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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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TABLE 1. Constants and Yields of Synthesized Compounds

Compound	mp, °C	Reaction time, h	IR spectrum (KBr), cm^{-1}		UV spectrum†, λ_{max}, nm (log ε)		Found, %				Empirical formula	Calculated, %				Yield, %
			SO_2 (*as*)	SO_2 (*s*)	anionic σ-complex	aromatic anion	C	H	N	S		C	H	N	S	
IIIa	153—154	1	1327, 1309	1160, 1130	555 (3,28)		65,9	4,9	6,8	9,6	$C_{36}H_{33}N_3O_5S_2$	66,3	5,1	6,4	9,8	92
IIIb	148—149	3	1310, 1280	1174, 1143	563 (3,00)	398 (3,39)	57,3	3,9	6,8	11,7	$C_{40}H_{32}Cl_2N_4O_7S_3$	57,1	3,8	6,6	11,4	71
IIIc	161—162	2	1327, 1307	1163, 1133	560 (3,28)		62,7	4,7	6,1	9,3	$C_{36}H_{32}ClN_3O_5S_2$	63,0	4,7	6,1	9,3	82
Va	168—169	7	1327, 1266	1160, 1131		454 (3,46)	66,0	5,2	6,3	9,6	$C_{36}H_{33}N_3O_5S_2$	66,3	5,1	6,4	9,8	95
Vd	133—134	1	1333, 1240	1167, 1133	555‡	377 (2,90)	65,1	4,4	6,8	10,2	$C_{34}H_{29}N_3O_5S_2$	65,5	4,7	6,8	10,3	71
Ve	135—136	3	1376, 1340	1160, 1127	555‡	380 (3,40)	66,0	4,5	6,6	10,1	$C_{35}H_{31}N_3O_5S_2$	65,9	4,9	6,6	10,0	60
Vf	158—159	3	1337, 1260	1166, 1130	565‡	377 (2,85)	62,2	4,4	6,5	9,8	$C_{34}H_{28}ClN_3O_5S_2$	62,1	4,3	6,4	9,7	85
Vg	143—144	3	1336, 1263	1160, 1129	565‡	377 (2,90)	63,3	4,8	6,1	9,6	$C_{36}H_{32}ClN_3O_5S_2$	63,0	4,7	6,1	9,3	72

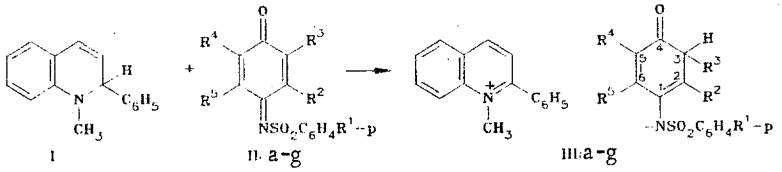
*Time of conclusion of reaction was determined spectrophotometrically.

†Absorption bands of cations of salts lie in 240-242, 265-269, and 328-330 nm regions.

‡Anion band determined spectrophotometrically.

The reaction of 1,2-dihydroquinoline I with 2-p-toluenesulfonylamino-4-p-toluenesulfonyliminobenzoquinone IIa in acetonitrile forms a dark violet crystalline adduct that contains the two components in 1:1 proportion. The absence of a signal in the EPR spectrum of a solution of this compound excludes the presence of a radical-ion pair. On the basis of UV, IR, and PMR spectra, adduct IIIa has been assigned the structure of a salt in which the cation is 1-methyl-2-phenylquinolinium and the anion is 3-p-toluenesulfonylamino-4-oxo-1,5-cyclohexadienyl-p-toluenesulfonyliminate.

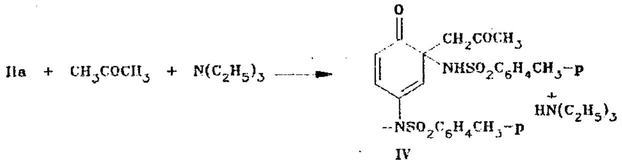
Evidence for the structure of the cation of IIIa is as follows: in the UV spectrum, a quinolinium cation absorption band with maxima at 240, 268, and 330 nm [14]; in the PMR spectrum, signals of the protons of the phenyl substituent at 7.76 ppm (5H), the quinoline ring at 8.00-9.27 ppm (6H), and the methyl at 4.39 ppm (3H, N-CH_3) [15]. In the IR spectrum the absorption at 707, 770, 817, and 1603 cm^{-1} corresponds to the quinolinium cation.



