confirmed that the main products of the dimerization of the corresponding anion radicals (ARs) are dimers of the "head–head" type (pinacones). However, according to recent presentations [2], the regioselectivity of the dimerization of the ARs is determined by the distribution of the electron density on their outer molecular orbitals, which far from always favors the dimerization at the carbonyl group. Therefore, as an example, the electroreduction (ER) of aromatic carbonyl derivatives under conditions permitting disregard of specific interaction with the components of the medium results either in the formation of a low yield of the corresponding pinacones [3] or in the situation where they are not found at all [4]. At the same time, the dimers of the "tail–tail" type, which should be one of the main products of the reaction under consideration according to the theory of [5], are actually isolated in a high yield on the ER of anthracene derivatives in nonaqueous media [4, 6]. The dianions formed by the dimeriza-

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TABLE 1. Influence of the Composition of the Electrolyte on the Yield of the Products of the Electrolysis of 0.1 M Solutions of 1-Acetylnaphthalene in DMF

No. of the experiment	Electrolyte	Number of electrons	Isolated after chromatography, %			
			I	II	III	IV
1	0,1 M Bu_4NClO_4	0,9	20	30	10	–
2	0,1 M Bu_4NClO_4+0,1 M $Ba(ClO_4)_2$	1,1	25	40	–	10
3	0,3 M $Ba(ClO_4)_2$ *	1,5	10	15	–	60
4	0,2 M $LiClO_4$	1,1	15 †	50	–	–

*The yield of (VI) was 10%.

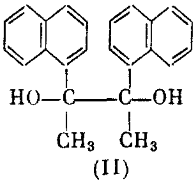
†The total yield of (I) and (VII).

tion of their ARs are probably stabilized on account of the significant delocalization of the negative charge. In the case of the carbonyl derivatives with a smaller size of the aromatic system than that of anthracene, one of the routes for the stabilization of the dimeric dianion may be provided by the formation of the ion pairs with the cations of metals. For this purpose, the utilization of the cations of divalent metals, e.g., the cations of barium, seems the most promising. However, it should thereby be taken into consideration that the cation of the metal present in the catholyte will form ion pairs not only with the dimeric dianions, but also with the ARs. The displacement of the electron density to the carbonyl group, which thereby occurs, should be accompanied by an increase in the yield of the pinacone and the decrease in the yield of the non-pinacone dimers (see, for example, [3]). In our opinion, it is precisely this circumstance which also served as the reason that the corresponding pinacones could be isolated in a high yield by Egashira et al. [1] using the ER of aromatic carbonyl derivatives in solutions containing the mixture of tetrabutylammonium and lithium salts.

In the given work, the object of the investigation, which we selected, was 1-acetylnaphthalene (I) for which the difference in the density of the unpaired electron on the carbon atoms of the carbonyl group and at the position 4 of the aromatic ring is adequately high (0.070 and 0.194 correspondingly according to the data of the CNDO/2 calculation). It could therefore be expected that the redistribution of the electron density in the ARs with the formation of the ion pairs should, in far from all cases, lead to the complete suppression of the reactions for the formation of dimers of the non-pinacone type. The ER of (I) was investigated by the method of electrolysis at a controlled potential for the experimental verification of these proposals.

RESULTS AND DISCUSSION

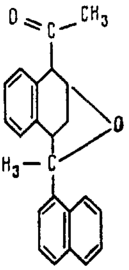
The ER of (I) was performed at the potential of the limiting current of the first polarographic wave (−1.8 to −1.9 V relative to the saturated calomel electrode) until the complete disappearance of the depolarizer was achieved. The monitoring of the concentration of (I) in the catholyte during the electrolysis was accomplished polarographically. It can be seen from Table 1 that the number of the electrons transferred to the molecule of the depolarizer in the process of the ER is close to unity in all cases (with the exception of Experiment 3). This is in complete agreement with the results of the investigation [1] of the mechanism of the ER of (I) by electroanalytical methods, according to which the formation of the corresponding AR occurs at the potentials of the first wave of this compound. At the same time, it is shown by the analysis of the reaction mixture (Table 1) that the conclusion of Egashira et al. [1] that the main reaction of these ARs is the dimerization at the carbonyl group does not correspond with the actuality. In particular, it can be seen from Table 1 that the yield of 2,3-dimethyl-2,3-di(1-naphthyl)butane-2,3-diol (II) does not exceed 30% when the cations of the metals are absent from the catholyte.



