CYCLIC β-AMINOVINYLIMINES

VI. Formation of Isoquinolones and Isoindolones in the Oxidation of 2-Aryl-1-phenylamino-3-phenyliminoindenes*

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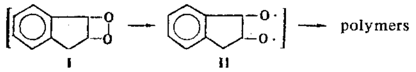
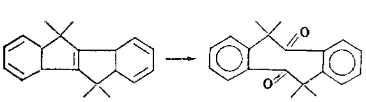
2-Substituted 1-phenylamino-3-phenyliminoindenes have been found to be readily oxidized by atmospheric oxygen. The structure of the resulting 3-aryl-3-hydroxy-2-phenyl-4-phenyliminodihydroisoquinol-1-ones has been shown by chemical and spectroscopic methods. The comparative oxidizability of enamines of several types is discussed on the basis of quantum-mechanical calculations by the LCAO MOH method.

In a study of aminoindenes [1], it was found that when 2-aryl-1-phenyl-amino-3-phenyliminoindenes (Va–Vc) were boiled in inert solvents (chloroform, dichloroethane, carbon tetrachloride, toluene, heptane), the double bond of the five-membered ring was cleaved by the action of atmospheric oxygen. Such ready oxidizability of these aminoindenes appeared unusual and required a more detailed study. The literature contains relatively few examples of the oxidation of the double bond of the five-membered ring of indene. A case is discussed of the oxidation of indenes by organic peracids to 1,2-epoxyindans [2] and by phthaloyl peroxide to cyclic phthalic esters of indan-1,2-diol [3]. In a study of the oxidation of indenes by atmospheric oxygen [4] the formation of cyclic peroxides I giving the short-lived free biradicals II is mentioned [4]. The oxidation of tetrahydroindenoindene (III) by chromium trioxide was terminated by the oxidative cleavage of the double bond of the five-membered ring with the formation of the dicarbonyl compound IV [5].

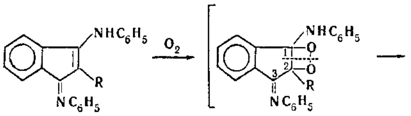


I II



III IV

In our case, we regard the process of oxidation as the initial addition by the aminoindenes of a molecule of oxygen with the formation of the cyclic peroxides VI, similar to those reported previously [4]. Then the peroxide ring opens with the cleavage of the C_1—C_2 bond of the five-membered ring. The intermediate benzyl derivatives VII then rearrange to form 3-aryl-3-hydroxy-2-phenyliminodihydroisoquinol-1-ones (VIII) which give the urethanes XIII with phenylisocyanate. The IR spectrum of the latter contains the bands most important for the carbamates [6]. The IR spectra of the isoquinolones VIII themselves also confirm the structure adopted for them (Table 1).



V VI

Table 1

Infrared Spectra of the Compounds Obtained*

VIII a	VII b	VIII c	IX a	IX c	X	XI	XI according to [9]	XII	XIII	Assignment of the bands according to [6]
1493 (8)	1493 (6)	1505 (4)	1502 (9)	1498 (9)	1502 (7)	1496 (6)	1501 (7)	1504 (6)	1494 (7)	ν of aromatic rings
1544 (9)	1541 (10)	1534 (6)								?
1599 (9)	1599 (10)	1596 (5)	1599 (8)	1598 (6)	1600 (8)	1594 (5)	1594 (6)	1598 (4)	1594 (4)	ν of aromatic rings
1658 (10)	1650 (8)	1658 (10)	1682 (9)	1679 (8)	1676 (10)	1688 (10)	1691 (10)	1694 (10)	1692 (10)	$\nu_{C=O}$ of a cyclic amide
			1702 (10)	1712 (10)						$\nu_{C=O}$ of an aroyl group
								2977 (10)		ν vibrations of CH_3 for an ethoxy group
3358 (10)	3348 (10)	3337 (10)	3391 (10)	3377 (10)	3409 (10)	3379 (10)	3377 (10)		3302 (10)	ν of NH and OH groups

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*For part V, see [1].

