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ELECTROCHEMICAL DIMERIZATION OF 9-ACETYLANTHRACENE

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Previously we showed [1-4] that the direction and rate of dimerization reactions involving radical anions and dianions of aromatic compounds can be predicted quantitatively on the basis of quantum-chemical reactivity indexes. The use of these indexes in the case of aromatic carbonyl derivatives leads [2] to the conclusion that in the absence of specific interactions of the radical anions with components of the medium the yield of dimeric tail—tail-type products should be higher than the yield of the corresponding pinacols. Indeed, as was established [4], the yield of pinacol in the electrochemical reduction of acetophenone in DMFA in a Bu_4NClO_4 supporting electrolyte is close to that predicted by the theory and does not exceed 30%. However, it was not possible to recover nonpinacol-type products in this case, possibly because of their increased tendency to resinify. At the same time, the stability of such dimers should be significantly higher in the case of carbonyl derivatives of anthracene. In this regard, it is appropriate to use the example of derivatives of this series in carrying out the experimental proof of the predominant formation of tail—tail-type dimers under the conditions of electrochemical generation of ambident radical anions. In the present paper, we discuss the direction of electrochemical hydrodimerization under the conditions of preparative electrochemical reduction of 9-acetylanthracene (I) at a controlled potential in DMFA in a Bu_4NClO_4 supporting electrolyte.

RESULTS AND DISCUSSION

The results of a quantum-chemical calculation by the CNDO/2 method show that the density of the unpaired electron of the C atom of the carbonyl group in the acetophenone radical anion is significantly higher than in the radical anion of (I) (0.169 and 0.033, respectively). In its turn, the distribution of the spin density in the aromatic fragments of these species is qualitatively similar. The maximum density of the unpaired electron in the radical anion of (I) (0.216) is localized on the C^{10} atom, and that in the acetophenone radical anion is localized in the para position (0.192). A calculation carried out with a correlation equation relating the values of the dimerization rate constants of the radical anions and the values of the electron density on the reaction center [3] shows that in the case of (I) the yield of a tail—tail-type dimer can reach 85-90%, whereas the yield of pinacol (head—head dimer) should be insignificant, not more than 4-5%. For comparison, we can mention that the experimentally determined yield of pinacol in the electrochemical reduction of acetophenone is close to that predicted by the theory and is 25% [4].

The electrolysis of (I) was carried out in solutions of DMFA in a Bu_4NClO_4 supporting electrolyte at the potential of the first stage of its electrochemical reduction. During the electrolysis, the current changed little with respect to time, although polarographic monitoring of the electrochemical-reduction process indicated practically complete exhaustion of the depolarizing agent after the passage of 1 F per mole. Because hardly any new

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reduction waves of the products were observed in the polarograms at the end of the electrolysis, we can assume that the practical constancy of the current during the electrolysis was related to the phenomenon of "secondary catalysis" [5]. Apparently, the latter was due to hydrogen evolution [6] or solvent decomposition under the effect of free-radical intermediate species. Acidification of the catholyte without access of the oxygen of air resulted in the precipitation of a yellowish precipitate from the solution. Analysis of the mass spectrum (with chemical ionization) and the proton NMR spectrum of this precipitate enabled us to assign the structure of the dimer 9,9-diacetyl-9,9',10,10'-tetrahydrobianthryl (II) to the obtained product. The mass spectrum of (II) contained peaks of the molecular ion (M^+ 442) and fragments with m/z 221 and 179, and the proton NMR spectrum contained characteristic multiplets of aromatic protons (6.3-7.4 ppm) and singlets of methine protons (3.75 and 5.06 ppm) and methyl protons (2.58 ppm). According to the data of the proton NMR method with adamantane as the internal standard, the yield of (II) with respect to (I) having entered into the reaction in the series of runs was ~70%. According to the proton NMR spectrum, the filtrate contained not only a small amount of (II), but also the starting (I), anthraquinone, and trace amounts of a compound of undetermined structure. Specially carried out experiments showed that the decomposition of the dimeric anion, which was a primary product of electrochemical reduction and was formed from (II) in alkaline DMFA solutions, afforded the same products in the presence of oxygen of air. The data suggest that the actual yield of the dianion of dimer (II) after electrolysis was probably higher than 70%, but it decomposed partially during treatment.

Thus, the main product under the conditions of electrochemical generation of radical anions of (I) was the dimeric dianion with tail—tail-type structure. Because the yield of the analogous dimer in the electrochemical reduction of 9-nitroanthracene is also high [7] and close to the calculated yield, we can conclude that such a direction of the process is indeed characteristic of radical anions of 9-substituted anthracenes, as is evident from theoretical concepts.

EXPERIMENTAL

9-Acetylanthracene (I) was obtained by the procedure of [8], and Bu_4NClO_4 of polarographic-purity grade was dried under vacuum at 75°C. The DMFA was dried over 4-Å molecular sieves and distilled under vacuum.

