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N-ALKYLATION OF VINYLOXYANILINES WITH GLYCIDYL ETHERS OF PHENOLS AND A STUDY OF THEIR BASICITY IN ACETONITRILE

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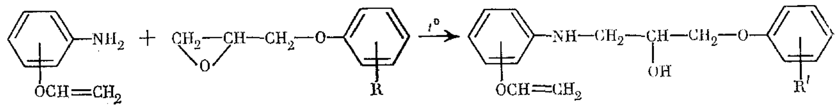
The interaction of vinyloxyanilines (I) with alkyl bromides and dimethyl sulfate leads to tertiary N,N-dialkylvinyloxyanilines [1] but with alkyl iodides stable quaternary ammonium salts of (I) are formed [2]. There has been little work on the synthesis of alkylated vinyloxyanilines with a secondary amino group and these were devoted in the main to the vinylation of the corresponding aminophenols [3, 4].

While continuing investigations on the synthesis of substituted vinyloxyanilines we have studied the reaction of (I) with the epoxypropyl ether of phenol (II), of p-chlorophenol (III), and of o-cresol (IV) in the present work. The influence of the structure of the resulting substituted vinyloxyanilines on their basicity has been investigated by potentiometric nonaqueous titration.

It is known that the glycidyl ethers (II)-(IV) alkylate aromatic amines with the formation of 3-aroxyanilinopropan-2-ols [5, 6], while there is no information on the interaction of vinyloxyanilines with epoxy compounds. It was established in [7] that the o-, m-, and p-isomers of (I) and also N-methyl-p-vinyloxyaniline (V) react at 110-115°C with ether (II) with fission of the oxirane ring and the formation in high yield of p-, m-, and o-N-(2-hydroxy-3-phenoxypropyl)vinyloxyanilines (VI)-(VIII) or N-methyl-N-(2-hydroxy-3-phenoxypropyl)-p-vinyloxyaniline (IX). Glycidyl ethers (III), (IV) behave similarly in this reaction:



(I) (II)-(IV) (VIa, c), (VIIa)-(VIIIc)

where R = H (a), p-Cl (b), o-CH_3 (c).

It was noticed that the presence of an electron-accepting substituent in the aromatic nucleus of the glycidyl ether increased the yield of N-(aroxypropanolyl)vinyloxyanilines (VIIb), (VIIIb) and the pressure of an electron-donating substituent reduced the yield of (VIc-VIIIc). In the series of isomeric (I) a regular decrease was observed in the yield of its reaction products with glycidyl ethers on going from the p to the o isomer. This is evidently explained both by steric screening of the reaction center and by a possible fall in the basic properties of the o isomers of (I).

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TABLE 1. Characteristics of the Obtained Compounds $RC_6H_4N(R^*)CH_2CH(OH)CH_2OC_6H_4R'$†

Compound	R	R′	Yield, %	Bp (p, mm Hg) or mp, °C	n_D^{20}	d_4^{20}	MR_D Found/Calculated	Empirical formula	Found/calculated, %		
									C	H	N
(VIa)	*p*-OCH=CH₂	H	76,6	100–101	–	–	–	$C_{17}H_{19}NO_3$	72,02/71,58	7,12/6,93	4,47/4,90
(VIc)	*p*-OCH=CH₂	*o*-CH₃	75,3	86–87	–	–	–	$C_{18}H_{21}NO_3$	72,25/72,24	7,25/7,00	4,14/4,67
(VIIa)	*m*-OCH=CH₂	H	71,8	230–235 (2)	1,5945	1,1743	82,40/81,45	$C_{17}H_{19}NO_3$	70,96/71,58	6,66/6,93	4,22/4,38
(VIIb)	*m*-OCH=CH₂	*p*-Cl ‡	73,3	240–245 (2)	1,6015	1,2847	86,52/86,59	$C_{17}H_{18}NO_3Cl$	63,40/63,87	5,32/5,64	4,68/4,38
(VIIc)	*m*-OCH=CH₂	*o*-CH₃	69,2	238–240 (2,5)	1,5874	1,1538	87,10/86,28	$C_{18}H_{21}NO_3$	72,35/72,24	7,48/7,00	4,66/4,67
(VIIIa)	*o*-OCH=CH₂	H	58,7	230–235 (3)	1,5854	1,1765	81,81/81,45	$C_{17}H_{19}NO_3$	71,34/71,58	6,73/6,93	4,54/4,90
(VIIIb)	*o*-OCH=CH₂	*p*-Cl ‡	60,3	236–240 (3)	1,5950	1,2653	85,81/85,69	$C_{17}H_{18}NO_3Cl$	63,42/63,87	5,36/5,64	4,10/4,38
(VIIIc)	*o*-OCH=CH₂	*o*-CH₃	57,8	225–230 (2,5)	1,5745	1,1423	86,45/86,28	$C_{18}H_{21}NO_3$	72,65/72,24	7,20/7,00	4,32/4,67
(IX)	*p*-OCH=CH₂	H	66,9	225–230 (1,5)	1,5855	–	–	$C_{18}H_{21}NO_3$	73,08/72,24	6,87/7,00	4,62/4,68
(X)	*p*-OC₂H₅	H	62,5	109	–	–	–	$C_{17}H_{21}NO_3$	71,51/71,05	7,05/7,36	4,55/4,87