*The spectra were recorded on an IKS-14 instrument. In the 1480-1800 cm^{-1} region the samples of the substances were examined in paraffin oil and in the 2400-3600 cm^{-1} region in hexachlorobutadiene. The relative intensities of the bands (background taken as zero and the strongest band as 10) are given in brackets.

Table 2

Results of Calculation of a Number of β-Aminovinylimines

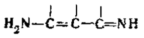
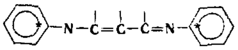
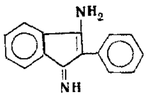
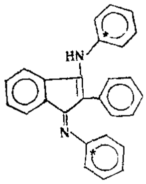
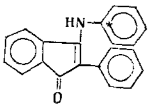
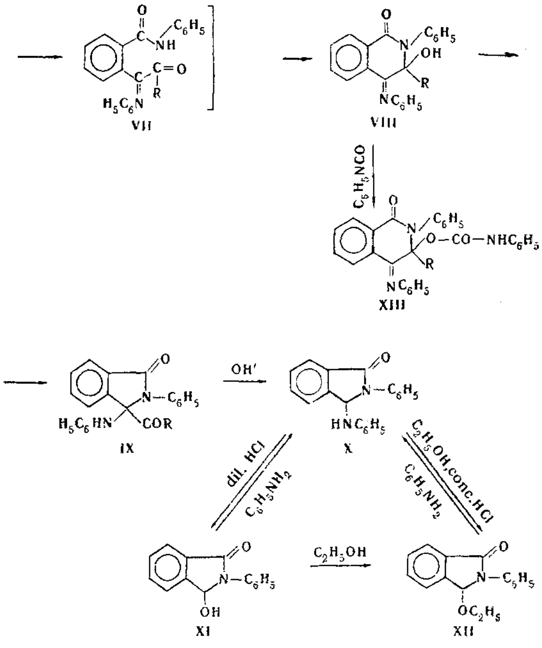
Formula for π skeleton of the system	Angles of rotation around ordinary bonds relative to a coplanar arrangement of the groups	Energies of the highest occupied orbital in β_0 units
 $H_2N-\overset{\mid}{C}=\overset{\mid}{C}-\overset{\mid}{C}=NH$		0.6824
	$\overset{*}{C}$—N 50°;	0,5812
	C—C 20°;	0,5004
	C—N and $\overset{*}{C}$—N 25°; C—C 20°;	0,4647
	C—N and $\overset{*}{C}$—N 25°; C—C 20°;	0,5115

Table 3

3-Aryl-3-hydroxy-2-phenyl-4-phenyliminodihydroisoquinol-1-ones

Compound	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
VIIIa	175—177	$C_{27}H_{20}N_2O_2$	80.21	5.09	6.93	80.19	4.95	6.93	80
VIIIb	178—179	$C_{28}H_{22}N_2O_3$	77.62	5.38	6.57	77.56	5.07	6.46	75
VIIIc	193—195	$C_{31}H_{22}N_2O_2$	82.31	5.23	6.35	82.18	4.85	6.17	81



V-IX R= a) C_6H_5; b) p-$CH_3OC_6H_4$; c) α-$C_{10}H_7$

The duration of the reaction described depends on the amount of the starting material. The passage of oxygen through the reaction mixture while it is boiling does not accelerate the reaction and does not increase the yield. When the aminoindenes were boiled in inert solvents in an atmosphere of carbon dioxide, only traces of the isoquinolones were obtained and the starting materials were unchanged. This experiment confirms the decisive role of atmospheric oxygen in this reaction. In hydroxyl-containing solvents (alcohols, acids) the aminoindenes V are not oxidized. In this case the molecules of V are probably stabilized by association.

All the isoquinolones VIII obtained are yellow crystalline substances readily soluble in halogenohydrocarbons and in the usual aromatic hydrocarbons and sparingly soluble in heptane and petroleum ether.

