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DUAL REACTIVITY OF 1,2-DISUBSTITUTED DIHYDRO-N-HETEROAROMATIC SYSTEMS.

2.* MECHANISM OF THE DEHYDROGENATION OF N-ACYLDIHYDROQUINOLINES AND ISOQUINOLINES WITH 2,2,6,6-TETRAMETHYL-1-OXOPIPERIDINIUM PERCHLORATE

Z. M. Skorobogatova, V. A. Golubev, and A. K. Sheinkman

UDC 541.124:542.941.8:547.751.831.833

The mechanism of the heterolytic dehydrogenation of various N-acyl derivatives of α-substituted 1,2-dihydroquinolines and isoquinolines with 2,2,6,6-tetramethyl-1-oxopiperidinium perchlorate was investigated.

In a previous communication we demonstrated [1] that the aromatization of partially hydrogenated nitrogen heterocycles can be realized by means of various organic and inorganic cations, during which the heterocycles are converted to aromatic systems both as a result of splitting out of hydrogen and as a consequence of the loss of a geminal substituent [2, 3].

New selective dehydrogenating agents for the aromatization of α-substituted N-acyldihydroquinolines and isoquinolines, viz., oxo ammonium salts, were recently discovered [1, 4]. To obtain information regarding the mechanism of dehydrogenation by these salts and to develop the optimum methods for the synthesis of previously difficult-to-obtain α-substituted N-acylquinolinium and isoquinolinium salts we investigated the reactions of N-benzoyl-α-(3-indolyl)-1,2-dihydroquinoline (I) and the corresponding isoquinoline II with 2,2,6,6-tetramethyl-1-oxopiperidinium perchlorate (III).

The stoichiometry and kinetics of oxidation of dihydrobenzopyridines (DHP) I and II were studied in acetonitrile solution, in which both the starting reagents and the final products are stable. The experiments were carried out in air or in an oxygen or argon atmosphere.

Dihydrobenzopyridines I and II are dehydrogenated quantitatively by oxopiperidinium salt III to the corresponding benzopyridinium cations (BP^+) IV and V. Oxopiperidinium

*See [1] for Communication 1.

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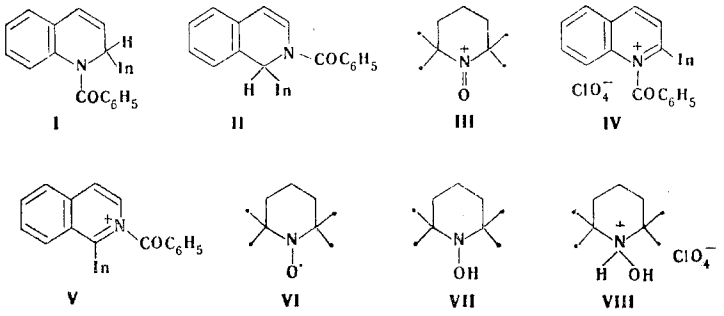
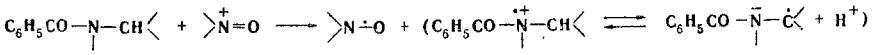
cation III is simultaneously reduced to 2,2,6,6-tetramethylpiperidine-1-oxyl (VI) and the corresponding hydroxypiperidine VII and hydroxypiperidinium cation VIII:



I II III IV V VI VII VIII

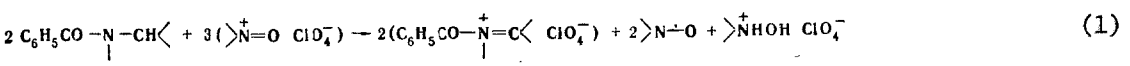
in = 3-indolyl

The oxidation of the DHP to the corresponding benzopyridinium salts may proceed via two [5-8] alternative mechanisms, viz., a heterolytic mechanism that includes transfer of a hydride ion from the DHP to the oxidizing agent, and a homolytic mechanism that is realized through the successive transfer of two electrons and a proton to the oxidizing agent. Active (with respect to oxygen) benzopyridinyl radicals should develop in the latter case:



However, such radicals cannot be detected by EPR spectroscopy or from the change in stoichiometry and rate of dehydrogenation of the DHP in the presence of oxygen. The dehydrogenation of N-acylhydrobenzopyridines by oxopiperidinium salts, like the oxidation of alcohols by these cations [9], is therefore evidently realized via a heterolytic mechanism.