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†R* is always H, in (IX) $R^* = CH_3$.

‡Found, %: Cl 11.53 (VIIb); 11.61 (VIIIb). Calculated, %: Cl 11.12.

TABLE 2. Values of the Ionization Constants of N-(3-Aroxy-2-hydroxypropyl)anilines $RC_6H_4NHCH_2CH(OH)CH_2OC_6H_4R'$ in Acetonitrile at 25°C

Compound	R	R′	pK_a, MeCN	σ, for R
(VIa)	p-CH_2=CHO	H	10,78	−0,089 *
(VIc)	p-CH_2=CHO	o-CH_3	10,72	−0,089 *
(VIIa)	m-CH_2=CHO	H	9,78	+0,21 *
(VIIb)	m-CH_2=CHO	p-Cl	9,71	+0,21 *
(VIIc)	m-CH_2=CHO	o-CH_3	9,70	+0,21 *
(VIIIa)	o-CH_2=CHO	H	9,65	+0,21 *
(VIIIb)	o-CH_2=CHO	p-Cl	9,67	+0,21 *
(VIIIc)	o-CH_2=CHO	o-CH_3	9,70	+0,21 *
(X)	p-C_2H_5O	H	11,32	−0,25
(XI) †	H	H	10,39	0

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*According to data of [8].

†Obtained according to the method in [5].

The obtained N-(2-hydroxy-3-aroxypropyl)vinyloxyanilines (VI)-(IX) were thermally stable crystalline or oily substances. Their properties and data of their elemental analysis are shown in Table 1. The basicity constants of N-(2-hydroxy-3-aroxypropyl-p-, -m-, and -o-vinyloxyanilines (VI)-(VIII), N-(2-hydroxy-3-phenoxypropyl)-p-ethoxyaniline (X), and N-(2-hydroxy-3-phenoxypropyl)aniline (XI) are given in Table 2. The degree of purity of compounds (VI)-(XI) was 99.85%.

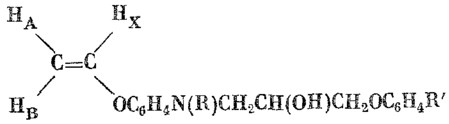
The main properties of the N-(2-hydroxy-3-aroxypropyl)vinyloxyanilines can be considered in three separate series of compounds according to the special features of their structure, viz. (VIa, c), (VIIa-c), and (VIIIa-c), characterized by the fixed position of the vinyloxy group with variations of the nature and position of the substituent in the phenoxyl fragment. Comparison of the pK_a value (see Table 2) within each series showed that the center of basicity in the molecules is not sensitive to a structural change in the phenoxyl fragment. This result is in agreement with known ideas on the attenuation of the polar effect of a substituent at a sufficiently large displacement from the reaction center. For the same reason the contribution of the —I effect of the phenoxy group to the electron density on the N atom must be extremely insignificant. (Calculation on the additivity constant σ^* of the $PhOCH_2 \cdot CH_2CH_2$ group gave a value of 0.1.)