II, III a, c, g $R^1=CH_3$; b $R^1=Cl$; d, e, f $R^2=NHSO_2C_6H_5$; g $R^2=NHSO_2C_6H_4CH_3$-*p*; a, c $R^3=NHSO_2C_6H_4CH_3$-*p*; b $R^3=NHSO_2C_6H_4Cl$-*p*; e $R^4=CH_3$; c, f, g $R^4=Cl$; b $R^5=$ $=NHSO_2C_6H_5$; all undefined R=H

The structure of the anion of IIIa is proved by its PMR spectrum, which shows, besides the signals mentioned above, the signals of a four-spin ABCD system; the 6-H and 2-H protons appear as two doublets, at 6.71 (1-H, $J_{6,5}$ = 10.2; $J_{6,2}$ = 2.7 Hz) and 7.01 ppm (1-H, $J_{2,5}$ = 9.8 and $J_{2,6}$ = 2.7 Hz). The 3-H and 5-H proton signals consist of a multiplet with its center at 6.36 ppm (2-H). The aryl sulfonamide protons (an AA'BB' system) resonate in the 7.22-7.78 ppm region (8-H) as complex signals superimposed on those of the quinolinium protons. The IR spectrum of the anion shows a set of bands of C=O 1680, $SO_{2(as)}$ 1327 and 1309, and $SO_2(s)$ 1160 and 1130 cm^{-1}. The UV spectrum of III has intense absorption in the visible with λ_{max} 555 nm (log ε 3.28) that is typical of cyclohexadienate anions [16].

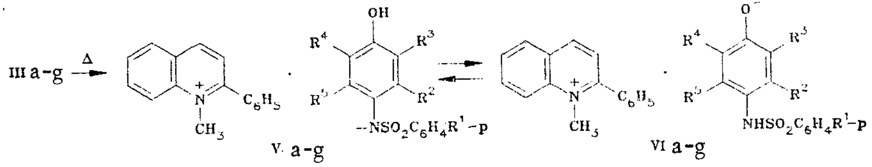
To confirm the structure of the IIIa anion under the conditions of the Yanovskii reaction [17], quinonimine IIa was reacted with acetone in the presence of triethylamine. It gave the dark violet salt IV, viz., triethylammonium 3-p-toluenesulfonylamino-3-acetonyl-4-oxo-1,5-cyclohexadienyl-p-toluenesulfonyliminate.



The UV spectra of IIIa and IV are identical in the visible region [sic]. In the PMR spectrum of IV, along with the signals of the protons of the two methyls at 2.37 ppm (3-H, CH_3) and 2.36 ppm (3-H, CH_3), and of the ethyls of triethylammonium at 3.09 (6-H, CH_2) and 1.17 ppm (9-H, CH_3), and the multiplets of the aromatic protons of the two tolyl fragments at 7.73-7.96 and 7.27-7.33 ppm, there are two doublets of 2-H and 5-H protons at 6.93 (1H) and 6.31 ppm (1H) with spin-spin coupling constants of 2.7 and 10.0 Hz, respectively, and a doublet of doublets at 6.71 ppm (1H), that belong to the 6-H proton. The acetonyl residue is characterized by the CH_2 singlet at 2.07 ppm (2-H). The identical locations of the 2-H and 6-H proton signals in the anions of IIIa and IV point to the location of the acetonyl residue at the 3 position.

When IIIa is heated its anion aromatizes, so that the melting point of the salt changes. In the visible region the UV spectrum shows an appreciable hypsochromic shift of the absorption band from 555 to 454 nm; this is typical for the change of a cyclohexadiene structure to aromatic [18]. In the IR spectrum the C=O band at 1680 cm^{-1} disappears, and an OH band appears at 3413 cm^{-1}. A separate communication will be devoted to our comparison of N-H and O-H acidities in substituted aminophenols and the corresponding tautomerism of the anions of salts Va-g and VIa-g.

Aromatization of 1-methyl-2-phenyl-1,2-dihydroquinoline by quinonimines IIa-g is a general reaction. The process goes through the formation of salt III with a cyclohexadienate anion, as evidenced by the intense violet color of the reaction solution, and the presence in the UV spectrum of that solution of absorption at λ_{max} 555 nm (Table 1). But salt III could be separated on a preparative scale only in the reactions with quinonimines IIa-c, which have a sulfonylimine substituent at the 3 position. In the other cases, III aromatized to salts Vd-g during the reaction at room temperature.



The R^1-R^5 values correspond to those given above.

Thus, since the formation of hydridic σ-complexes in the aromatization of dihydroquinolines by quinonimines has been demonstrated, we can conclude that the reaction mechanism is ionic, with transfer of a hydride ion, probably in the solvent cage, from dihydroquinoline to quinonimine.

EXPERIMENTAL

PMR spectra were obtained on a Bruker WH-90 instrument (90 MHz) in DMSO-D_6. IR spectra were obtained on a Specord IR-75 instrument in KBr tablets. UV spectra were obtained on a Specord UV-Vis instrument in acetonitrile.

The properties of compounds IIIa-c and Va,d-g, and the reaction conditions are given in Table 1.

