ELECTRON TRANSFER IN THE REDUCTION OF THE ACRIDINIUM CATION WITH BOROHYDRIDE

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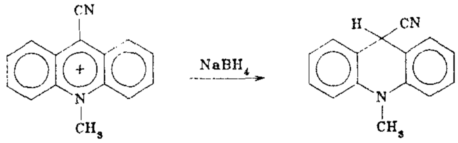
The reaction between the cyanoacridinium cation and sodium borohydride was studied by EPR spectroscopy and cyclical voltammetry. It is shown that the formation of a cyanoacridinyl radical precedes the formation of the reaction product, viz., N-methyl-9-cyano-9,10-dihydroacridine. It is concluded that the borohydride anion may be an electron-donor in this reaction.

The reduction of unsaturated compounds by means of complex metal hydrides, which is widely used in organic synthesis, has traditionally been regarded as a result involving direct transfer of a hydride ion [1, 2]. However, in the last 2-3 years there have been reports of SET mechanisms in the reaction of aluminum hydrides and borohydrides with heterocyclic bases [3], alcohol [4], aromatic ketones [5], aryl and alkyl halides [6-8], and the dipyrazolinyl dication [9].

In the present research we investigated the reaction of sodium borohydride with a heteroaromatic cation of the azinium series, viz., the 9-cyano-10-methylacridinium cation (I). This cation has clearly expressed acceptor properties (its one-electron reduction potential is 0.04 V [10]) and is capable of readily adding H^- to give a stable dihydro derivative of acridine.

The reaction was carried out at room temperature in dimethylformamide (DMF). The color of the reaction solution changes from dark purplish red to light yellow as a result of a vigorous process that is accompanied by significant gas evolution. An analysis of the gas by IR spectroscopy showed that boron hydride products are absent and that the characteristic absorption at 945-974, 1140-1205, 1180, and 1600-2220 cm^{-1} that is due to vibrations of the B—H bond is not observed in the spectra. A colorless hydrogenation product, viz., 9-cyano-10-methyl-9,10-dihydroacridine (II), which was identical to the product of addition of KCN to N-methylacridine [11], was isolated from the reaction solution by precipitation with water.



I II

To ascertain the possibility of one-electron transfer in hydrogenation with sodium borohydride we made a study of this reaction by EPR spectroscopy. The presence in cation I of annelated benzene rings attached to the pyridine ring and the presence of a nitrile group, which promotes delocalization of the unpaired electron, made it possible to hope that this sort of transfer is possible. In a study of the reaction mixture in the spectrometer cell (with an equimolar reagent ratio, DMF as the solvent, and a nitrogen atmosphere) we were able to observe the formation of an intense well-resolved spectrum that belongs to the 9-cyanoacridinyl radical (III) [11, 12]. Precisely the same spectrum was recorded under conditions corresponding to the electrochemical one-electron reduction of cation I in dimethylformamide ($E_{1/2}$ = 0.04 V,* i = 9.6 μA). A mixture of cation I with triethylamine,

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*Here and subsequently, the potentials are reduced relative to an aqueous saturated calomel electrode with a solution of tetrabutylammonium perchlorate as the inert electrolyte.

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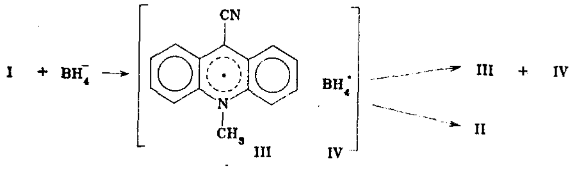
which is an electron donor that is incapable of releasing hydrogen, also has a similar spectrum.

In order to obtain an electrochemical model of the reaction with sodium borohydride we studied the behavior of the latter in the case of oxidation on an electrode amalgamated with gold. Electrochemical oxidation takes place in one one-electron step (half-wave potential $E_{1/2} = -0.19$ V). Recording of the cyclical voltammetric spectrum on the same stationary electrode (at a potential-scan rate of 0.136 V/sec) made it possible to establish that the oxidation is an irreversible process ($E_{pa} = -0.19$ V). Consequently, sodium borohydride may be an electron donor in the electrochemical reaction. However, it must be noted that, since the oxidation of $NaBH_4$ is an irreversible process, the potential can serve only to qualitatively characterize its donor properties.

The data presented above and the previously obtained data [3-9] make it possible, with a sufficient foundation, to propose that the first step in the reaction of sodium borohydride and the 9-cyano-10-methylacridinium ion is electron transfer from the metal hydride to the heteroaromatic cation to give a radical pair (III and IV).



