7-Cyanoamino-2H,3,4-dihydropyrano[2,3-d]pyrimidine (XIIb). A 0.84-g (10 mmole) sample of N-cyanoguanidine and 2.8 g (10 mmole) of complex X were added to a solution of sodium ethoxide (from 0.5 g of sodium and 30 ml of alcohol), and the mixture was refluxed for 3 h. The alcohol was evaporated, the residue was dissolved in water, and the aqueous solution was acidified to pH 7 with 1 N HCl. The resulting precipitate was removed by filtration, washed with alcohol, and dried to give 0.77 g (43.8%) of XIIb with mp > 320°C (from DMF). IR spectrum: 1580 (C=C), 1645 (C=N), 2150 (C≡N), and 3010 cm^{-1} (NH). Found: C 54.3; H 4.6; N 32.5%; M^+ 176. $C_8H_8N_4O$. Calculated: C 54.6; H 4.6; N 31.8%; M 176.

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POLYARALKYLATION OF PRIMARY AROMATIC AMINES WITH 6-HYDROXY-2,4-DIMETHYL-1,3-BENZODIOXANE

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6-Hydroxy-2,4-dimethyl-1,3-benzodioxane is cleaved with opening of the 1,3-dioxane ring in a mixture of acetic and hydrochloric acids. The resulting hydroquinone-containing fragments N-aralkylate the primary amines (aminoanthraquinone, p-nitroaniline, and p-aminoazobenzene) which are added to the reaction mixture to give the corresponding N-(polyethylidenehydroquinone)arylamines.

Azo and anthraquinone dyes that contain hydroquinone residues have been used as developers for color photography [1-4]. The existing methods for the preparation of such dye-developers are usually multistep processes. In order to develop a method for the introduction of hydroquinone residues into aromatic compounds we studied the reaction of primary aromatic amines with 6-hydroxy-2,4-dimethyl-1,3-benzodioxane (I), which can be readily obtained from hydroquinone and acetaldehyde [5]. Bearing in mind the ability of 1,3-benzodioxanes to undergo cleavage to give fragments that are capable of aralkylating alcohols and thio alcohols [6, 7], we assumed that benzodioxane I would be a suitable reagent for the introduction of a hydroquinone residue into arylamine molecules. The amines that are usually employed in the synthesis of dyes, viz., p-nitroaniline (II), 1-aminoanthraquinone (III), 1,4-diaminoanthraquinone (IV), 1,4-diamino-5,8-dihydroxyanthraquinone (V), and p-aminoazobenzene (VI), were used as the starting compounds.

We found that benzodioxane I is cleaved with opening of the 1,3-dioxane ring in solution in acetic acid under the influence of concentrated hydrochloric acid and that the cleavage products react with the arylamine added to the reaction mixture to give several reaction products. However, by using a sufficiently large amount of hydrochloric acid (more than 20 moles per mole of benzodioxane I) one can direct the reaction to give primarily an N-substituted arylamine containing hydroquinone residues in the side chain. Compounds of this type were obtained in the reaction of benzodioxane I with all of the amines listed above (II-VI). On

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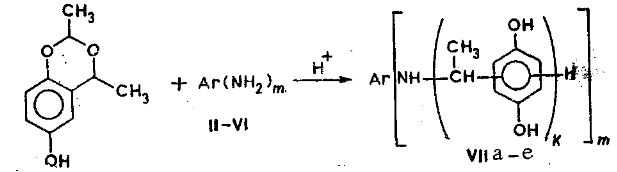
TABLE 1. PMR Spectra of N-(Polyethylidenehydroquinone)arylamines

