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SYNTHESIS AND THE INVESTIGATION OF SOME 4H-β-QUININDINES, THE HETEROCYCLIC ANALOGS OF AZULENE

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The investigation of the chemical properties of 4-methyl-1,2-dihydro-4H-β-quinindine (I) has demonstrated that electrophilic reactions take place at $C_{(3)}$ with a great ease. For example, during the reaction in ether of I, obtained by the action of alkali on methiodide of β-quinindane (II) (1), and C_6H_5COCl we obtained at once a precipitation of 3-benzoyl-4-methyl-1,2-dihydro-4H-β-quinindine (IIIa) with a yield of 87%, m.p. 193-194° (EtOH), orange. $C_{20}H_{17}NO$.* R_f 0,41**. λ_{max}^{EtOH} mμ (logε): 230 (4.42), 265(4.09) 320 (3,65 - shoulder), 455 (4.40). Similar to this, when PhNCO was added to the ether solution of I, 3-N-phenylcarbamyl-4-methyl-1,2-dihydro-4H-β-quinindine (III) precipitated with an almost quantitative yield, m.p. 178-180° (EtOH), yellow. $C_{20}H_{18}N_2O$. R_f 0,1**. λ_{max}^{EtOH} mμ (logε): 253 (4.10, fine structure), 329 (4.09, fine structure), 416 (4.28).

The high reactivity of I was due to a high electronic density at $C_{(3)}$, and a significant contribution by the limiting structure (IVc). In contrast to I, the substances IIIa and IIIb were stable, as the introduction of electronegative substituents stabilized the compounds due to resonanse (IIIa,b $\leftrightarrow$ IVa,b $\leftrightarrow$ Va,b).

The compounds IIIa and IIIb are strong bases. Their salts - methiodide of 3-benzoyl-β-quinindane (VIa) and methiodide of 3-N-phenylcarbamyl-β-quinindane (VIb) - were obtained by the addition of KJ in acetic acid to IIIa,b. VIa, m.p. 215-216° (decomp., EtOH). $C_{20}H_{18}JNO$. λ_{max}^{EtOH} mμ (logε): 238 (4.72), 330 (4.26). VI b, m.p. 221-222° (decomp., EtOH). $C_{20}H_{19}JN_2O$. λ_{max}(0,1N HCl, 5% EtOH) mμ (logε): 243 (4.93), 328 (3.45).

The compounds IIIa,b are 1,2-dihydroderivatives of the appropriate 4H-β-quinindines - "pseudoaromatic" substances (heterocyclic analogs of azulene), which have an abundant electronic density in the five-membered ring and an unsufficient electronic density in the pyridine ring (2,3).

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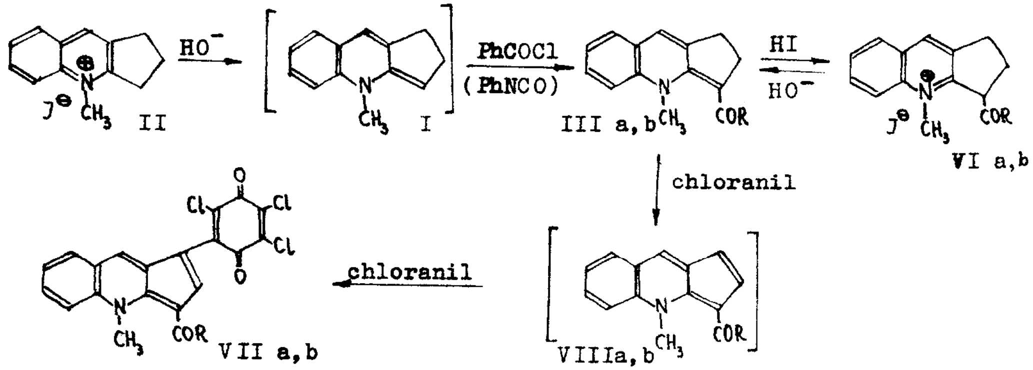
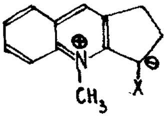
* Elemental analyses of all new compounds were satisfactory.

**TLC, Al_2O_3, $CHCl_3$



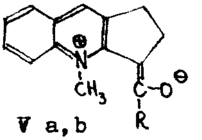


IV a-c

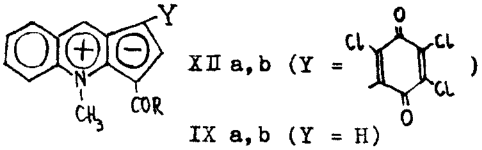
a X=COPh

b X=CONHPh

c X=H

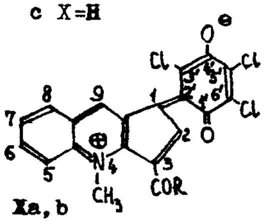


V a,b

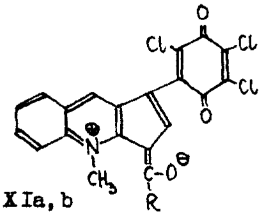


XII a,b (Y =)

IX a,b (Y = H)



Xa,b



XIa,b

a R=Ph

b R=NHPh

of IIIb the shift of a CO-band to shorter wavelength, as compared with methiodide VIb ($\Delta \sim 70 cm^{-1}$), is significantly less than that of IIIa as compared with VIa ($\Delta \sim 190 cm^{-1}$). This testifies to a smaller contribution of the limiting structure V to IIIb as compared with IIIa. The pK_a's also agree with this: IIIb is a more strong base (pK_a 8.68, 80% EtOH) than IIIa (pK_a 6.15, 80% EtOH) by more than two orders. Therefore it can be assumed [considering preferential protonation at $C_{(3)}$(5)] that the limiting structure IVb makes a greater contribution to IIIb than IVa to IIIa.

