RING – CHAIN TRANSFORMATIONS WITH THE PARTICIPATION OF THE C = N GROUP

III.* 3-ARYL-3-ARYLAMINOPERINAPHTHALIDES AND 2,3-DIARYL-3-HYDROXY-2,3-DIHYDRO-1H-BENZ[d,e]ISOQUINOLIN-1-ONES

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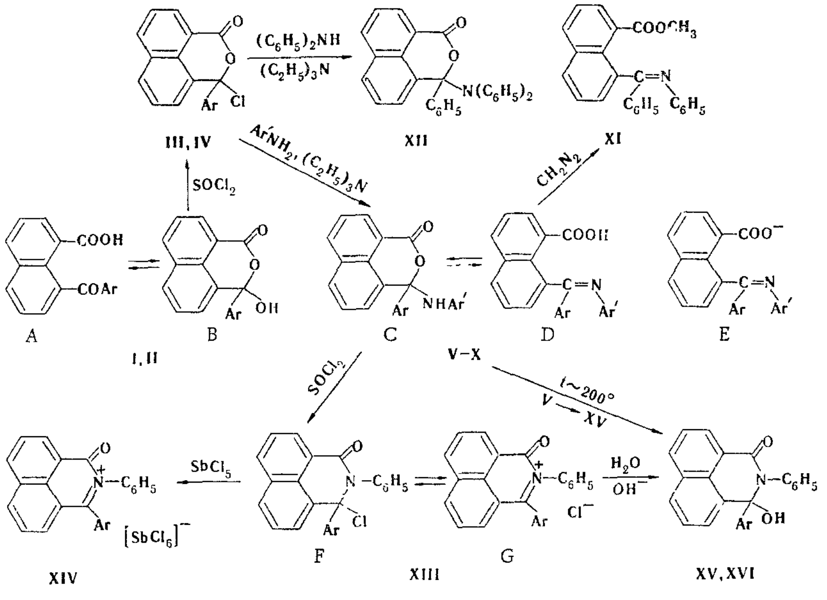
In reaction with primary aromatic amines, 3-aryl-3-chloroperinaphthalides form 3-aryl-3-arylaminoperinaphthalides. The ring–chain tautomerism of these compounds has been studied and isomerization has been realized in the 2,3-diaryl-3-hydroxy-2,3-dihydro-1H-benz[d,e]isoquinolin-1-ones.

It has been established previously [2] that in reaction with 3-chloro-3-phenylphthalide primary aromatic amines attack the carbon atoms in positions 1 and 3 with the formation of a mixture of 2,3-diaryl-3-hydroxyisoindolinones and 3-arylamino-3-phenylphthalides. In the present work we have investigated the reaction of 3-aryl-3-chloroperinaphthalides (II, IV) with primary aromatic amines in order to determine the predominant direction of attack of the nucleophilic agent and to study the ring–chain isomeric transformations of the products of this reaction.

8-Benzoyl- and 8-(p-methoxybenzoyl)naphthoic acids (I, II) were obtained by the action of the appropriate diarylcadmiums on naphthalic anhydride [3]. Judging from their IR spectra, in the crystalline state, the acid (I) has the ring structure (IB) and acid (II) the open structure (IIA). In dioxane solution there is tautomeric equilibrium A ⇌ B (see [4, 5]). The higher intensity of the diaryl ketone C = O band in the



I, III, V, VII, IX, XIII–XV Ar = C_6H_5; II, IV, VI, VIII, X, XVI Ar = $p\text{-}CH_3OC_6H_4$, V, VI Ar′ = C_6H_5, VII, VIII Ar′ = $p\text{-}CH_3OC_6H_4$, IX, X Ar′ = $p\text{-}NO_2C_6H_4$

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*For Communication (II), see [1].