Compound	Solvent	δ, ppm			
		CH_3	CH	OH	C_6H_2
VIIa	d_6-Acetone	1,37 (m)	4,53 (m)	7,65 br	6,62 (m)
	d_4-Methanol	1,40 (d, $J=7$ Hz)	4,27—4,80 (m)	4,80 (s)	6,63 br
VIIb	d_4-Methanol	1,30 (d, $J=7$ Hz)	4,42 (q, $J=7$ Hz)	4,80 (s)	6,60 (m)
VIIc	d_4-Methanol	1,38 (m)	4,30—4,90 (m)	4,76 (s)	6,59 (m)
	d_6-Acetone	1,37 (d, $J=7$ Hz)	4,53 (q, $J=7$ Hz)	7,60 br	6,60 br
VIId	d_4-Methanol	1,40 (d, $J=6{,}5$ Hz)	4,49—4,80 (m)	4,80 (s)	6,67 (m)
VIIe	d_4-Methanol	1,37 (m)	4,40—4,80 (m)	4,86 (s)	6,67 br

the basis of analytical and spectral data, as well as the properties that are peculiar to the compounds obtained, we concluded that they are N-(polyethylidenehydroquinone)arylamines (VIIa-e).



II, VIIa Ar= p-nitrophenyl, m=1; III, VIIb Ar=1-anthraquinonyl, m=1;IV, VIIc Ar=1,4-anthraquinonylene, m=2; V, VIId Ar=5,8-dihydroxy-1,4-anthraquinonylene, m=2; VI, VIIe Ar=p-phenylazophenyl, m=1; in all cases k=5-20

Absorption bands that indicate the presence of a $CHCH_3$ group (three bands at 2880-2980 cm^{-1} and a band at 1430 cm^{-1}) and a hydroquinone residue (broad band at 3100-3600 cm^{-1} and a band at ~1200 cm^{-1}) are observed in the IR spectra of polymers VIIa-e. The secondary amino group shows up in the spectra of VIIa-e only as an inflection (at 3200-3300 cm^{-1}) on the band of the stretching vibrations of the hydroxy group. Absorption bands at 1640-1680 cm^{-1}, which should be assigned to the C=O vibrations, are observed in the spectra of anthraquinone derivatives VIIb-d.

The PMR spectra of VIIa-e confirm the presence of an ethylidene group and a hydroquinone residue in their molecules (see Table 1).

The electronic absorption spectra of polymers VIIa-e contain a band with a maximum at ~300 nm, which is due to absorption of hydroquinone fragments, and bands that correspond to the chromophore systems of arylamines; the long-wave band in the spectra of polymers VIIa-e is shifted bathochromically as compared with the long-wave band observed in the spectra of the corresponding amines II-VI.

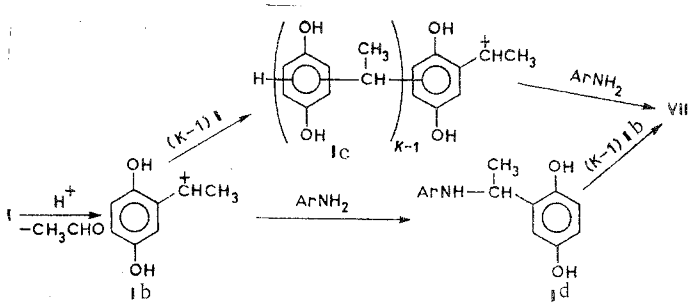
The determination of the molecular mass of samples of polymer VIIa obtained by condensation of benzodioxane I with amine II under various conditions shows that polyaralkylation of the amino group occurs even when equimolar amounts of the reagents are used (part of amine II remains unchanged) and that a polymer that contains approximately eight hydroquinone links is formed. A polymer with a higher molecular mass is formed when the amount of benzodioxane I in the reaction mixture is increased and also when the reaction time is increased (see Table 2).

The formation of polymers VIIa-e can be represented by a scheme that includes conversion of benzodioxane I under the influence of acid to polymeric carbonium ion Ic, which then aralkylates the amino group of the primary amine (II-VI) added to the reaction mixture. Another pathway, which consists in initial aralkylation of the amine by monomeric carbonium ion Ib with subsequent growth of the side chain in the intermediately formed monoaralkyl derivative Id, also is not excluded.

Polymers VIIa-e are colored solids that do not have distinct melting points and gradually decompose when they are heated above 200°C. They are soluble in aqueous alkali, acetone, alcohol, dioxane, and pyridine, only slightly soluble in chloroform, and insoluble in water, benzene, and hexane.