The formation of VII was likely the result of a secondary process. In all probability, the intermediate substance was the product of dehydrogenation - 3-benzoyl- or 3-N-phenylcarbamyl-4-methyl-4H-β-quinindine(VIIIa,b). The compound VIIIa was probably a red substance, which we observed during chromatographing. This substance has a structure IX similar to azulene. 3-Acyl-4H-β-quinindine has an abundant electronic density at $C_{(1)}$ and $C_{(3)}$ (like azulene) and the electrophilic attack of chloranil with a mobile chloro-group is probably directed to the unsubstituted position 1. Like azulene the

Only two derivatives of 4H-β-quinindine (2,3) are known so far, and some compounds of this class were prepared as complexes with trinitrobenzene (4); the properties of 4H-β-quinindines being poorly studied. For this reason the dehydrogenation of IIIa,b was of interest. We chose chloranil as a dehydrogenating agent. In carrying out the reaction with ketone IIIa in boiling benzene in an argon atmosphere, we obtained at first three coloured substances (TLC). The blue and blue-green substances have the close R_f(0,89 and 0,92, respectively) and the red substance has R_f 0,62 (TLC, Al_2O_3 + + 2,5% CH_3COOH, $CHCl_3$).

The starting compound IIIa and the red substance disappeared almost completely in 1.5 hours. Two products of the reaction (the blue substance, R_f 0,26* and the blue-green substance R_f 0,83*) were separated by preparative TLC.

The blue-green substance is 1-(3',5',6'-trichlor-1',4'-benzoquinonil-2'-)-3-benzoyl-4-methyl-4H-β-quinindine (VIIa), yield 64%, m.p.236-237° (decomp.). $C_{26}H_{14}Cl_3NO_3$. R_f~0.80* $\lambda_{max}^{CHCl_3}$ mμ (log ε): 275 (4.45), 317(4.40) 335 (4.38), 488 (3.25), 730 (3.78). The structure of the blue substance has not been established due to a low yield of this compound.

In the case of IIIb the reaction with chloranil takes place similarly to the reaction of IIIa, but faster. The starting material has disappeared in 10 minutes. As a result we obtained only a blue substance (R_f 0.66 *, the substance was purified by chromatography on Al_2O_3 column), which represents 1-(3',5',6'-trichlor-1',4'-benzoquinonil-2'-)-3-N-phenylcarbomyl-4-methyl-4H-β-quinindine (VIIb), temperature of decomposition 270-300°, yield 21%. $C_{26}H_{15}Cl_3N_2O_3$. $\lambda_{max}^{CHCl_3}$ mμ (log ε): 304 (4.30), 355 (4.02), 500 (3.23), 725 (3.88).

In all probability, the increased rate of the reaction with chloranil in the case of IIIb is due to the smaller electronegativity of PhCONH-group compared with PhCO-group. As a result of this, the electrophilic reactions in the five-membered ring are made easier in the case of IIIb as compared with IIIa (for example, dehydrogenation and protonation). Therefore, the electronic density at $C_{(3)}$ is higher in anilide IIIb than in ketone IIIa, but that at the oxygen atom in IIIb is lower than in IIIa. This is confirmed by the dipole moments, pK_a and the IR spectra of these compounds. The dipole moment of IIIa is 3.32 D and that of anilide (IIIb) is 2.87 D (benzene). This agrees with the suggestion of increased negative charge at the oxygen atom in IIIb.

This fact finds reflection also in IR spectra (Table 1). In the case

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obtained compounds (VIIa,b) are weak bases: their chloroform and benzene solutions have a blue colour, but the solutions VIIa,b in concentrated H_2SO_4 or H_3PO_4 have a yellow colour.

The UV spectra has confirmed the formation of a VIIa (and VIIb) substance with a charge in the conjugated system of bonds. All four observable absorption bands were shifted to the visible region compared with IIIa.

In the NMR spectrum of VIIa in DMSO + CCl_4 (10:1) no protons are found besides aromatic protons (7.7 - 9.0 ppm) and protons of the N-methyl group (δ 4.50 ppm).

Table 1

Substance		III	VI	VII		
				at $C_{(1')}$	at $C_{(4')}$	at $C_{(3\ )}$
ν_{CO}, cm^{-1}	a, R = C_6H_5	1500	1689	1674	1659	1615
	b, R = NHC_6H_5	1620	1690	1678	1660	1627

Three bands were observed in the IR spectrum of VIIa,b (see Table 1). Two of them were nearly coincide and that is why we can attribute them to the vibration of the carbonyl groups of benzoquinone. As carbonyl at $C_{(4')}$ was conjugated with nitrogen atoms (X) the bands at 1659 and 1660 cm^{-1} could be attributed to carbonyl at $C_{(4')}$.

The bands 1615 and 1627 cm^{-1} can be attributed to ketone carbonyl in VIIa and amide carbonyl in VIIb correspondingly. The increased frequences of absorption of these carbonyl groups as compared with carbonyl bands observable in carbonyls of IIIa,b (115cm^{-1} for VIIa and 7cm^{-1} for VIIb) testify to the decreasing involvement of the carbonyl COR-groups in the conjugation. This implies a smaller contribution of the limiting structure XI to compounds VII compared with that of the structure V to dihydroderivatives III. This is probably due to a considerable contribution by the energetically favourable "pseudoaromatic" structure XII and to some contribution by the structure X.

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