On being boiled in polar media, compounds VIII rapidly and irreversibly isomerize into the corresponding 1-aroyl-1-phenylamino-2-phenylisoindol-3-ones (IX). This indicates that in the ternary ring-chain tautomeric system VII–VIII–IX the isomer with the five-membered ring is the most stable, as in [7]. In polar solvents the migration of the proton necessary for this prototropic conversion is considerably facilitated. In inert solvents the isomerization of VIII into IX requires prolonged boiling.

The isoindolones IX obtained are colorless crystalline substances moderately soluble in chloroform and alcohol and readily soluble in acetic acid. The IR spectra confirm the structure IX. As was to be expected, the frequency of the amide band in IX at 1690 cm^{-1} is higher than that for the six-membered isomer VIII at 1650 cm^{-1} (see Table 1).

The isoindolones IX are hydrolyzed by alcoholic alkalies and alkoxides to the same compounds 2-phenyl-1-phenylaminoisoindol-3-one (X), with the elimination of the respective organic acid. In the IR spectrum of X the aroyl band has disappeared.

On hydrolysis with dilute mineral acids in ethanolic solution, the 1-phenylaminoisoindolone X loses aniline and forms 1-hydroxy-2-phenylisoindol-3-one (XI), which has been obtained independently by the reduction of phthalanil [8]. The vibrational spectra of compounds X and XI are given in Table 1. We have found that the spectroscopic data given in the literature for the 1-hydroxyisoindolone XI [9] (amide $\nu_{C=O}$ 1652 cm^{-1} and ν_{NH} 3280 cm^{-1}) are erroneous.

On being boiled with aniline in acetic acid, the 1-hydroxyindolone XI formed the initial 1-phenylaminoisoindolone X, and on being boiled with conc HCl in ethanol it was etherified to form 1-ethoxy-2-phenylisoindol-3-one (XII).

The hydrolysis of the 1-phenylaminoisoindolone X with conc HCl in ethanol also led to the 1-ethoxyisoindolone XII. The reaction of XII with aniline in acetic acid reformed X. All these reactions confirmed the structure of the compounds obtained and described by us previously.

Only N-phenyl-substituted 1-amino-3-iminoindenes (V) take part in such an oxidation reaction; aliphatic β-aminovinylimines and N-unsubstituted 1-amino-3-imino-2-phenylindene are stable to the action of oxy-

Table 4

1-Aroyl-2-phenyl-1-phenylaminoisoindol-3-ones

Compound	Mp, °C	Empirical formula	Found, %			Calculated, %		
			C	H	N	C	H	N
IXa	171—172	$C_{27}H_{20}N_2O_2$	80.24	5.06	6.91	80.19	4.95	6.93
IXb	181—183	$C_{28}H_{22}N_2O_3$	76.89	5.12	6.23	77.56	5.07	6.45
IXc	188—190	$C_{31}H_{22}N_2O_2$	81.85	4.92	6.11	82.18	4.85	6.17

gen. This appeared unexpected since the oxidizability of the N-phenyl derivatives should be lower because of the electron-attracting effect of the aromatic rings. However, quantum mechanical calculations by the LCAO MOH method (see Table 2) explain the experimental results fully. The majority of the parameters h and k for the determination of the resonance and Coulomb integrals were taken from a published paper [10]; the values of the others were: $h_N = 0.5$; $k_{C=N} = 1.0$. The resonance integral was calculated additionally in cases where the structure of the molecule requires rotations of groups round an ordinary bond. The angles of rotation were evaluated roughly from molecular models of the substances.

As can be seen from the results of the calculation, it is just the aminovinylimines of type V that have the greatest oxidizability. The phenyl group does not decrease but, rather, increases the tendency of the given π-systems to give up electrons. The replacement of a phenylimino group by a carbonyl group markedly reduces the oxidizability of the system as compared with substances having a β-aminovinylimine structure.

