B. A mixture of II and III hydrochlorides was recrystallized once from abs. alcohol. Then it was converted to the free base mixture by treatment with sodium bicarbonate to yield 4.8 g (60%). The mixture was dissolved in 30 ml of methylene chloride, 1.7 g of triethylamine was added, then with stirring, a solution of 2.4 g of benzoyl chloride in 5 ml of methylene chloride. The mixture was stirred for 2 h at room temperature, then extracted with three 20-ml portions of 5% hydrochloric acid, then with 20 ml of water. The combined extracts were used for the isolation of III. The organic phase was dried over Na_2SO_4, and the solvent was evaporated in vacuum to give 4.3 g (64%) of 2-benzoyl-3-carbethoxymethyl-4-oxo1,2,3,6,7,11b-hexahydro-4H-pyrazino[2,1-a]-isoquinoline (IV). Mp 100-102° (from ethyl acetate). R_f 0.9. IR spectrum: 1628, 1660 (amide CO), 1742 cm^{-1} (ester CO). Found: C 70.6; H 6.4; N 7.4%. $C_{23}H_{24}N_2O_4$. Calculated: C 70.4; H 6.2; N 7.1%.

The hydrochloric acid solution was neutralized with sodium bicarbonate to pH 7 and the precipitate was extracted with 20 ml of methylene chloride and dried over Na_2SO_4. After distillation of the solvent, 0.9 g (17%) of base III was obtained. After recrystallization from chloroform-hexane mixture it was identical in mp, TLC, and IR spectrum with the sample obtained by procedure A.

LITERATURE CITED

1. J. Seubert, R. Pohlke, and F. Loebich, Experientia, 33, 1036 (1977).
2. J. Seubert, BDR Patent 2,504,250; Chem. Abstr., 85, 142,999 (1976).
3. J. Seubert, BDR Patent 2,457,971; Chem. Abstr., 85, 160,160 (1976).
4. S. Sharma, R. Bindra, R. Iyer, and N. Anand, J. Med. Chem., 18, 913 (1975).
5. K. Masuzawa, M. Masaki, and M. Onta, Chem. Pharm. Bull., 14, 194 (1966).

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

6.* ELECTROCHEMICAL OXIDATION OF N-ACYL DERIVATIVES OF 2-PHENYL-1,2-DIHYDROQUINOLINES

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In the electrochemical oxidation of 1-acyl-2-phenyl-1,2-dihydroquinolines, first the radical cations of the starting compounds form; these then lose a benzoyl radical and go over to the 2-arylquinoline cations.

The oxidation of substituted dihydroheteroaromatic compounds can proceed via a monomolecular mechanism [2], in which there first forms an ion pair of heteroaromatic cation and substituent anion [1], which then reacts with the aromatizing agent (the so-called nucleophilic alkylation [3]). An alternative is the bimolecular aromatization mechanism, in which the aromatizing agent first oxidizes the starting compound to a radical cation, then (depending on the electron density distribution) removes either hydrogen or a geminal substituent [2]. The direct removal of substituent or hydrogen with an electron pair is also not excluded in those cases where the aromatizing agent is a strong electrophile but its reduction potential is lower than the oxidation potential of the dihydro derivative. The behavior of dihydroheteroaromatic compounds in oxidations can be predicted when their electrochemical oxidation has first been studied at a rotating platinum disk electrode with a ring [4].

Thus we have previously shown [4] that in the electrochemical oxidation of N-acyl derivatives of α-(γ)-(indolyl-3)-1,2-dihydroheteroaromatic compounds an unstable radical

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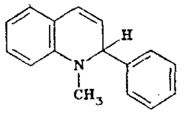
cation forms; it then loses either a proton and a second electron to form an N-acyl indolyl-substituted heteroaromatic cation, or an acyl cation and a second electron or acyl radical to form the corresponding indolyl-substituted heteroaromatic cation [4]. In accordance with this it becomes understandable why strong oxidants such as 2,2,6,6-tetramethyl-1-oxopiperidinium perchlorate ($E_{1/2}$ = 0.60 V in acetonitrile), which oxidize dihydroheteroaromatics to the radical cation, remove hydrogen, whereas weaker oxidants that function only as electrophiles (e.g., trityl perchlorate, $E_{1/2}$ = 0.34 V in acetonitrile) remove the indole residue by a monomolecular mechanism.