When the dehydrogenation of DHP is carried out in spectrally pure and dry acetonitrile, 3 moles of cation III, of which 2 moles are reduced to the VI radical, and 1 mole is reduced to the VIII cation, are consumed per 2 moles of DHP:



(1)

The oxidation of DHP under these conditions is virtually irreversible, and stoichiometry (1) is strictly observed over the investigated range of reagent concentrations from 10^{-4} to 0.3 mole/liter at 20 to 55°C.

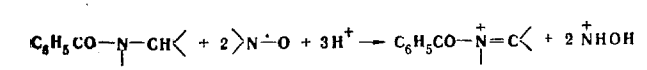
Oxygen dissolved in the acetonitrile at an oxygen pressure of less than 1 atm does not affect the stoichiometry of this reaction, which is also retained when excess oxopiperidinium salt III is used but changes when insufficient oxidizing agent is present.

The stoichiometry of the reaction of DHP with oxopiperidinium perchlorate III depends on the acidity of the medium: The degree of conversion of cation III to radical VI decreases and the fraction of cation VIII increases as the acidity is increased. At hydrogen ion activities $\geqslant 10^{-2}$ mole/liter in the reaction mixture the reaction proceeds in accordance with the equation

(2)

For the realization of this stoichiometry it is necessary to have an excess of acid HX, which depends on the strength of HX and on the initial concentrations of the reagents. In the case of $HClO_4$ and CF_3COOH, a 1% excess of the acid is required when $[DHP]_0 = [\overset{+}{=}O]_0 \approx 0.1$ mole/liter, whereas a twofold to threefold excess is necessary when the weaker CCl_3COOH is used.

In addition to cation III, the product of its one-electron reduction, viz., piperidine oxyl VI, is also a dehydrogenating agent. In an acidic medium this radical quantitatively oxidizes dihydroquinolines I and II to the corresponding benzopyridinium salts IV and V in accordance with the equation



(3)

TABLE 1. Rate Constants for the Oxidation of Dihydrobenzopyridines I and II with 2,2,6,6-Tetramethyl-1-oxopiperidinium Perchlorate in Acetonitrile in Air

Oxidized compound	t°	10^4 C_0	10^4 $[III]_0$	10^4 k', sec^{-1}	10^2 k_1, liters/mole-sec
		moles/liter			
I	25	1	50	2,7±0,01	5,3±0,2
I	25*	1	50	2,8±0,01	5,6±0,2
I	25	5	30	1,62±0,06	5,4±0,2
I	25	5	50	2,9±0,04	5,8±0,1
I	25	5	100	5,4±0,2	5,4±0,2
I	25†	5	200	10,9±0,4	5,4±0,2
I	25‡	5	200	11,4±0,2	5,7±0,1
I	25	10	100	5,6±0,2	5,6±0,2
I	25	30	1	2,6±0,04	5,7±0,1
I	25	50	1	4,1±0,08	5,4±0,1
I	25*	50	1	2,8±0,01	5,6±0,2
I	35	5	100	15,1±0,3	15,1±0,3
I	45	5	100	35,4±0,3	35,4±0,3
I	55	5	100	65,7±0,4	65,7±0,4
II	25	5	30	1,55±0,002	5,16±0,05
II	25	5	50	2,62±0,02	5,24±0,05
II	25	5	100	5,19±0,05	5,19±0,05
II	25	5	200	10,0±0,2	5,0±0,1

*In the presence of 0.01 M CCl_3COOH.
†In an O_2 atmosphere.
‡In an inert atmosphere.

For the preparative synthesis of perchlorates IV and V this reaction was carried out in acetonitrile solutions in the presence of a small excess of $HClO_4$. However, other acids can be used for the preparation of benzopyridinium salts with other anions.

The rate of oxidation of DHP I and II was determined from the accumulation of cations IV and V and piperidine oxyl VI, the concentrations of which were measured by spectrophotometry and EPR spectroscopy, respectively. The instantaneous concentrations of the reagents were calculated with allowance for the stoichiometry of the reaction from the difference in the initial concentrations of the reagents and the instantaneous concentrations of the reaction products.