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TABLE 1. 3-Aryl-3-arylaminoperinaphthalides (V-X, XII) and 2,3-Diaryl-3-hydroxy-2,3-dihydro-1H-benz[d,e]isoquinolin-1-ones (XV,XVI)

Compound	Ar	Ar′	mp, °C	Empirical formula	Found, %			Calc., %			IR spectra,* ν, cm⁻¹				R_f	Yield, %
											solid substances		solutions in dioxane			
													C=O			
					C	H	N	C	H	N	$\nu_{C=O}$	$\nu_{N-H,\ O-H}$	ν	ε (A)		
V	C_6H_5	C_6H_5	201—202	$C_{24}H_{17}NO_2$	81,8	4,9	4,0	82,0	4,9	4,0	1706, 1695	3313	1725	(3,6)	0,14	62
VI	p-$CH_3OC_6H_4$	C_6H_5	188—189	$C_{25}H_{19}NO_3$	78,5	5,2	3,6	78,7	5,0	3,7	1700	3307	1729	480	0,09	65
VII	C_6H_5	p-$CH_3OC_6H_4$	181—182	$C_{25}H_{19}NO_3$	78,8	5,0	3,6	78,7	5,0	3,7	1703	3318	1725	(4,2)	0,05	30
VIII	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	167—168	$C_{26}H_{21}NO_4$	76,0	5,0	3,1	75,9	5,2	3,4	1704	3316	1723	505	0,05	63
IX	C_6H_5	p-$NO_2C_6H_4$	209—210	$C_{24}H_{16}N_2O_4$	72,6	4,1	6,9	72,7	4,1	7,1	1709	3273	1734	(3,9)	0,14	86
X	p-$CH_3OC_6H_4$	p-$NO_2C_6H_4$	182—183	$C_{25}H_{18}N_2O_5$	70,0	4,3	6,6	70,4	4,3	6,6	1714	3271	1731		0,05	48
XII			204—205	$C_{28}H_{21}NO_2$	83,5	4,9	3,3	83,6	5,3	3,5	1714	—	1727	(3,7)		50
XV	C_6H_5		180—181	$C_{24}H_{17}NO_2$	82,0	5,1	3,8	82,0	4,9	4,0	1661пл 1634	3281ш	1663	(3,0)	0,89	67
XVI	p-$CH_3OC_6H_4$		203—204	$C_{25}H_{19}NO_3$	78,8	5,0	3,6	78,7	5,0	3,7	1643	3274ш	1662	(2,7)	0,89	53

*Abbreviations: br, broad band; sh, shoulder; A, integral intensity in practical units of measurement equal to 10^4 liter · mole^{-1} · cm^{-2} (ln).

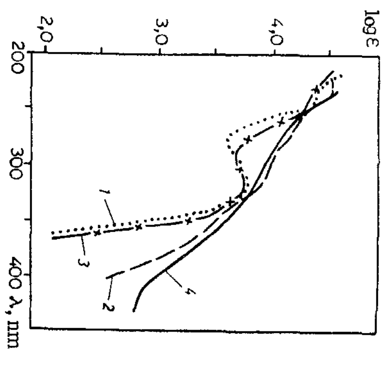

Fig. 1. UV spectra in ethanol: 1) (V); 2) (XI); 3) (XII); 4) (V) in the presence of 0.1 N KOH.

spectrum of the acid (II) indicates that in the solution of (II) the tautomeric equilibrium is shifted further in the direction of the open form A than in the solution of (I). Obviously, under the influence of the +C effect the methoxy group lowers the electrophilicity of the carbon atom of the keto group and, consequently, decreases the tendency of the acid (II) to exist in the ring form. In the IR spectra of 8-aroylnaphthoyl chlorides in dioxane there is only one C=O band of a six-membered chlorolactone [6] at 1735 cm^{-1}, showing their ring structure as 3-aryl-3-chloroperinaphthalides (III, IV).