It was therefore of interest to study the electrochemical oxidation of 1-alkyl-(I) or the 1-acyl-2-aryl-1,2-dihydroquinolines IIa-h, because these compounds have different oxidation potentials, but they apparently cannot be aromatized by a monomolecular mechanism even in highly ionizing solvents; consequently the determining factor in the choice of aromatizing agent is not the medium but the ratio of the redox potentials of the reacting substances.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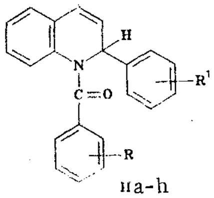
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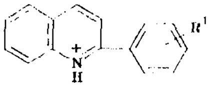
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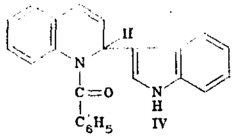
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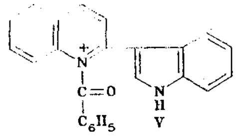
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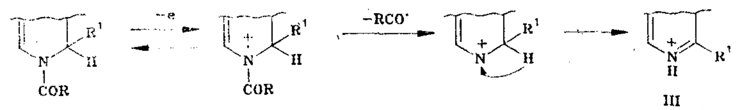
II a-d, h R=H, e R=-P-NO_2, f R=3,5-$(NO_2)_2$, g R=-P-OCH_3; II, III a R^1=H, b R^1= =-o-OCH_3, c R^1= P-CH_3, d R^1=-m-CH_3; II e-g R^1=H, h R^1=-P-$N(CH_3)_2$

It turned out that electrochemical oxidation of IIa-f at a rotating platinum ring-disk electrode in acetonitrile formed protonated salts of quinolines III (Table 1). A preliminary study of the reduction of these compounds in acetonitrile showed that because of adsorption their wave potential varied over the −0.32 to −0.40 V range. The limiting oxidation current of Ia-f varies over wide limits, but is always larger than the current corresponding to a one-electron transfer. As Table 1 shows, the formal number of transferable electrons, n, increases with increase in the acceptor properties of the acyl group. For IIa-f at constant ring potential equal to the plateau of the limiting reduction current of the III cation at the ring, there is a III-cation reduction wave, the current efficiency coefficient of which, Q, is somewhat too low. The probable reason is that the III cations are partly adsorbed on the disk. When the voltamperogram at the ring electrode is recorded at a constant disk potential equal to the start of the plateau of the limiting oxidation current of dihydroquinolines, only one reduction wave appears; it corresponds to the reduction of the protonic salt III (the proton wave potential is acetonitrile is -0.15 to -0.20 V). The reason is that N-protonated heteroaromatic cations are known to be reduced at platinum with catalytic hydrogen evolution at the same potential [5]. At a constant ring current corresponding to the base of the dihydro derivative oxidation wave at the disk, an appreciable wave could not be recorded at the ring ($i_{pr} \leq 0.02$ μA). This is evidence of the low stability of the radical cation that forms when the first electron is detached.

It may be pressumed from the data the oxidation of dihydro derivatives goes by the scheme:



Evidence for this view is the absence of proton oxidation waves in the polarization curves of the ring electrode, in contrast to what was observed in [4]. When the radical cation decomposes, the acyl group probably splits off as a radical. This radical, in turn, can undergo various conversions: it can react with the solvent, dimerize, be oxidized to a cation, or be adsorbed on the electrodes. Depending on the ratios of the rates of these reactions the number of electrons transferred from the dihydro compound can vary from one to two. Recording of the voltamperogram at the ring electrode at a constant ring potential (which corresponds, by our assumption, to the limiting reduction current of acyl cations, +0.5 V, Table 1), showed that their concentration is insignificant (∿2%). This may be related to the fact that some of the radicals are not oxidized to cations, and those cations

TABLE 1. Electrochemical Oxidation of 1,2-Dihydroquinoline Derivatives I, IIa-h, IV, at Rotating Platinum Ring-Disk Electrode in Acetonitrile