When a large excess of one of the reagents is present, the oxidation of the DHP or the reduction of III proceeds in accordance with pseudofirst-order equations. The pseudomonomolecular rate constants are directly proportional to the concentrations of the excess reagent, while the bimolecular rate constants $K_1 = K'[=\overset{+}{N}=O]_0 = \alpha K'/[DHP]_0$ are independent of the stoichiometry of the reaction and the initial concentrations of the reagents (Table 1). Thus the reaction rate is described by the second-order equation

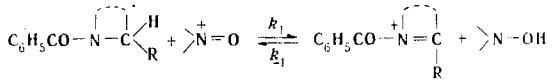
$$W = -\frac{d[\text{DHP}]}{d\sigma} = -\alpha\frac{d[=\overset{+}{N}=O]}{d\sigma} = K_1[\text{DHP}][=\overset{+}{N}=O], \quad (4)$$

where α is the ratio of the stoichiometric coefficients from Eqs. (1) and (2) and is 2/3 or 1.

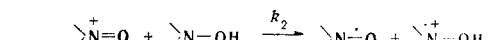
The rates of dehydrogenation of dihydroquinoline I and dihydroisoquinoline II differ insignificantly, while the bimolecular rate constants (K_1) at 25°C are $(5.5 \pm 0.1)\cdot10^{-2}$ and $(5.1 \pm 0.1)\cdot10^{-2}$ liter/mole•sec for I and II, respectively, with a probability of 95%. As the temperature is raised, the rate of oxidation of dihydroquinoline I increases in accordance with the equation $\log K_1 = 10.77 - 16{,}390/4.575T$. The activation energy of this reaction is 16.39 kcal/mole (68.6 kJ/mole), while the preexponential factor, viz., $5.93\cdot10^{10}$, is close to the average value for normal bimolecular reactions [10].

The rates of oxidation of the DHP, like the stoichiometry of these reactions, do not depend on the concentration of oxygen dissolved in the acetonitrile.

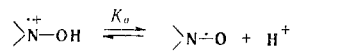
The results with respect to the kinetics and stoichiometry of the oxidation of DHP with 2,2,6,6-tetramethyl-1-oxopiperidinium perchlorate are in complete agreement with the following reaction mechanism:



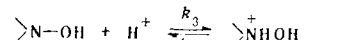
(5)



(6)



(7)



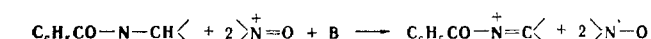
(8)

According to this scheme, the oxidation of DHP with oxopiperidinium perchlorate III and piperidine oxyl VI occurs via the reaction of the DHP with oxopiperidinium salt III. The resulting hydroxypiperidine VII subsequently undergoes reversible oxidation by the oxopiperidinium cation to radical VI or is protonated by acid to give cation VIII. According to this mechanism, the rate of consumption of the DHP and accumulation of benzopyridinium cations is independent of the empirical stoichiometry of the reaction and will be determined by kinetic Eq. (4) when $V_1 > V_{-1}$. The irreversibility of step (5) is explained by the higher redox potential of cation III than in the case of benzopyridinium cations. The standard potentials for the reduction of cation III to radical VI and hydroxypiperidine VII are 0.75 and 0.68 with respect to a standard hydrogen electrode [11], while the potentials for the reduction of pyridinium cations to dihydropyridines are ±0.2 V [12]. The inequality $V_1 > V_{-1}$ is therefore valid even in the case of virtually complete conversion of the reagents. In conformity with this, the experimental rate constants (k_1) are the rate constants for transfer of a hydride ion from the DHP to cation III.

Schemes (5)-(8) completely explain the observed stoichiometry of the reactions of DHP with oxopiperidinium perchlorate III.

The experimentally observed stoichiometry of reaction (1) is explained by the fact that $HClO_4$ is a stronger acid (by 17 orders of magnitude) than the VIII cation, for which pK_a = 6.9 [13]. The $HClO_4$ formed via Eqs. (6) and (7) is therefore converted quantitatively to hydroxypiperidinium perchlorate VIII, and when $V_2 > V_1$, the final products of the reduction of cation III are piperidine oxyl radical VI and cation VIII.