Compounds (III) and (IV), unlike 3-chloro-3-phenylphthalide [2], undergo nucleophilic attack by arylamines only in position 3 with the formation of 3-aryl-3-arylaminoperinaphthalides (V-X, Table 1). In order to study the tautomeric equilibrium VC ⇌ VD, we synthesized fixed model open and ring forms – the anil of 1-benzoyl-8-methoxycarbonylnaphthalene (XI) and 3-diphenylamino-3-phenylperinaphthalide (XII). In the IR spectrum of a dioxane solution of (V), the naphthalide C=O band is similar in frequency and integral intensity to the C=O band in the spectrum of the fixed model (XII). Ethanolic solutions of these compounds (V and XII) have identical absorption curves in the UV region of the spectrum (Fig. 1). Consequently, in neutral solutions, the equilibrium VC ⇌ VD is, within the limits of sensitivity of the methods of UV and IR spectroscopy, displaced completely in the direction of VC. On comparing these results with information [2] on the tautomeric equilibrium of the 3-arylamino-3-phenylphthalides it can be seen that the stability of the ring form C is higher for the 3-aryl-3-arylaminoperinaphthalides. Using three-dimensional models it is possible to convince oneself that in the molecule of (VD) the C=N and COOH groups, the intramolecular reaction between which leads to the ring form (VC), are closer in space than in the anil of 2-benzoylbenzoic acid.

The action of bases on (V) forms the anion of the open structure (VE). This is confirmed by the similarity of the UV spectrum of (V) in 0.1 N ethanolic caustic soda solution and the spectrum of the model substance (XI) (Fig. 1). The ring form (C) also predominates in dioxane solutions of the other 3-aryl-3-arylaminoperinaphthalides (VI-X) within the limits of sensitivity of the IR-spectroscopic method.

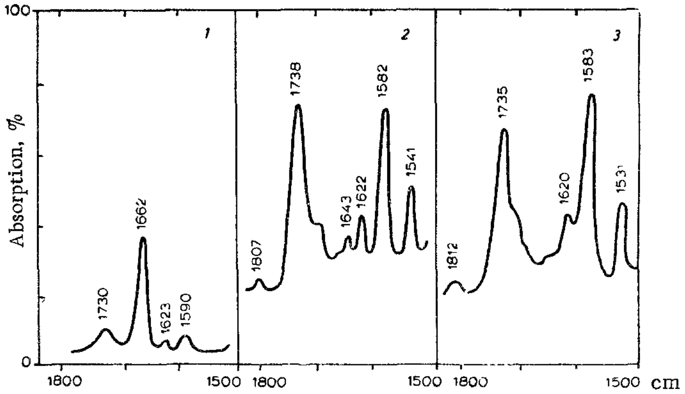

Fig. 2. IR spectra: 1) (XIII) in dioxane; 2) (XIII) as a mull in paraffin oil; 3) (XIV) in a KBr tablet.

The isomerization of the 3-aryl-3-phenylaminoperinaphthalides (V, VI) into the 2,3-diaryl-3-hydroxy-2,3-dihydro-1H-benz[d,e]isoquinolin-1-ones (XV, XVI) was brought about thermally or by the successive treatment of compounds (V, VI) with thionyl chloride and aqueous sodium carbonate solution. In the IR spectra of the crystalline substances (XV and XVI) there are broad OH bands at 3300 cm^{-1}. The frequency of the C=O bands is lowered in comparison with the spectra of solutions in dioxane (Table 1), which shows the presence of C=O ··· H–O intermolecular hydrogen bonds in the crystal lattice. Compounds (XV) and (XVI) are cyclic isomers of anilides of 8-aroylnaphthoic acids, but it proved to be impossible to effect their thermal isomerization into the corresponding anilides.

The action of thionyl chloride on (V) forms 3-chloro-2,3-diphenyl-2,3-dihydro-1H-benz[d,e]quinolin-1-one (XIII). The crystalline substance (XIII) is yellow and in its IR spectrum there is an intense C=O band at 1738 cm^{-1}. In the spectrum of a dioxane solution of (XIII) a very intense C=O band appears at 1662 cm^{-1}, which corresponds well to the spectra of compounds (XV) and (XVI). When substance (XIII) is dissolved in dioxane the intensity of the yellow coloration falls sharply. Consequently, in dioxane, compound (XIII) exists predominantly in the form (XIIIF) and in the crystalline state in the tautomeric form (XIIIG).