Preparative electrolysis of (I) was carried out in an Ar atmosphere at $E = -1.72$ V in a cell with a glass diaphragm with a P-5848 potentiostat. The cathode was solid-phase mercury (~20 cm^2), the anode was a Pt screen, the reference electrode was a saturated calomel electrode, and the catholyte was 20 ml of 0.1 M Bu_4NClO_4 in DMFA (0.2-0.3% H_2O in the solution after electrolysis determined according to Fischer).

After the completion of electrolysis and separation of the anolyte in an Ar stream, 50 ml of dilute (~1%) AcOH was added to the catholyte, and the precipitate was filtered after 3 h, washed with water, and dried in a vacuum desiccator. The filtrate was extracted with ether and dried over $MgSO_4$, and the solvent was removed.

The proton NMR spectra were recorded on a Varian-250 spectrometer with respect to TMS, the IR spectra were obtained on a UR-20 instrument, and the mass spectra were obtained on a Kratos Ms-30 mass spectrometer (with direct sample injection at ionization-chamber temperature 100°C with ionizing-electron energy 200 eV and CH_4 reagent gas).

9,9'-Diacetyl-9,9',10,10'-tetrahydrobianthryl. IR spectrum (ν, cm^{-1}): 580, 800, 1160, 1360, 1480, 1710, 3030 ($CHCl_3$). Proton NMR spectrum (δ, ppm): 2.58 singlet (6H, CH_3), 3.75 singlet (2H, HC^{10}, $HC^{10'}$), 5.06 singlet (2H, HC^9, $HC^{9'}$), 6.3-6.33 multiplet (4H, $HC^{4,5}$, $HC^{4',5'}$), 6.92-6.98 multiplet (4H, $HC^{3,6}$, $HC^{3',6'}$), 7.22-7.28 multiplet (4H, $HC^{2,7}$, $HC^{2',7'}$), 7.42-7.45 multiplet (4H, $HC^{1,8}$, $HC^{1',8'}$). Mass spectrum (m/z, %): M^+442(100), 223(36.6), 221(96.5), 179(41), 151(40.6), 83(37.5). Found, %: C 86.86, H 5.86. $C_{32}H_{26}O_2$, mol. wt. 442.30. Calculated, %: C 86.87, H 5.88.

CONCLUSIONS

It was shown that the main product of the one-electron electrochemical reduction of 9-acetylanthracene in an aprotic solvent is a tail—tail-type 9,9-diacetyl-9,9',10,10'-tetrahydrobianthryl dimer.

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REACTION OF POLYFLUOROAROMATICS WITH o- AND p- AMINOPHENOLS IN DMF

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The reaction of aromatic and heteroaromatic compounds containing an activated halogen atom with aminophenols can lead to hydroxydiarylamines or aminodiphenyl ethers depending upon the basicity of the medium [1-9]. In the latter case a strong base or an alkali metal aminophenolate is required. The reaction with o-aminophenols may be complicated by conversion of the o-aminodiphenyl esters to o-hydroxydiarylamines (the Smiles Rearrangement) [1-3, 10, 11].

There are literature reports of the reactions of polyfluoroaromatics of the type C_6F_5X (X = F, H, Cl, C_6F_5) with o- and p- aminophenols in pyridine with NaOH [12-14] and also with potassium p-aminophenolate in DMF [15] which led to substitution of one or two fluorine atoms by the aminophenoxy group. The possibility of obtaining diphenylamines as well was not investigated.

In this work we studied the reaction of hexafluorobenzene and pentafluoronitrobenzene (I) with o- and p-aminophenols in DMF under neutral and basic conditions. It was found that C_6F_6 did not react with aminophenols in DMF when heated to 80°C, in agreement with the inertness of polyfluoroaromatic when compared with aromatic amines [16, 17]. In basic media, where the $H_2NC_6H_4O^-$ nucleophile is formed, a reaction occurred forming a mixture of products involving substitution of one or two F atoms by the aminophenoxy group (II, III). As was to be expected [14, 15] the disubstituted compounds of type II had the aminophenoxy group in positions 2 or 4. Isomeric hydroxydiarylamines were not discovered in the reaction mixtures. (See Scheme at top of next page.)

By contrast pentafluoronitrobenzene (I), with a significantly higher fluorine nucleophilic lability [18], reacted readily with aminophenols both with and without base. In neutral medium the reaction occurred completely at the amino group giving hydroxydiarylamines IVa, b (see Scheme (I) on next page).

Reaction of I with aminophenols in anhydrous DMF with solid NaOH gave a complex mixture of products even when cooled to −20°C. In the case of o-aminophenol the process occurred more simply in the presence of aqueous NaOH solution at 0°C to give 4-nitro-2,3,5,6-tetra-

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