If the $HClO_4$ is tied up by a base (B) that is stronger than VII, the stoichiometry of the reaction of the DHP with III should correspond to the equation



(9)

The oxidation of DHP with oxopiperidinium salts of weak acids such as oxopiperidinium acetate should proceed in accordance with a similar equation. In addition if the primary product of reduction of III, viz., hydroxypiperidine VII, is tied up by excess hydrochloric acid, the stoichiometry of the dehydrogenation of the DHP will be equal to the sum of Eqs. (5) and (8) and will coincide with the experimentally observed stoichiometry (2).

Mechanism (5) and (8) also explains the dehydrogenating activity of piperidine oxyl VI in an acidic medium, which is due to its disproportionation to cations III and VIII and reaction of the former with the DHP. When pH < 2, equilibria (6)-(8) are shifted to favor the disproportionation products [13], and the oxidation of the DHP by piperidine oxyl VI therefore proceeds via Eq. (3), which is in agreement with the experimental results.

With respect to their selectivity, the oxopiperidinium salts differ substantially from other oxidizing agents used for the aromatization of heterocyclic dihydro compounds. The difference consists in the fact that cation III is exclusively a dehydrogenating agent, while oxidizing agents such as trityl perchlorate or heteroaromatic cations aromatize dihydrobenzopyridines in a number of cases by detachment of a geminal substituent [2, 3]. The high selectivity of oxopiperidinium salts is evidently explained by the fact that they are very strong oxidizing agents with $E^\circ_{\overset{+}{N}=O/=NOH} = 0.6$ and extremely mild electrophilic agents with pK_a = 14.5 [14]. Oxopiperidinium cation III therefore detaches a hydride ion at a high rate virtually without involvement of the geminal substituents.

Thus oxopiperidinium perchlorate quantitatively oxidizes dihydrobenzopyridines to the corresponding benzopyridinium salts. In the rate-determining step of the reaction a hydride

ion is evidently transferred from the DHP to the III cation, and the resulting hydroxypiperidine VII is converted by reaction with oxopiperidinium ion III to piperidine oxyl VI and by protonation to hydroxypiperidinium ion VIII.

In an acidic medium at pH < 2 tetraalkyl nitroxyl radicals VI quantitatively dehydrogenate the DHP to the corresponding benzopyridinium salts. The intermediate in this reaction is cation III, which is formed by disproportionation of radical VI.

EXPERIMENTAL

Starting benzoyldihydroquinoline I and benzoyldihydroisoquinoline II were obtained by the method in [15] and were recrystallized twice from acetonitrile. Oxopiperidinium perchlorate III was obtained by the method in [16] and was crystallized from acetonitrile. The percentage of piperidinium perchlorate III in the samples used for the kinetic measurements was 90.5 ± 0.3% according to the results of iodometric titration. The IR spectra were recorded with a UR-20 spectrometer. The melting points were determined with a Boetius heating stage.

Method Used for the Kinetic Measurements. The kinetic measurements were made with RÉ-1301 and ÉPA-2M radiospectrometers and a Specord UV-vis spectrophotometer. Solutions of the reagents in spectrally pure acetonitrile were mixed at room temperature, and the reaction mixture was heated up rapidly to the experimental temperature and transferred to thermostatable cuvettes for the spectrophotometric measurements or ampuls for the EPR measurements. The temperature during the experiments was maintained with an accuracy of ±0.5°C. The reaction rate during the spectrophotometric measurements was determined from the change in the optical density of the reaction mixture at 23,250 and 24,490 cm^{-1} due to the formation of quinolinium and isoquinolinium cations IV and V respectively. During the EPR measurements the reaction rate was determined from the accumulation of piperidine oxyl VI in the reaction mixture. When the experiments were carried out in an argon or oxygen atmosphere, these gases were bubbled by means of a fine capillary through the ampul for recording of the EPR spectra.