On the strength of the realization of the π-donor saturation effect in molecules of aromatic amines the size of the electronic influence of the p-vinyloxy group (as also others +M substituents) in these compounds depends on the extent of the steric inhibition of resonance. Thus, in the series of primary anilines, the electronic effect of the CH_2 = CHO group characterizes it as an electron-donating substituent $\sigma_n = -0.089$ [9], while in the series of structurally hindered N,N-dialkylvinyloxyanilines the effect of this substituent proved to be close to the effect of a H atom $\sigma_n = 0$ [8].

In the investigated series of secondary anilines the p-vinyloxy group proved to have an electron-donating influence on the basicity of the N atom [cf. (VIa) and (XI)]. The marked electron-donating character of the influence of the CH_2 = CHO group on the distribution of electron density on the N atom indicates that in the molecules of these compounds, just as in molecules of anilines (I) [8], this substituent enters into an intramolecular electronic interaction with a π-donating reaction center, viz., the nitrogen atom. The presence of a splendid linear relationship between the pK_a values of the investigated compounds (VIa), (VIIa), (X), and (XI), and the averaged Hammett constants $pK_a = (10.45 \pm 0.02) - (3.26 \pm 0.33)\sigma$, $S_0 = 0.07$, $r = 0.991$ indicates that such an effect actually takes place in the series of anilines (VIa-c).

When calculating the correlation relationship, a value of the constant $\sigma_{p\text{-}CH_2=CHO} = -0.089$ was used, allowing for the contribution of the π-donor saturation effect of this substituent with the reaction center. In accordance with the obtained data, the appearance of this effect in the investigated N-(3-aroxy-2-hydroxypropyl)vinyloxyanilines (VIa)-(VIIc) indicated that the functional substituent on the N atom $CH_2CH(OH)CH_2OAr$ did not prove to have an appreciable steric influence on the extent of p—π-conjugation of the N atom with the π-system of the benzene ring.

TABLE 3. Parameters of the PMR Spectra of Compounds*



Compound	Chemical shifts, ppm							
	H_A	H_B	H_X	NCH_2 †	CH_2O	CH(O)	C_6H_4	CH_3
(VIa)	4,23	4,54	6,53	3,25 3,30	4,00	4,20	6,68 7,25–6,80	–
(VIc)	4,21	4,53	6,50	3,25 3,28	4,00	4,06	7,05–6,66	2,25
(VIIIa)	4,22	4,56	6,42	3,15 3,28	3,82	4,02	7,18–6,47	–
(IX)	4,16	4,30	6,53	3,32	3,92	4,05	7,05–6,65	2,81
(X)	–	–	–	3,16	3,9 ‡	3,9 ‡	7,23–6,63	1,33

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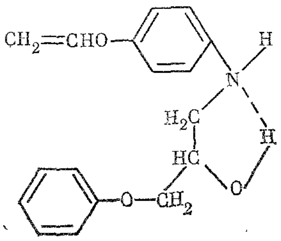
*The spin–spin interaction constants of the protons of the vinyloxy group were characterized by equal J values for compounds (VIa)-(IX): $^3J_{trans} = 13.5$, $^3J_{cis} = 6.0$, and $^2J = 2.0$ Hz (in IX) $^2J = 1.5$ Hz).

†The chirality of the methyl group carbon atom of compounds (VIa)-(VIIIa) causes anisochronicity of the geminal protons $-N-CH_2$ (but not CH_2O). For them, $^2J = 12.5$, $^3J = 7.0$ and 4.0 Hz.

‡Superposition of multiplets of groups CH(OH), CH_2O, and CH_2O in C_2H_5O group.