TABLE 2. Effect of the Reagent Ratio and the Reaction Time on the Results of Polyaralkylation of Amine II with Benzodioxane I in a Mixture of Acetic and Hydrochloric Acids (4:1) at 20°C

Molar ratio of amine II and benzodioxane I	Reaction time, h	Yield of polymer VIIa in % of the mass of the starting compounds (I + II)	Molecular mass of polymer VIIa
1 : 1	4	42	1198
1 : 2	1	40	1210
1 : 2	4	53	1430
1 : 2	8	56	1850
1 : 4	4	55	1980
1 : 8	4	55	2180



The examined compounds are capable of reactions through the polymeric aralkyl chain, which contains hydroquinone links. Thus when polymer VIIb is treated with acetic anhydride in pyridine, it forms the aqueous alkali-insoluble acetate (VIII), which indicates esterification of the hydroxy groups.

Like the known hydroquinone-containing polymers [8], VIIa-e may likely find application as reducing reagents in photography.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The electronic absorption spectra of alcohol solutions were obtained with a Specord UV-vis spectrophotometer. The PMR spectra of solutions in deuteromethanol or deuteroacetone were recorded with a Tesla radiospectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The molecular masses of the polymers obtained were determined by isothermal distillation in acetone.

N-(Polyethylidenehydroquinone)-4-nitroaniline (VIIa). A 0.38-g (2.75 mmole) sample of p-nitroaniline was added to a solution of 0.5 g (2.75 mmole) of benzodioxane I [5] in 20 ml of acetic acid, after which 5 ml (55 mmole) of concentrated hydrochloric acid (sp. gr. 1.18) was added, and the mixture was stirred at 20°C for 4 h. The mixture was poured into water (100 ml), and the resulting yellow precipitate was removed by filtration, washed with water, and dried. The dry finely ground precipitate was extracted with chloroform until slightly colored extracts were obtained (the low-molecular-weight compounds were removed with the chloroform). This procedure gave 0.37 g (42% of the mass of benzodioxane I and amine II) of polymer VIIa. Reprecipitation from a mixture of acetone and benzene (1:1) by means of hexane gave the reaction product in the form of a yellow powder that decomposed at 310-320°C. IR spectrum: 3100-3600 broad (O–H); 2980, 2945, 2885, 1430 ($CHCH_3$); 1320 (NO_2); 1190 cm^{-1} ($C_6H_4O_2$). UV spectrum, λ_{max} ($\log \varepsilon$): 205 (5.09), 300 (4.51), and 400 nm (4.25). See Table 1 for the PMR spectrum. Found: C 67.6; H 5.8; N 2.4%; M 1198. $C_6H_4NO_2(C_8H_8O_2)_kH$. Calculated (for k = 8): C 68.5; H 5.7; N 2.3%; M 1225.

The effect of the reagent ratio and the reaction time on the polyaralkylation of amine II with benzodioxane I is shown in Table 2.

N-(Polyethylidenehydroquinone)-1-aminoanthraquinone (VIIb). Similarly, the reaction of 0.5 g of benzodioxane I and 0.61 g (2.75 mmole) of amine III in 50 ml of a mixture of acetic and hydrochloric acids (4:1) gave 0.36 g (32% of the mass of the starting compounds) of polymer VIIb in the form of a red-violet powder that decomposed on heating above 220°C [reprecipitation from methanol—benzene (1:2) by means of hexane]. IR spectrum: 3430 broad (O—H); 3260 inflection (N—H); 3070, 3040 (=C—H); 2975, 2940, 2880, 1430 ($CHCH_3$); 1660, 1630 (C=O); 1190 cm^{-1} ($C_6H_4O_2$). UV spectrum, λ_{max} (log ε): 203 (5.40), 250 (4.86), 299 (4.56), and 522 nm (4.05). See Table 1 for the PMR spectrum. Found: C 70.6; H 4.9; N 1.3%; M 1357. $C_{14}H_8NO_2(C_8H_8O_2)_kH$. Calculated (for k = 8): C 71.3; H 5.5; N 1.1%; M 1311.