Compound	Electrode	Constant potential, V	$E_{1/2}$, V	i_{pr}, μA	n	Q, %
I	Disk	—	0,67	33,5	1,48	
	Range	E_k −0,7	0,70	2,00		
IIa	Disk	—	1,44	27,40	1,36	84
	Range	E_k −0,7	1,45	2,04		
	Range	E_k 0,5	1,40	0,03		
	Range	E_D 1,55	−0,39	0,86		
IIb	Disk	—	1,44	26,40	1,33	81
	Range	E_k −0,7	1,41	1,92		
	Range	E_k 0,5	1,39	0,04		
	Range	E_D 1,55	−0,32	1,61		
IIc	Disk	—	1,46	27,0	1,36	79
	Range	E_k −0,7	1,49	1,88		
	Range	E_k 0,5	1,52	0,02		
	Range	E_D 1,60	−0,40	0,72		
IId	Disk	—	1,44	31,6	1,60	92
	Range	E_k −0,7	1,46	2,56		
	Range	E_k 0,5	1,39	0,02		
	Range	E_D 1,65	−0,35	2,79		
IIe	Disk	—	1,54	33,0	1,74	84
	Range	E_k −0,7	1,53	1,92		
	Range	E_k 0,5	1,48	0,02		
	Range	E_D 1,65	−0,39	1,88		
IIf	Disk	—	1,97	38,5	2,12	82
	Range	E_k −0,7	1,97	1,19		
	Range	E_k 0,5	2,03	0,03		
	Range	E_D 2,15	−0,35	1,08		
IIg	Disk	—	1,41	20,0	1,04	87
	Range	E_k −0,7	1,41	2,00		
	Range	E_k 0,5	1,36	0,03		
	Range	E_D 1,55	−0,19	0,61		
			−0,48	0,55		
IIh	Disk	—	0,83	18,8	0,95	
	Range	E_k 0,5	0,84	2,10		
IV	Disk	—	1,20	43,5	2,46	
	Range	E_k −0,7	1,22	5,65		
	Range	E_k −0,3	1,24	2,2		
	Range	E_D 1,40	−0,2	8,75		

that are formed quickly undergo further conversions. In our view, this is specifically the reason for the changes in the limiting oxidation current of the various dihydroquinolines.

One of the oxidation routes for N-acyl derivatives of dihydroheteroaromatic compounds with detachment of an acyl radical has been previously considered in our mass spectrometric study of these compounds [6] and some of their reactions [7]. But the process was not studied in detail. The compounds considered in the present work are convenient for studying this particular aromatization route because in this case it is the only route. Oxidation of 1-benzoyl-2-(indolyl-3-)-1,2-dihydroquinoline (IV) under analogous conditions proceeds (as in the cases described previously [4]) with stepwise detachment of hydrogen ($E_{1/2}$ = -0.2 V) and formation of the corresponding N-acyl quinoline cation V. Here the oxidation potential is much more negative than for phenyl derivatives of 1,2-dihydroquinolines (Table 1); this is evidently what determines the decomposition route of the radical cations of these compounds. Indeed, the p-methoxybenzoyl derivative of IIg is oxidized just as easily, and the radical cation that forms then loses a proton and one more electron, but not an acyl radical; this is obvious from the two-electron oxidation wave for this compound.

1-Methyl-2-phenyl-1,2-dihydroquinoline I is oxidized analogously with stepwise detachment of hydrogen to form the 1-methyl-2-phenylquinoline cation, which was identified by comparison with the reduction potential of a sample of known structure ($E_{1/2}$ = -0.75 V).

The dimethylaminophenyl derivative IIh behaves anomalously. Reverse transfer of the first electron from the p-dimethylaminophenyl substituent forms a radical cation that is quite stable (under the experimental conditions) and does not undergo further oxidation before the potential corresponding to the discharge of the support electrolyte.