The hydroxyethyl group ($\sigma^*CH_2CH_2OH = 0.20$) reduces the basicity of the N atom in aromatic amines (n-hydroxyethylaniline is a weaker base than N-methylaniline in aqueous solution by 0.83 units of pK_a [10]). Proceeding from the electron-accepting nature of the hydroxyalkyl fragment $CH_2CH(OH)$ in the investigated molecules (VI)-(XI), it was possible to expect a similar influence of it on their basicity. However, comparison of the basic properties of aniline (V) ($pK_a = 10.95$) and of the hydroxyalkyl derivative (VIa) (see Table 2) shows that in a medium of MeCN the influence of the hydroxyalkyl group on the basicity of the N atom differed from the effect which this substituent showed in aqueous solution. As is evident, in MeCN the basic properties of the compared compounds were practically equal to one another ($\Delta pK_a = 0.17$). On going from water to MeCN, the observed drop in electron-accepting properties of the hydroxyalkyl substituent in N-(aroxypropanolyl)anilines (VI)-(XI) is, in our view, linked with the fact that in MeCN this substituent realizes its potential to enter into an intramolecular hydrogen bond [11, 12].



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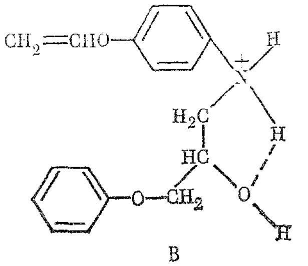

B

The increase in basicity in the studied series of compounds (VI)-(XI) in comparison with that expected from the size of the –I effect of the hydroxyalkyl substituent indicates that in MeCN an intramolecular hydrogen bond is formed not in the actual base (in structure A the basicity is reduced), but in the protonated form (structure B).

The correctness of the stated hypothesis regarding the reasons for the weakening of the electron-accepting properties of the hydroxyalkyl substituent (the generation of an intramolecular hydrogen bond in the cation) was confirmed by an investigation of the basic properties of aniline (V) (pK_a MeOH = 5.79 [8]) and aniline (VIa) (pK_a MeOH = 5.00) in a medium of MeOH the solvating ability of which is close to that of water. As is evident in methanol, the difference in basicity of compounds (V) and (VIa) ($\Delta pK_a = 0.79$) was practically in complete agreement with the ratio, of basic properties of the N-substituted anilines PhNHR (R = Me, EtOH) in aqueous solution ($\Delta pK_{a_{H_2O}} = 0.83$) [10] and differed from that established in a medium of MeCN ($\Delta pK_{a_{MeCN}} = 0.17$). If it is considered that in aqueous solution the influence of the hydroxyalkyl and methyl substituents on the basicity of the nitrogen atom in N-substituted anilines correspond completely with the inductive constant of these substituents, then the practical equality of the ΔpK_a values in methanol and in water for the compared pair of compounds indicates that in methanol (as in aqueous solution) the action of the $CH_2—CH(OH)$ fragment on the basicity of the nitrogen atom in N-(aroxypropanolyl)anilines (VI)-(XI) corresponds to its inductive effect.

The influence of the hydroxyalkyl substituent on the basicity of the N atom in the aromatic amines $ArNHCH_2CH(OH)$ therefore depends on the nature of the solvent in which determination of the basic properties is carried out.

The vinyloxy group located in the ortho position of the aromatic nucleus in anilines (VIIIa-c) exerts an electron-accepting influence on the basicity of the N atom [cf. (VIII) and (XI) in Table 2]. The size of its electronic effect is no different from the effect exerted by the m-$CH_2 = CH—O$ group which follows from the identical basicity of o- and m-substituted compounds of the series (VIIa-c) and (VIIIa-c).

The data obtained on analysis of the PMR and IR spectra additionally confirmed the structure of the synthesized N-(aroxypropanolyl)anilines (VI)-(XI). Values of the chemical shifts of functional group protons and spin—spin interaction constants are shown in Table 3. There were absorptions at 1640-1638 and 965-960 ($CH_2 = CH$), 1255-1230 (COC), 3260 (NH, except compound IX), and a wide band near 3400 (OH) in the IR spectra (ν, cm^{-1}) of compounds (VI)-(IX).