Acetate VIII was formed when acetic anhydride (10 mmole) was added to a solution of polymer VIIb (0.2 mmole) in pyridine (5 ml) and the mixture was maintained at 20°C for 20 h. The red crystals had mp 204-209°C (reprecipitation from benzene by means of hexane). IR spectrum (KBr): 1765 cm^{-1} ($COCH_3$). Found: N 1.1%. $C_{14}H_8NO_2(C_{12}H_{12}O_4)_kH$. Calculated (for k = 8): N 0.7%.

N,N'-Bis(polyethylidenehydroquinone)-1,4-diaminoanthraquinone (VIIc). A solution of 0.75 g (4 mmole) of benzodioxane I in 10 ml of acetic acid was added in the course of 30 min to a suspension of 0.5 g (2 mmole) of amine IV in 25 ml of acetic acid and 25 ml of hydrochloric acid, and the mixture was stirred at 25°C for 2.5 h. It was then poured into water (150 ml), and the precipitate was removed by filtration, washed with water, and dried. The admixed low-molecular-weight compounds were removed by washing the precipitate with chloroform. The residue was dissolved in acetone—benzene (1:2), and the solution was chromatographed with a column packed with silica gel. The principal (blue) zone (elution with acetone) was collected to give 0.35 g (28% of the mass of the starting compounds) of polymer VIIc in the form of a blue powder that decomposed on heating above 200°C [reprecipitation from benzene—methanol (2:1) by means of hexane]. IR spectrum: 3400 broad (O—H); 3300 shoulder (N—H); 3050 (=C—H); 2975, 2940, 2880, 1430 ($CHCH_3$); 1650 (C=O); 1190 cm^{-1} ($C_6H_4O_2$). See Table 1 for the PMR spectrum. Found: M 2908. $C_{14}H_8N_2O_2(C_8H_8O_2)_{2k}H$. Calculated (k = 10): M 2958.

N,N'-Bis(polyethylidenehydroquinone)-1,4-diamino-5,8-dihydroxyanthraquinone (VIId). A mixture of 0.37 g (1.4 mmole) of amine V, 2 g (11 mmole) of benzodioxane I, 50 ml of acetic acid, and 12 ml (0.13 mmole) of hydrochloric acid was stirred at 25°C for 5 h, after which it was diluted with water, and the precipitate was separated, dried, and washed with chloroform to remove the low-molecular-weight compounds. Reprecipitation of the residue from acetone—benzene (1:1) by means of hexane gave 1.05 g (44% of the mass of the starting compounds) of polymer VIId in the form of a blue powder that decomposed on heating above 210°C. IR spectrum: 3100-3600 (O—H); 3300 inflection (N—H); 3080 (=C—H); 2975, 2940, 2880, 1430 ($CHCH_3$); 1655 (C=O); 1190 cm^{-1} ($C_6H_4O_2$). UV spectrum, λ_{max} (log ε): 205 (5.72), 242 (5.30), 299 (5.16); 578 shoulder (4.75), 625 (4.68), and 676 nm (4.75). See Table 1 for the PMR spectrum. Found: M 5580. $C_{14}H_8O_4N_2(C_8H_8O_2)_{2k}H$. Calculated (for k = 19): M 5438.

N-(Polyethylidenehydroquinone)-4-aminoazobenzene (VIIe). Condensation of 0.54 g (2.75 mmole) of amine VI with 1 g (5.5 mmole) of benzodioxane I in a mixture of acetic acid (20 ml) and hydrochloric acid (5 ml) as described above gave 0.82 g (53% of the mass of the starting compounds) of polymer VIIe in the form of a red powder that turned yellow on heating above 190°C and decomposed on further heating (above 250°C) (after reprecipitation from alcohol by means of benzene). IR spectrum: 3200-3600 (O—H); 3270 inflection (N—H); 2980, 2945, 2885, 1430 ($CHCH_3$); 1195 cm^{-1} ($C_6H_4O_2$). UV spectrum, λ_{max} (log ε): 204 (5.36), 300 (4.71), and 412 nm (4.45). See Table 1 for the PMR spectrum. Found: N 3.5%. $C_{12}H_{10}N_3 \cdot (C_8H_8O_2)_kH$. Calculated (for k = 8): N 3.6%.

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