TABLE 2. Properties of 1,2-Dihydroquinolines IIb-g and Their Respective Perchlorates IIIb-d

Compound	mp,* °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
IIb	113—114	80,5	5,4	4,2	$C_{23}H_{19}NO_2$	80,8	5,6	4,1	75
IIc	160—161	84,6	5,7	4,4	$C_{23}H_{19}NO$	84,9	5,8	4,3	72
IId	111—112	84,7	5,8	4,4	$C_{23}H_{19}NO$	84,9	5,8	4,3	75
IIe	139—140	72,2	4,6	7,9	$C_{22}H_{16}N_2O_3$	74,2	4,5	7,9	70
IIf	85—86	65,6	3,8	10,2	$C_{22}H_{15}N_3O_5$	65,8	3,7	10,5	68
IIg	190—191	80,6	5,6	4,3	$C_{23}H_{19}NO_2$	80,8	5,6	4,1	76
IIIb	210—211	57,5	4,3	4,1	$C_{16}H_{14}ClNO_5$	57,3	4,2	4,2	82
IIIc	195—196	60,0	4,4	4,6	$C_{16}H_{14}ClNO_4$	60,2	4,4	4,4	80
IIId	187—188	60,3	4,5	4,5	$C_{16}H_{14}ClNO_5$	60,2	4,4	4,4	83

*IIb-d were crystallized from ethanol, IIe from propanol, IIf from hexane, IIg from acetonitrile.

Thus the investigation of the electrochemical oxidation of the N-acyl derivatives of 2-phenyl-1,2-dihydroquinolines has shown that the radical cations decompose with detachment of the acyl group as a radical, and form protonated 2-arylquinoline cations.

EXPERIMENTAL

The construction and properties of the rotating platinum ring-disk electrode, the procedure for recording voltamperograms, and the calculation of the number of transferable electrons have been described in [8]. Acetonitrile (pure grade) was purified immediately before preparation of the solutions, as in [9]. The reference electrode was a saturated calomel electrode. The number of electrons transferred at the disk electrode was calculated under the assumption that the diffusion coefficient of the depolarizer was inversely proportional to the square root of the molecular weight. For recording voltamperogram, concentration was $5 \cdot 10^{-4}$ M. Support electrolyte concentration was 0.1 M.

1-Methyl-2-phenyl-1,2-dihydroquinoline was obtained by the procedure of [10]; 1-benzoyl-2-(p-dimethylaminophenyl)-1,2-dihydroquinoline, by the procedure of [11]; 1-benzoyl-2-(indolyl-3)-1,2-dihydroquinoline, by the procedure of [12].

N-Benzoyl-2-phenyl-1,2-dihydroquinoline (IIa). To a solution of 10.6 g (50 mmole) of 2-phenyl-1,2-dihydroquinoline [13] and 5.1 g (50 mmole) of triethylamine in 20 ml of ether was added 7.05 g of benzoyl chloride in 20 ml of ether. The mixture was helf for 3 h, then poured into water. The ether layer was separated, the water layer was extracted with ether and the ether layers were combined and dried with magnesium sulfate. The solvent was distilled off and 16.6 g (75%) of 1-benzoyl-2-phenyl-1,2-dihydroquinoline was obtained, mp 114-115° (from ethanol) [14]. Found: C 85.1; H 5.7; N 4.6%. $C_{22}H_{17}NO$. Calculated: C 84.9; H 5.5; N 4.5%.

Compounds IIb-g were obtained analogously (Table 2).

2-Phenylquinolinium Perchlorate (IIIa). To a solution of 0.26 g (1 mmole) of 2,2,6,6-tetramethyl-1-oxopiperidinium perchlorate in 5 ml of anhydrous acetonitrile was added 0.31 g (1 mmole) of 1-benzoyl-2-phenyl-1,2-dihydroquinoline over 10 min. The mixture was heated to 50° over 5 h, then it was poured into 100 ml of dry ether. The precipitate was filtered off and washed with ether. Yield 0.24 g (80%), mp 199-200°. Found: C 58.8; H 4.0; N 4.3%. $C_{15}H_{12}ClNO_4$. Calculated: C 58.9; H 3.9; N 4.4%.

Perchlorates IIIb-d were obtained analogously (Table 2).

1-Methyl-2-phenylquinolinium Perchlorate. To a solution of 0.77 g (3 mmole) of 2,2,6,6-tetramethyl-1-oxopiperidinium perchlorate in 5 ml of anhydrous acetonitrile was added 0.44 g (2 mmole) of 1-methyl-2-phenyl-1,2-dihydroquinoline over 10 min. After 2 h the solution was poured into 100 ml of dry ether. The precipitate was filtered off and washed with ether. Yield 0.58 g (90%), mp 210-211° (from ethanol), reduction potential $E_{1/2} = -0.75$ V (in acetonitrile). Found: C 62.7; H 4.6; N 4.5%. $C_{16}H_{14}ClNO_4$. Calculated: C 62.8; H 4.6; N 4.6%.

