Synthesis and Reactions of Azomethines Containing an m-Phenoxophenyl Group: III.*

N,N'-Bis(m-phenoxybenzylideneamino)arenes, -alicyclicnes and -polymethylene, Synthesis and Properties

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Abstract—Bis(m-phenoxybenzylideneamino)arenes, -alicyclicnes, and polymethylene were prepared, and the possibility to use them as ingredients of polymer compositions was investigated.

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The presence in diimine molecule of two C=N bonds makes it possible to use them not only as biologically active substances [2], but also as additives to polymer materials improving their service performance [3–5]. Therefore in extension of the previous studies [1, 6] on the synthesis and properties of azomethines with a m-phenoxophenyl group we investigated reactions of aromatic, alicyclic, and aliphatic diamines Ia–Ii with m-phenoxybenzaldehyde (II).

The process was carried out in the same fashion as the synthesis of N-aryl-m-phenoxybenzylideneamines [6] but at a molar ratio diamine : aldehyde 1:2:2. We established that the aliphatic diamines Ih and II reacted with aldehyde II more vigorously than aromatic diamines Ia–Ig. The reaction started spontaneously at 20–25°C and occurred with a considerable heat evolution resulting in self-heating of the reaction mixture to 45–55°C. The dimines obtained are colorless crystalline substances or viscous fluids of yellow or weak greenish tint. The products were purified by recrystallization or vacuum distillation.

To investigate the chemical properties of dimines IIIa–IIIi we subjected them to a reduction of the C=N bond. Lithium aluminum hydride and sodium borohydride were used as reductants [7]. The most plausible preparative method for reducing diimine IIIi was the treatment with sodium borohydride in the anhydrous methanol. The yield of the reduction product IVf attained 72%. However we failed to reduce by this procedure compounds IIIa, IIIc–IIIe, and IIIh due to their insolubility in the anhydrous methanol. Therefore the above cited dimines were reduced by lithium aluminum hydride in THF in 78–96% yields. All the reduction processes of dimines by sodium borohydride and lithium aluminum hydride were slightly exothermic.
To prove the structure of diamines obtained and to prepare therefrom water-soluble derivatives we by an example of diamines IVe–IVe synthesized their hydrochlorides Va—Ve in anhydrous solvents (dioxane, chloroform) at -5 to 0°C.

The composition and structure of all compounds obtained were proved by elemental analysis, IR and 1H NMR spectra.

An absorption band in the region 1630–1640 cm⁻¹ in the IR spectra of diamines IIIa–Illi belongs to the stretching vibrations of the C=N bonds. The presence in the IR spectra of the secondary diamines IVa–IVe of absorption bands in the region 3300–3500 cm⁻¹ corresponds to the stretching vibrations of the N–H bonds. In the IR spectra of hydrochlorides Va—Ve the wide bands in the region 2760–2960 cm⁻¹ indicate the presence of the -NH₂ moiety.

In the 1H MNR spectra of diamines IIIa–Illi the protons of the aromatic rings gave rise to a multiplet signal in the region δ 6.95–7.47 ppm. The protons of the methine group appear as a two-proton singlet at δ 8.05–8.42 ppm. This means that the protons of two imino groups coincided. In the 1H MNR spectra of diamines IVa–IVe a singlet in the region δ 4.32–4.58 ppm corresponded in the intensity to four protons indicating the overlapping of the signals of two methylene groups. The two-proton singlet in the region δ 2.24–2.59 ppm was attributed to the amino groups. The protons of aromatic rings give rise to a multiplet (18H) in the region δ 6.79–7.47 ppm: Here overlap proton signals from four aromatic rings.

We tested diamines IIIa, IIIc, and IIIh as curing agents for fluororubber SKF-26 in comparison with the prototype, bifurgin [8]. The results of the study demonstrated that the application of diamines IIIa, IIIc, and IIIh provided cured rubber with higher characteristics than those obtained with bifurgin. In addition at the investigation of the stabilizing properties of the compounds against thermooxidative aging diamine IIIh acted as an antiaging agent.

The application of diamine IIIa as an adhesion promoter ensured preparation of rubber items with a binding of the rubber to textile stronger by ~20% as compared with the known prototype (resorcinol) [9]. It should be noted that in the presence of this diamine the dynamic durability of the vulcanizates increased over 1.3 times.

The study of the efficiency of diamines IIIa, IIIh, and IIIi as retarders of acid corrosion of steel as compared with the inhibitor V-2 showed that the diamines exceed the inhibitor V-2 in reducing the specific corrosion rate by 25–65% (this rate for the inhibitor V-2 equals 0.2–0.3 g/(m²·h) [10]). This fact can be rationalized when it is considered that the reducing of the corrosion rate by diamines IIIa, IIIh, and IIIi introduced into the electrolyte solution occurs due to their stronger absorption on the metal surface blocking the active sites of dissolution. The presence in the structure of diamines IIIa, IIIh, and IIIi of nitrogen atoms capable of forming with the metal donor-acceptor bonds favors the absorption of the diamines on the metal surface.

The compounds obtained containing in the structure the m-phenoxyphenyl group presumably possess a wide range of medical and biological activity.

**EXPERIMENTAL**

IR spectra were recorded on a spectrophotometer Specord M-82 (prisms of NaCl or KBr) from thin films of fluids or mulls in the mineral oil of solids. 1H NMR spectra were registered on a spectrometer Tesla BS-487 (100 MHz) from solutions in CCl₄, CDCl₃, or (CD₃)₂CO, internal reference HMDS.

**Bis(m-phenoxybenzylideneamino)-arenes, -ali-cycloienes, and -polymethylene-IIIa–IIIi.** To 2.2 mol of aldehyde II was added at vigorous stirring and cooling 1 mol of an appropriate diamine Ia–ii, then the reaction mixture was heated for 1.5–2 h at 100–110°C. On completion of the process the reaction mixture crystalized. The product was purified by recrystallization.

**Bis(m-phenoxybenzylideneamino)-o-phenylene (IIIa).** Yield 65%, mp 199–200°C (from CCl₄). IR spectrum, cm⁻¹: 1620 (C=N), 1250 (C–O–C), 3055, 1572 (C–H). 1H NMR spectrum [(CD₃)₂CO], δ, ppm: 8.25 s (C–H), 6.93–7.54 m (Ar). Found, %: C 81.14; H 5.08; N 6.20. C₁₂H₁₂N₂O₂. Calculated, %: C 82.02; H 5.13; N 5.98.

**Bis(m-phenoxybenzylideneamino)-m-phenylene** (IIIb). Yield 85%, mp 98–100°C (from CCl₄). IR spectrum, cm⁻¹: 1620 (C=N), 1250 (C–O–C), 3058, 1570 (C–H). 1H NMR spectrum [(CD₃)₂CO], δ, ppm: 8.26 s (C–H), 6.95–7.60 m (Ar). Found, %: C 81.58; H 4.98; N 5.81. C₁₂H₁₂N₂O₂. Calculated, %: C 82.02; H 5.13; N 5.98.

**Bis(m-phenoxybenzylideneamino)-p-phenylene (IIIc).** Yield 80%, mp 126–128°C (from CCl₄). IR spectrum, cm⁻¹: 1620 (C=N), 1250 (C–O–C), 3060, 1570 (C–H). 1H NMR spectrum [(CD₃)₂CO], δ, ppm: 8.28 s (C–H), 6.95–7.58 m (Ar). Found, %: C 81.98;