Methods Used for Quantitative Analysis. The piperidine oxyl concentration in the reaction mixture was determined from the formula $[VI] = Ic_{st}/I_{st}$, where I and I_{st} are the amplitudes of the first components of the EPR spectra of the reaction mixture and solutions of piperidine oxyl VI in the corresponding solvent with known concentrations c_{st}. The solutions to be analyzed and the standard solutions were placed in the same ampul with a diameter of 0.8 mm, and the spectra were recorded under identical conditions. A linear dependence of I on [VI] was strictly observed at concentrations $5 \cdot 10^{-4} > [VI] > 10^{-5}$ mole/liter and at the uhf and hf modulation energy levels that we used. The accuracy in the determination of [VI] was ±3%.

The concentrations of perchlorates IV and V in the acetonitrile solutions were determined from the optical densities of the absorption bands of these substances at 23,250 and 24,490 cm^{-1} and the molar extinction coefficients [$(1.8 \pm 0.01) \cdot 10^{-4}$ and $(7.5 \pm 0.07) \cdot 10^{-3}$ liter/mole-cm, respectively] and at concentrations 10^2 [III] ≤ $[BP^+]$ ≥ 10^2 [VI] radical VI and cation III virtually do not interfere with the determination of cations IV and V. The accuracy in the determination of the BP^+ concentration was ±3%.

To determine the amount of hydroxypiperidinium perchlorate VIII formed we oxidized it in an aqueous alkaline medium to piperidine oxyl VI. For this, a known volume of the reaction mixture was diluted with a 0.1 NaOH solution containing 10^{-5} mole/liter $CuSO_4$ and shaken in air for 3-5 min. During this period, the hydroxypiperidine when $[VIII]_0 \approx (1\text{-}5) \cdot 10^{-4}$ mole/liter was oxidized to radical VI in accordance with the equation

$$\overset{+}{\rangle}NHOH + O_2 \xrightarrow{+Cu^{2+}} \rangle N\dot{-}O + H_2O_2$$

The amount of this radical was determined by EPR spectroscopy with respect to a solution of piperidine oxyl with $c_{st} = 5 \cdot 10^{-4}$ mole/liter in 0.1 N aqueous NaOH. The VIII concentration in the reaction solution was calculated from the formula

$$[VIII] = n[VI]_\Sigma - [VI],$$

where $[VI]_\Sigma$ and [VI] are the concentrations of the radical in the alkaline and starting solutions, and n is the dilution of the starting solution. The accuracy in the determination was ±5%. Cation III, which decomposes in an alkaline medium to give radical VI, interfered with the determination of [VIII].

The amount of unchanged oxopiperidinium perchlorate in the reaction product was determined by iodometric titration in an acetate buffer. For this, a solution containing 0.1-0.2 mmole of cation III was added to 10 ml of acetate buffer, the insoluble products were removed by filtration, and the filtrate was treated with 1 g of KI. The iodine liberated after 3 min was titrated with 0.2 N Na_2SO_3. The reaction proceeds in accordance with the stoichiometric equation

$$2\rangle\overset{+}{N}=O + 2I^- \longrightarrow 2\rangle N\text{–}O + I_2$$

Quinolinium and isoquinolinium salts IV and V interfered with the determination. Depressed results were obtained at comparable concentrations of cation III and cations IV and V.

Preparative Separation of the Products of the Reaction of Oxopiperidinium Perchlorate with Benzoyldihydroquinoline and Isoquinoline I and II. A 1-mmole sample of dihydroquinoline I or isoquinoline II was added in portions in 10 min at 25°C to a solution of 1.5 mmole of oxopiperidinium salt III in 10 ml of acetonitrile. At the end of the reaction (1.5-2 h), the concentrations of IV-VIII formed in the reaction mixture were determined by the methods presented above. Dry ether (100 ml) was then added to the reaction solution, as a result of which yellow salt IV or V, respectively, crystallized in 95-99% yield.

After separation of the crystals, the ether mother liquor was evaporated at 25°C, and the residual dark-red resin was crystallized by trituration with pentane. According to the IR spectrum [17] and analysis for the VIII cation, the residue contained small amounts of admixed salt IV or V and consisted primarily of hydroxypiperidinium perchlorate VIII, the yield of which was 50 mole % based on starting I or II. The piperidine oxyl passed into the pentane extract and, after evaporation of the pentane, was obtained as red crystals, the IR spectrum and the melting point of which were identical to those for the compound with a known structure. The yield of piperidine oxyl was 100% based on the starting dihydropyridines I and II.