LITERATURE CITED

1. A. K. Sheinkman, T. S. Chmilenko, and T. N. Nezdiiminoga, Khim. Geterotsikl. Soedin., No. 9, 1214 (1984).

2. A. K. Sheinkman, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., No. 4, 111 (1983).
3. A. K. Sheinkman, Z. M. Skorobogatova, T. S. Chmilenko, and T. M. Baranova, Dokl. Akad. Nauk SSSR, 267, 405 (1982).
4. I. M. Sosonkin, A. K. Sheinkman, Z. M. Skorobogatova, G. N. Strogov, and T. P. Ikher, Khim. Geterotsikl. Soedin., No. 3, 361 (1982).
5. R. F. Nelson and R. N. Adams, J. Electroanal. Chem., 16, 439 (1968).
6. N. A. Klyuev, G. A. Mal'tseva, R. A. Khmel'nitskii, A. K. Sheinkman, A. A. Deikalo, and T. V. Stupnikova, Izv. Timiryaz. Sel'skokhoz. Akad., No. 3, 200 (1974).
7. N. A. Klyuev, A. K. Sheinkman, and V. G. Zhil'nikov, Dokl. Akad. Nauk SSSR, 232, 618 (1977).
8. V. A. Subbotin, I. M. Sosonkin, N. V. Fedyainov, and V. I. Kumantsov, Khim. Geterotsikl. Soedin., No. 4, 516 (1978).
9. I. M. Sosonkin, A. N. Domarev, É. G. Kaminskaya, A. I. Tolstikov, F. F. Lakomov, and A. Ya. Kaminskii, Zh. Prikl. Khim., 44, 950 (1971).
10. R. C. Elderfield and Bruce A. Work, J. Org. Chem., 27, 543 (1962).
11. A. K. Sheinkman, A. N. Kost, A. N. Prilenskaya, and Zh. V. Shiyan, Zh. Org. Khim., 4, 1286 (1968).
12. H. Van Dobeneck and W. Goltzsche, Chem. Ber., 95, 1484 (1962).
13. C. E. Crawforth, O. Meth-Cohn, and C. A. Russell, J. Chem., Perkin Trans., Part 1, 22 2807 (1972).
14. A. K. Sheinkman and A. N. Prilenskaya, Khim. Geterotsikl. Soedin., No. 8, 1149 (1971).

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

7.* AROMATIZATION OF 1-METHYL-2-PHENYL-1,2-DIHYDROQUINOLINE BY QUINONIMINES

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In the aromatization of 1-methyl-2-phenyl-1,2-dihydroquinoline with substituted quinonimines, 1-methyl-2-phenylquinolinium salts of anionic hydride σ-complexes form, when then rearrange to iminyl anions. For comparison under Yanovskii reactions conditions, hitherto unknown acetonyl σ-complexes of quinonimines were synthesized.

Among the agents for homogeneous dehydrogenation the quinones occupy a special place; they are widely used to dehydrogenate organic compounds with a mobile hydridic hydrogen atom [2]. Such compounds include dihydroaromatic and dihydroheteroaromatic compounds [3-10], the dehydroaromatization of which can proceed by either an ionic or an SET mechanism [4-8]. The latter assumes a one-electron reduction of quinone to a radical anion, the so-called semiquinone, which adds a hydrogen atom or a proton to oxygen to form a radical, an anion, or neutral hydroquinone. The ionic mechanism assumes the addition of a hydride ion to one of the aromatic carbons to form an intermediate [11] like the Meisenheimer hydridic anionic σ-complexes [12]. But until now such intermediates have not been described, and distinct proof that they are formed is lacking.

The closest analogs of quinones are the quinonimines, which, having higher redox potentials than quinones [13], can be more efficient agents for dehydroaromatization.

In the present work, using the aromatization of 1-methyl-2-phenyl-1,2-dihydroquinoline as an example, we have studied the use of substituted quinonimines IIa-g in these reactions.

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*For Communication 6, see [1].

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