It has been shown [7] that the action of antimony pentachloride on 3-chloro-2,3-diphenylisoindolinone (XVII) forms 2,3-diphenyl-1-oxoisoindolium hexachloroantimonate. In the present work we have used this method to obtain 1-oxo-2,3-diphenyl-1H-benz[d,e]isoquinolinium hexachloroantimonate (XIV). The similarity of the IR spectra of the crystalline compounds (XIII) and (XIV) in the 1850-1500 cm^{-1} region (Fig. 2) is convincing proof of the fact that compound (XIII) has the immonium structure (XIIIG) in the crystalline state. This distinguished compound (XIII) from its five-membered analog (XVII) [2,7] and is apparently explained by the fact that the formation of a double bond in a six-membered ring is more favorable than in a five-membered ring.

EXPERIMENTAL

The IR spectra were obtained on an IKS-14A instrument using mulls in paraffin oil and hexachlorobutadiene and solutions in dioxane (c 5 · 10^{-2} M, l = 0.011 cm). The integral intensities of the C=O bands were calculated by the Wilson–Wells method with Ramsay's wing correction [8]. The calculation was performed by S. P. Valter and A. V. Burkevits, for which we express our thanks to them. The UV spectra were obtained on an SFD-2 instrument in ethanol (c 10^{-4} M).

The individualities of the substances were checked chromatographically in a thin layer of alumina of activity grade II. The thickness of the layer was 0.5 mm, the eluent benzene–acetone (10 : 1), and the chromogenic agent fluorescein. The R_f values are given in Table 1.

8-Benzoylnaphthoic Acid (I). Obtained by the method of Nightingale et al. [3]. IR spectrum, cm^{-1}: in Nujol, $\nu_{C=O}$ 1687 broad band, ν_{O-H} 3200 broad band; in dioxane, $\nu_{C=O}$ 1733 (ε 480), 1670 (ε 120).

8-(p-Methoxybenzoyl)naphthoic Acid (II). With stirring, 25.5 g (0.139 mole) of anhydrous cadmium chloride was added to a solution of 0.3 mole of p-methoxyphenylmagnesium bromide in 75 ml of ether cooled to 0°C, and then the solution was boiled for 2 h. The ether was evaporated off and to the dry residue were added 250 ml of anhydrous toluene and 20 g (0.1 mole) of naphthalic anhydride. The mixture was heated at 100°C and stirred for 4 h, after which it was cooled and 400 ml of dilute (1 : 1) hydrochloric acid was added. Stirring was continued, and after an hour the precipitate was separated off. The acid so obtained was reprecipitated with dilute hydrochloric acid from 500 ml of 10% aqueous sodium carbonate solution. Yield 23.6 g (77%). mp 192-193°C (from ethanol). IR spectrum, cm^{-1}: in Nujol, $\nu_{C=O}$ 1685 (carboxyl), 1647 (diaryl ketone), ν_{O-H} 2950 broad band; in dioxane, $\nu_{C=O}$ 1729 (ε 465), 1662 (ε 220). Found, %: C 74.5; H 4.4. $C_{19}H_{14}O_4$. Calculated, %: C 74.5; H 4.6.

3-Chloro-3-phenylperinaphthalide (III). This was obtained by the same method [3]. mp 126-128°C (lit. [3]: mp 127-128°C). IR spectrum (in dioxane): $\nu_{C=O}$ 1731 cm^{-1} (ε 630).