(II)

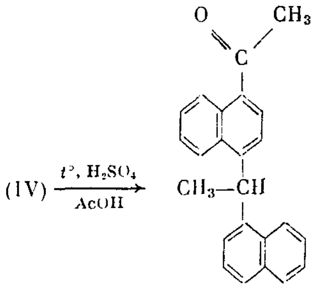
It should be emphasized that the given fact is difficult to explain by the losses occurring in the isolation of (II) since the total yield of all the products of the ER (including the resin-forming products) exceeds 90%. It is also impossible to explain the comparatively low yield of (II) under the given conditions by the marked contribution of the reactions of homogeneous (disproportionation) or heterogeneous transfer of the electron to the AR, which compete with the dimerization, since the yield of the product of the two-electron ER — 1-naphthylmethylcarbinol (III) — comprises ~10%. At the same time, the reaction mixture contains a significant amount of resin-forming products, the formation of which may be associated with the process of anion polymerization with the participation of dimeric dianions of the non-pinacone type [3]. The formation of dianions of the non-pinacone type is also indicated by the fact that the partial regeneration of the initial compound (up to 20%) is observed (Table 1, Experiment 1) with the treatment of the catholyte after the exhaustive ER. By the analogy with the chemical behavior of the products of the dimerization of the AR of 9-nitroanthracene [6] and methyl benzoate [7], it can be assumed that the regeneration of (I) is a consequence of the oxidative destruction of the dimeric dianions of the non-pinacone type.

Therefore, the isolation of dimeric products with the non-pinacone structure only seems to be possible when the ER of (I) is performed under conditions which are unfavorable for the participation of the corresponding dimeric dianion in the reactions of anionic polymerization. In fact, there are data in the literature [8] indicating that a dimer of the "head-tail" type can be isolated from the reaction mixture when the ER of (I) is performed in an alcoholic medium.



(IV)

We successfully achieved the analogous effect in an aprotic medium on account of the utilization of a barium salt. The introduction of barium cations into the catholyte noticeably stabilized the dimeric dianions of the non-pinacone type, as expected, decreasing their tendency for polymerization. This is indicated both by the decrease in the amount of the resin-forming products (Table 1, Experiment 2), and by the isolation of the dimer, to which the structure 5-acetyl-1,2,4,5-tetrahydro-2-methyl-2-(1-naphthyl)-1,4-methano-3-benzoxepine (IV) was assigned by us on the basis of spectral data (PMR, IR, and mass spectra). Additional evidence for the structure of the indicated product is the isolation of 1-(4-acetyl-1-naphthyl)-1-(1-naphthyl)ethane (V) as the result of the treatment of (IV) with a mixture of acetic and sulfuric acids.

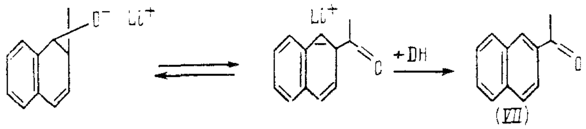


(V)

The maximal yield of (IV) was obtained by the ER of (I) using the base electrolyte of 0.3 M $Ba(ClO_4)_2$ (Table 1, Experiment 3). Under these conditions, 1-acetyl-1,4-dihydronaphthalene (VI), with which there is also evidently associated an increase in the number of electrons transferred to the molecule of the depolarizer, is formed together with the dimeric products (II) and (IV). The formation of (VI) is probably the consequence of the increase in the rate of disproportionation of the AR (I) in the presence of the metal cation with the formation of the dianion, which then undergoes protonation

$$(I)^{\overline{\cdot}} + (I)^{\overline{\cdot}} \rightarrow (I) + (I)^{=} + \xrightarrow{DH} (I) + (VI)$$

It should be noted that, as can be seen from Table 1 (Experiments 3 and 4), the substitution of the barium cation in the base electrolyte by the lithium cation leads to an increase in the yield of the pinacone (II) and the complete disappearance of (IV). One more significant feature of the ER in the 0.2 M solution of $LiClO_4$ is the presence of small amounts (~5%) of 2-acetylnaphthalene (VII) among the electrolysis products. The formation of (VII) is also evidently associated with the formation, due to the disproportionation of the AR, of the corresponding dianion; the protonation of this leads to the monoanion which forms an ion pair with the lithium cation. The migration of the functional group in the indicated anion probably proceeds by the mechanism of acylotropic tautomerism [9] via the intermediate cyclic product stabilized by the cation.



(VII)

The difference in the character of the products of the cathodic reduction of (I) in the presence of the Ba and Li cations indicates that the influence of the nature of the counterion on the regioselectivity of the dimerization of the ARs of aromatic carbonyl compounds is determined not only by the redistribution of the electron density as a result of the formation of ion pairs by the anion radicals, but also by the ability of the cation to stabilize the corresponding dimeric dianions.

EXPERIMENTAL

The instruments and methods utilized in the work were previously described [3, 4]. Compound (I) was isolated from the mixture of (I) and (VII) by chromatography on SiO_2 using hexane–2% ether, with the subsequent monitoring by NMR spectroscopy. The yield of the products was determined after the chromatography of the ether extract of the catholyte on SiO_2 following the electrolysis with the mixture of hexane–ether (up to 20% of ether) (Experiments 1 and 4) or the mixture of hexane–chloroform (up to 50% of chloroform) (Experiments 2 and 3). The products were identified by the comparison of the IR, NMR, and mass spectra with those described in the literature.

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