Radicals III and IV react with one another to give acridan II. Some of the radicals are capable of emerging from the reaction cage. The acridinyl radical is so stable that it is recorded by EPR spectroscopy. The subsequent transformations of radicals III and IV probably proceed via the schemes described in [3-9, 11].

The reaction of radical III with a solvent proton with subsequent reduction of the resulting cation radical to dihydro compound II may be an alternative to transfer of hydrogen from the borohydride to the cation. To verify this, we carried out the investigated reaction in $DMF-D_2O-CD_3OD$. Recording of the ^1H NMR spectrum of product II showed that deuterium exchange with the solvent does not occur.

Thus in the present research we have shown that sodium borohydride displays electron-donor properties not only in the reaction with an organic cation that is capable of accepting only electrons [9] but also in the reaction with a hydride hydrogen acceptor; this was also demonstrated in the case of the heteroaromatic N-methyl-9-cyanoacridinium cation.

EXPERIMENTAL

The electrochemical investigation was conducted in solution in DMF at a concentration of $5 \cdot 10^{-4}$ mole/liter. The amalgamated gold disk electrodes (r = 1 mm) [both rotating (n = 3000 rpm) and stationary] had designs similar to those in [13]. The voltammetric curves were recorded via a three-electrode scheme with a P-5848 potentiostat and a PDP-004 two-coordinate potentiometer. An external source of triangular pulses was used to record the cyclical voltammetric curves. The half-conversion lifetimes of the azinyl radicals were estimated from cyclical voltammetric data. The EPR spectra were recorded with a Rubin radiospectrometer at room temperature; the concentration of the compounds was $2 \cdot 10^{-3}$ mole/liter. The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Perkin–Elmer R12B spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard.

N-Methyl-9-cyano-9,10-dihydroacridine (II) was obtained by the reaction of solutions of 9-cyano-N-methylacridinium perchlorate (I) and $NaBH_4$ in DMF (the concentration of the compounds was 0.05 mole/liter). The acridan was precipitated by means of water and was crystallized from alcohol. PMR spectrum: 5.18 (1H, s, 9-H) and 3.52 ppm (3H, s, CH_3).

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THREE-DIMENSIONAL STRUCTURES AND CHEMICAL-IONIZATION MASS SPECTRA OF ISOMERIC OXIMES OF 2-SUBSTITUTED 3-QUINUCLIDONES

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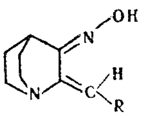
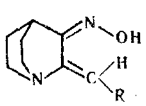
The chemical-ionization (CI; isobutane and ammonia as the reactant gases) mass spectra of 2-arylmethylene-3-quinuclidone oximes, which can exist in syn-cis, anti-cis, and syn-trans isomeric forms, were studied. A significant difference in the CI spectra of the cis and trans isomers, which makes it possible to unambiguously determine the configuration of the substituent in the 2 position, was established. It was found that the CI spectra of the syn and anti isomers differ substantially with respect to the ratios of the intensities of the MH$^+$ and $[MH - CH_4]^+$ ion peaks ($I_{MH^+}/I_{[MH - CH_4]^+}$), and this makes it possible to identify the syn and anti isomers by comparison of their individual CI spectra. The spatial configurations of 2-furyl- and 2-thienylmethylene-3-quinuclidones were established on the basis of the principles found.

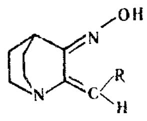
The three-dimensional structures of 2-arylmethylene-3-quinuclidone oximes, for which existence in four isomeric forms is possible owing to cis-trans and syn-anti isomerism, were established in [1] by NMR spectroscopy and electron-impact (EI) mass spectrometry:



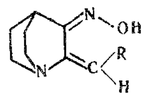
syn-cis



anti-cis



syn-trans



anti-trans

However, the formation of an anti-trans isomer was not observed in a single case, evidently because of pronounced steric hindrance, and three geometrical isomers, viz., syn-cis, anti-cis, and syn-trans, are primarily realized.

Chromatographic mass-spectrometric analysis makes it possible to reliably distinguish the cis and trans isomers from the relative retention times and the characteristic differences observed in the EI mass spectra. However, a necessary condition for the successful performance of this sort of analysis is a comparative study of a pair of geometrical isomers in each case. In the analysis of only one isomer neither data on the retention times nor the EI mass spectra make it possible to obtain unambiguous information regarding its stereo-

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