EXPERIMENTAL

3-Aryl-3-hydroxy-2-phenyl-4-phenyliminodihydroisoquinol-1-ones (VIII). The appropriate initial aminovinylimine V (0.2 g) was boiled in chloroform for 3 hr. The reaction mixture was cooled and two volumes of heptane were added with rubbing with a glass rod, and the mixture was placed in the refrigerator. On the following day the yellow crystals were separated off and recrystallized from toluene. After the separation of the **VIII** from the mixture of chloroform and heptane, the evaporation of the latter in the air yielded the initial substance unchanged: 0.06 g of **Va**, 0.05 g of **Vb**, and 0.05 g of **Vc**. The yields were calculated on the V that had reacted.

1-Aroyl-2-phenyl-1-phenylaminoisoindol-3-ones (IX). An isoquinolone VIII was dissolved in a small amount of ethanol by boiling and boiling was continued until the yellow color of the solution had changed to light yellow or colorless. On cooling, the corresponding compound IX crystallized out in colorless form.

2-Phenyl-2-phenylaminoisoindol-3-one (X). A compound IX (0.1 g) was boiled with 3 ml of 3% sodium methoxide or in a mixture of 5 ml of ethanol and 2 ml of 10% aqueous caustic soda for 5 min. On cooling, 0.05 g (76%) of the white substance **X** crystallized out. Mp 159–160° C (from ethanol). Found, %: C 79.72; H 5.54; N 9.38. Calculated for $C_{20}H_{16}N_2O$, %: C 80.00; H 5.35; N 9.34. The corresponding acid was detected in the filtrate.

A mixture of 0.2 g of **XI** or **XIII**, 3 ml of acetic acid, and 0.2 ml of aniline was boiled for 3 min. The reaction mixture was cooled, diluted with 3 volumes of water, and the resin that deposited was washed with water. On trituration with ethanol the substance crystallized. Yield 0.18 g (67–75%) of **X**.

1-Hydroxy-2-phenylisoindol-3-one (XI). A mixture of 0.1 g of the phenylaminoisoindolone **X**, 6 ml of ethanol, and 1.5 ml of dil (1 : 1) HCl was boiled for 1 hr. The reaction mixture was cooled, 12 ml of water was added, and 13 ml of liquid was distilled off. The residue was crystallized from ethanol. This gave 0.05 g (69%) of colorless acicular crystals with mp 167–169° C. A mixture with an authentic sample [9] gave no depression of the melting point. Aniline was detected in the filtrate.

1-Ethoxy-2-phenylisoindol-3-one (XII). A) A mixture of 0.4 g of the phenylaminoisoindolone **X**, 25 ml of ethanol, and 5 ml of conc HCl was boiled for 1.5 hr and was then cooled and diluted with 20 ml of water. On the following day, 0.22 g (63%) of **XII** was separated off in the form of small colorless needles with mp 79–80° C (from dil ethanol). Found, %: C 75.54; H 5.74; N 5.82. Calculated for $C_{16}H_{15}NO_2$, %: C 76.00; H 5.93; N 5.82.

B) A mixture of 0.1 g of the hydroxyisoindolone **XI**, 2 ml of ethanol, and 0.5 ml of conc HCl was boiled for 1 hr. The mixture was cooled and diluted with three volumes of water. On the following day 0.06 g (46%) of **XII** was separated off.

Phenylurethane of 3-hydroxy-2,3-diphenyl-4-phenyliminodihydroisoquinol-1-one (XIII). A mixture of 0.2 g of **VIIIa** and 0.058 g (1 : 1) of phenylisocyanate was heated until a homogeneous red-violet solution had been formed. Then it was cooled and 1 ml of absolute benzene was added. On rubbing with a glass rod, a colorless substance crystallized out. After 1 hr, the precipitate was separated off and washed with heptane, giving 0.13 g (50%) of **XIII** with mp 251–252° C (from ethanol). Found, %: C 78.47; H 5.09; N 8.28. Calculated for $C_{34}H_{25}N_3O_3$, %: C 78.00; H 4.78; N 8.03.

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