Oxidation of Dihydrobenzopyridines I and II with 2,2,6,6-Tetramethylpiperidine-1-oxyl (VI). A 3.1-mmole sample of 72% $HClO_4$ and 1 mole of dihydrobenzopyridine I or II were added at 25°C to a solution of 2 mmole of piperidine oxyl VI in 10 ml of acetonitrile. At the end of the reaction (1.5-2 h), 100 ml of dry ether was added to the reaction mixture, and the precipitated yellow salt IV or V was separated by filtration. The yield of IV or V was 95-98%.

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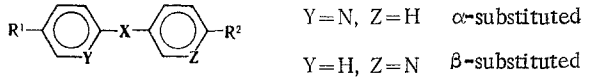
SYNTHESIS OF MESOMORPHIC 2-ALKYL-5-(p-CYANOPHENYL)PYRIDINES

A. I. Pavlyuchenko, E. I. Kovshev, and V. V. Titov

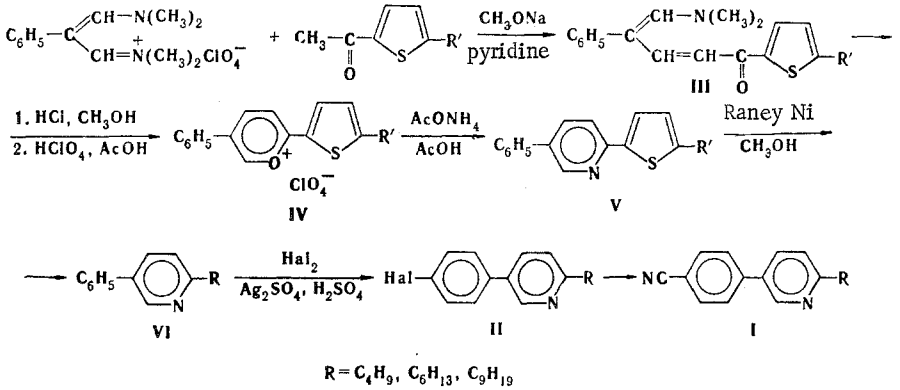
UDC 547.82

A new series of liquid-crystal derivatives of 2-alkyl-5-(p-cyanophenyl)pyridines were obtained by halogenation of 2-alkyl-5-phenylpyridines under the conditions of the Birckenbach-Gubo-Waters reaction with subsequent conversion of the 2-alkyl-5-(p-bromo- or iodophenyl)pyridines to the cyano derivatives.

In previous research on the liquid-crystal properties of α- and β-substituted pyridines [1-3] it was shown that in the case of β-X-substituted pyridines both the thermal stability of the mesophase and the melting point decrease significantly (when X = CH=N, X = COO). In the case of α- and β-phenylpyridines (X = a single bond) the melting point and the thermal stability of the mesophase, as well as the dielectric properties, of the liquid crystals obtained have a more complex relationship [4, 5].



It seemed of interest to compare two series of mesomorphic compounds, viz., our previously described 2-cyano-5-(p-alkylphenyl)pyridines [6] and 2-alkyl-5-(p-cyanophenyl)pyridines, which differ with respect to the position of the nitrile group. The synthesis of the latter was realized via the scheme



R = C_4H_9, C_6H_{13}, C_9H_{19}

We presented the method used to obtain the intermediate 2-alkyl-5-phenylpyridines (VI) in [4, 7]. In a preparative respect this method is simpler, it seems to us, than the known scheme for the synthesis of VI through organolithium derivatives [8]. Since exclusively the p-substituted compounds have mesomorphic properties, we made a detailed study of the orientation of the incorporation of substituents in the halogenation of β-phenylpyridines (VI) by the bromine or iodine cation under the conditions of the Bircenbach-Gubo-Waters reaction [9]. The para isomer was isolated in 64% yield in the nitration of β-phenylpyridine in sulfuric acid at 100°C [10]. We therefore expected that the principal product in the halogenation of β-phenylpyridine would also be the para isomer. An analysis of the reaction mixture by means of gas-liquid chromatography (GLC) shows that the principal product in the iodination of VI is actually the para isomer (R = H, 82% IIa; R = C_4H_9, 66% IIb; R = C_6H_{13},

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