3-Chloro-3-(p-methoxyphenyl)perinaphthalide (IV). A solution of 4.3 g (0.014 mole) of the acid (II) and 3.3 ml (0.046 mole) of thionyl chloride in 35 ml of anhydrous benzene was boiled for 1 h and filtered, and to the filtrate was added 25 ml of hexane. After 24 h the crystals that had formed were separated off. Yield 3.0 g (65%), mp 170-172°C. IR spectrum (in dioxane): $\nu_{C=O}$ 1735 cm^{-1} (ε 490). Found, %: Cl 10.5. $C_{19}H_{13}ClO_3$. Calculated, %: Cl 10.9.

3-Aryl-3-arylaminoperinaphthalides (V-X). A solution of equimolar amounts (0.0035 mole) of (III) or (IV), an arylamine, and triethylamine in 10 ml of anhydrous dioxane was heated at 100°C for 2 h. Then it was cooled and the triethylamine hydrochloride was separated off. The solution was evaporated in vacuum and the residue was recrystallized from benzene, giving compounds (V-X) (Table 1).

Anil of 1-Benzoyl-8-methoxycarbonylnaphthalene (XI). An excess of diazomethane in ethereal solution was added to a solution of 0.22 g of (V) in 10 ml of dioxane. After 24 h the solution was evaporated in vacuum. The yield of light yellow crystals was 0.18 g (75%). mp 160-161°C (from cyclohexane–n-hexane). IR spectrum, cm^{-1}: in Nujol, $\nu_{C=O}$ 1727, $\nu_{C=N}$ 1617; in dioxane, $\nu_{C=O}$ 1727 (ε 430), $\nu_{C=N}$ 1161 (ε 150). Found, %: C 82.7; H 5.2; N 3.9. $C_{25}H_{19}NO_2$. Calculated, %: C 82.2; H 5.2; N 3.8.

3-Diphenylamino-3-phenylperinaphthalide (XII). A solution of equimolar amounts (0.0035 mole) of (III), diphenylamine, and triethylamine in 10 ml of dioxane was kept at room temperature for 24 h, and the triethylamine hydrochloride was separated off. The solution was evaporated in vacuum and the residue was recrystallized from benzene to give (XII) (Table 1).

3-Chloro-2,3-diphenyl-2,3-dihydro-1H-benz[d,e]isoquinolin-1-one (XIII). A solution of 0.3 g of (V) and 0.2 ml of thionyl chloride in 10 ml of anhydrous benzene was boiled for 30 min and was then evaporated in vacuum to give 0.25 g (76%) of yellow crystals. These were dried in vacuum over phosphorus pentoxide. mp 220-222°C. The IR spectra are given in Fig. 2. Found, %: Cl 9.5; N 3.6. $C_{24}H_{16}ClNO$. Calculated, %: Cl 9.6; N 3.8.

1-Oxo-2,3-diphenyl-1H-benz[d,e]isoquinolinium Hexachloroantimonate (XIV). With cooling and stirring, a solution of 0.05 ml of antimony pentachloride in 5 ml of benzene was slowly added to a solution of 0.08 g of (XIII) in 25 ml of anhydrous benzene. The resulting yellow crystalline precipitate was separated off, washed with benzene, and dried in a vacuum desiccator over phosphorus pentoxide, mp 243-245°C (decomp.). Found, %: Cl 31.8. $C_{24}H_{16}Cl_6NOSb$. Calculated, %: Cl 31.8.

2,3-Diaryl-3-hydroxy-2,3-dihydro-1H-benz[d,e]isoquinolin-1-ones (XV, XVI). A. Compound (V) (0.3 g) was heated at 200°C for 5 min and was then cooled, after which recrystallization from benzene yielded colorless crystals of (XV).

B. A solution of 0.0015 mole of (V or VI) and 0.3 ml of thionyl chloride in 20 ml of anhydrous benzene was boiled for 30 min and evaporated in vacuum. The residue was triturated with 10 ml of 3% aqueous sodium carbonate solution. The undissolved matter was separated off, washed with water, dried, and recrystallized from benzene. This gave colorless crystals of (XV) or (XVI), respectively (Table 1).

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