EXPERIMENTAL

PMR spectra were taken on a Tesla BS-487 B spectrometer (80 MHz) in CCl_4 ($CDCl_3$) relative to HMDS. IR spectra were taken on a UR-20 instrument (with KBr or in a thin film). Ionization constants were determined potentiometrically in anhydrous MeCN by the method of [13] (standard with diphenylguanidine with $pK_a = 17.90$ [14]) for compounds (V) and (VIa) in absolute methanol by the method of [15].

N-(2-Hydroxy-3-aryloxypropyl)vinyloxyanilines (VIa, c). Ether (II) or (IV) (10 mmoles) was added dropwise over 1 h to the p-isomer of aniline (I) (1.35 g:10 mmole) heated to 110-115°C. The mixture was kept at 115°C for 5 h and then cooled. The reaction products were recrystallized repeatedly from a chloroform—petroleum ether mixture.

In the same way, N-(2-hydroxy-3-arylpropyl)vinyloxyanilines (VIIa)-(VIIIc) were obtained by the interaction of the m- and o-isomers of aniline (I) with ethers (II)-(IV). The reaction products were fractionated by distillation in vacuum.

Compound (IX) was obtained in a similar manner by the interaction of ether (II) with aniline (V) and compound (X) with p-phenetidine. The characteristics and yields of the obtained N-(2-hydroxy-3-aryloxypropyl)anilines (VIa)-(X) are shown in Table 1.

CONCLUSIONS

1. N-(2-Hydroxy-3-aryloxypropyl)vinyloxyanilines have been obtained for the first time by reaction of vinyloxyanilines with glycidyl esters of phenols.

2. A linear relationship has been established linking the size of the pK_a with the Hammett constants of substituents in an aromatic series of anilines ($\rho = 3.26$).

3. In acetonitrile the basicity of N-(2-hydroxy-3-aryloxypropyl)vinyloxyanilines was increased as a result of additional stabilization of the conjugate acids of these bases by an intramolecular hydrogen bond.

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OXIDATION OF STERICALLY HINDERED PHENOLS BY MANGANESE TRIACETATE AND POTASSIUM DICHROMATE IN NEUTRAL AND ACIDIC MEDIA

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Detailed studies have been carried out on the oxidation of sterically hindered phenols (SHP) in basic and neutral media by O_2, salts and oxides of Fe, Pb, Ag, and Mn, and phenoxyl, nitroxyl, and peroxide radicals [1]. There is much less information on the oxidation of SHP in acidic media, apparently as a result of the changes in the redox potentials of SHP on protonation, with the consequent need for more powerful oxidants. In some instances, however, this requirement may give favorable results, since in protonic media the selectivity of SHP toward some oxidants should increase, and this can be used, notably, to protect SHP from uncontrolled thermal oxidation by atmospheric oxygen. In addition, increasing the acidity of the medium may result in a change in the mechanism of oxidation. For example, according to Vermillion and Pearl [2], in the electrochemical oxidation of 2,6-di-tert-butyl-4-methylphenol and the corresponding phenoxide, the anion undergoes one-electron oxidation, whereas the undissociated form of the phenol is involved in a two-electron reaction.

The object of the present investigation was to study the oxidation of the para-substituted SHP 2,6-di-tert-butyl-4-methylphenol (I), 2,4,6-tri-tert-butylphenol (II), 2,6-di-tert-butyl-4-dimethylaminophenol (III), and 2,6-di-tert-butyl-4-methoxymethylphenol (IV) by $Mn\cdot(OAc)_3$ and $K_2Cr_2O_7$ (Scheme 1).

Oxidation of (I) with $Mn(OAc)_3$ in MeOH affords the phenol (IV) and the quinol methyl ether (V) in yields of 80 and 20%. When the reactant ratio is 1:1, half of the original phenol (I) remains unconsumed. Complete reaction of (I) requires two equivalents of the oxidant.

These observations lead to a mechanism for the oxidation of (I) involving a stepwise two-electron process.

The ether (IV) may be formed by addition of MeOH to the methylenequinone (IX), formed by the disproportionation of radicals (VIII), and by the prototropic dienone—phenol rearrangement of the quinol ether (V). We have demonstrated experimentally the possibility of

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