Reaction of 1-Methyl-2-phenyl-1,2-dihydroquinoline with 1,4-Benzoquinon-2-R^2-3-R^3-5-R^4-6-R^5-4-(R^1-sulfonyl)imine. Into a solution of 1 mmole of IIa-g in 5 ml of dry acetonitrile was sprinkled 1 mmole of 1-methyl-2-phenyl-1,2-dihydroquinoline. At the end of the reaction the mixture was poured into ether and salts IIIa-c (Vd-g) were separated.

1-Methyl-2-phenylquinolinium 3-p-Toluenesulfonylamino-4-hydroxyphenyl-p-toluenesulfonyliminate (Va). A solution of 0.65 g (1 mmole) of N-methyl-2-phenylquinolinium 1-p-toluenesulfonylimino-3-p-toluenesulfonylaminocyclohexadienate-1,5-one-4 (IIIa) in 5 ml of dry acetonitrile was boiled under reflux for 7 h. After cooling the solution was poured into 100 ml of dry ether, and the precipitate was separated and washed with ether.

Triethylammonium 1-p-Toluenesulfonylamino-3-acetonyl-4-oxo-1,5-cyclohexadienyl-p-toluenesulfonyliminate (IV). To a solution of 0.43 g (1 mmole) of 2-p-toluenesulfonylamino-N-p-toluenesulfonyl-1,4-benzoquinonimine (IIa) in 5 ml of abs. acetone was added 0.3 ml (2 mmole) of triethylamine. After 1 h the dark-vio violet crystals of salt IV were separated. Yield 0.4 g (72%), mp 98-99°. UV spectrum (acetone), λ_{max} (log ε): 555 nm (3.30). Found: C 59.4; H 6.6; N 7.0; S 10.6%. $C_{29}H_{39}N_3O_6S_2$. Calculated: C 59.1; H 6.6; N 7.1; S 10.9%.

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

8.* AROMATIZATION OF N-ACYL PARTLY HYDROGENATED PYRAZINE AND QUINOXALINE DERIVATIVES

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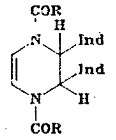
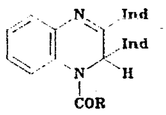
N-mono- and N,N-diacyl 2,3-diindolyl-substituted 1,2-dihydro- and 1,2,3,4-tetrahydropyrazines and quinoxalines were aromatized with triphenylmethyl perchlorate and 2,2,6,6-tetramethyl-1-oxo-piperidinium perchlorate. The hitherto unknown N-acylquinoxalinium perchlorates were obtained.

Continuing our study of the aromatization of N-acyl partly hydrogenated N-heteroaromatic systems [2, 3], we have studied the reactivity of the most difficulty aromatizable N-acyl derivatives of di- and tetrahydro-1,4-diazinium bases, having substituents at the sp^3 carbons of the heterocycle, under the influence of perchlorates of various organic cations. Moreover we have studied the synthesis by aromatization (by analogy with the synthesis of stable N-acyl pyridinium and benzopyridinium salts [2]) of hitherto unknown N-acyl salts of 1,4-diazines. Their participation *in situ*, however, was postulated for the synthesis of Reissert's compounds [4] and in the heteroarylation of nucleophilic organic compounds under the simultaneous action of acyl chlorides and diazines [5]. Until now, aromatization has been described for N-methyl and N-hydro derivatives of di- and tetrahydro-1,4-diazine systems [6-10], by the action of neutral oxidants of various strengths: chloranil, oxygen, sulfur, and $KMnO_4$. From the data of [6-10] it follows that the ease of aromatization of these systems decreases substantially in going from their N-methyl to their N-hydro derivatives, from dihydro to tetrahydro derivatives, and from the products of mono-addition of various nucleophiles to the products of binucleophilic addition to quaternary and protonated 1,4-diazine salts.

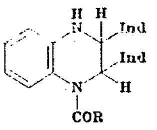
We aromatized a series of 2,3-diindolyl-substituted N,N-diacyl-1,2,3,4-tetrahydropyrazines (I), mono-N-acyl-1,2-dihydro- (II), 1,2,3,4-tetrahydro- (III), and N,N-diacyl-2,3-di(indolyl-3)-1,2,3,4-tetrahydroquinoxalines (IV) by the action of various hydride ion acceptors.



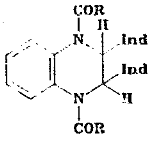
Ia,b



IIa-e



IIIa-e



IVb

I—IV Ind=3-indolyl; I—III a $R=C_6H_5$; I—IV b $R=CH_3$; II, III c $R=C_6H_4—Cl$-*p*; d $R=C_6H_4—NO_2$-*p*; e $R=C_6H_4—CH_3$-*o*

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*For Communication 7, see [1].

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