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Synthesis and Reactions of Azomethines Containing an *m*-Phenoxyphenyl Group: III.* *N,N'*-Bis(*m*-phynoxybenzylideneamino)arenes, -alicyclenes and -polymethylenes, Synthesis and Properties

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Abstract—Bis(*m*-phenoxybenzylideneamino)arenas, -alicyclenes, and polymethylenes were prepared, and the possibility to use them as ingredients of polymer compositions was investigated.

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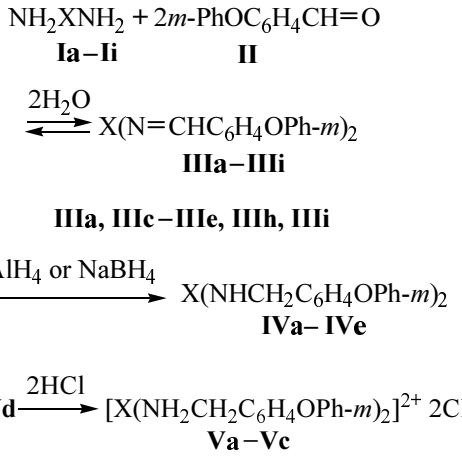
The presence in diimine molecule of two C=N bonds makes it possible to use them not only as biologically active substances [2], but also as additives to polymer materials improving their service performance [3–5]. Therefore in extension of the previous studies [1, 6] on the synthesis and properties of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



I, III, X = *o*-C_6H_4 (**a**), *m*-C_6H_4 (**b**), *p*-C_6H_4 (**c**), *p,p'*-$C_6H_4OC_6H_4$ (**d**), *p,p'*-$C_6H_4C_6H_4$ (**e**), 1,8-di(*p*-phenylene)fluorene (**f**), 1,4-di(*p*- phenylene)cyclohexane (**g**), $(CH_2)_6$ (**h**), $(CH_2)_2$ (**i**); **IV, X** = *o*-C_6H_4 (**a**), *p*-C_6H_4 (**b**), *p,p'*-$C_6H_4OC_6H_4$ (**c**), *p,p'*-$C_6H_4C_6H_4$ (**d**), $(CH_2)_6$ (**e**), $(CH_2)_2$ (**f**); V, X = *p*-C_6H_4 (**a**), *p,p'*-$C_6H_4OC_6H_4$ (b), *p,p'*-$C_6H_4C_6H_4$ (**c**).

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 diimines 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 chamical properties of diimines **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 diimines were reduced by lithium aluminum hydride in THF in 78–96% yields. All the reduction processes of diimines by sodium borohydride and lithium aluminum hydride were slightly exothermic.

* For Communication II, see [1].

To prove the structure of diamines obtained and to prepare therefrom water-soluble derivatives we by an example of diamines **IVc–IVe** synthesized their hydrochlorides **Va-–Vc** 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 ^{1}H NMR spectra.

An absorption band in the region 1630–1640 cm^{-1} in the IR spectra of diimines **IIIa–IIIi** 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-–Vc** the wide bands in the region 2760–2690 cm^{-1} indicate the presence of the $^+NH_2$ moiety.

In the ^{1}H MNR spectra of diimines **IIIa–IIIi** 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 ^{1}H 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 diimines **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 diimines **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 diimine **IIIh** acted as an antiaging agent.

The application of diimine **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 diimine the dynamic durability of the vulcanizates increased over 1.3 times.

The study of the efficiency of diimines **IIIa**, **IIIh**, and **IIIi** as retarders of acid corrosion of steel as compared with the inhibitor V-2 showed that the diimines 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/(m^2 h) [10]}. This fact can be rationalized when it is considered that the reducing of the corrosion rate by diimines **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 diimines **IIIa**, **IIIh**, and **IIIi** of nitrogen atoms capable of forming with the metal donor-acceptor bonds favors the absorption of the diimines 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. ^{1}H NMR spectra were registered on a spectrometer Tesla BS-487 (100 MHz) from solutions in CCl_4, $CDCl_3$, or $(CD_3)_2CO$, internal reference HMDS.

Bis(*m*-phenoxybenzylideneamino)arenes, -alicyclenes, and –polymethylenes 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 crystallized. The product was purified by recrystallization.

Bis(*m*-phenoxybenzylideneamino)-*o*-phenylene (IIIa). Yield 65%, mp 199–200°C (from CCl_4). IR spectrum, cm^{-1}: 1620 (C=N), 1250 (C–O–C), 3055, 1572 (C–H). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 8.25 s (C–H), 6.93–7.54 m (Ar). Found, %: C 81.14; H 5.08; N 6.20. $C_{32}H_{24}N_2O_2$. Calculated, %: C 82.02; H 5.13; N 5.98.

Bis(*m*-phenoxybenzylideneamino)-*m*-phenylene (IIIb). Yield 85%, mp 98–100°C (from CCl_4). IR spectrum, cm^{-1}: 1620 (C=N), 1250 (C–O–C), 3058, 1570 (C–H). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 8.26 s (C–H), 6.95–7.60 m (Ar). Found, %: C 81.58; H 4.98; N 5.81. $C_{32}H_{24}N_2O_2$. Calculated, %: C 82.02; H 5.13; N 5.98.

Bis(*m*-phenoxybenzylideneamino)-*p*-phenylene (IIIc). Yield 80%, mp 126–128°C (from CCl_4). IR spectrum, cm^{-1}: 1620 (C=N), 1250 (C–O–C), 3060, 1570 (C–H). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 8.28 s (C–H), 6.95–7.58 m (Ar). Found, %: C 81.98;

H 5.32; N 6.12. $C_{32}H_{24}N_2O_2$. Calculated, %: C 82.02; H 5.13; N 5.98.

***p,p′*-Bis(*m*-phenoxybenzylideneamino)diphenyl oxide (IIId).** Yield 65%, mp 120–122°C [from $(CH_3)_2CO$]. IR spectrum, cm^{-1}: 1620 (C=N), 1260 (C–O–C), 2930, 1580 (C–H). ^1H NMR spectrum (CCl_4), δ, ppm: 8.33 s (C–H), 6.95–7.50 m (Ar). Found, %: C 81.24; H 5.59; N 5.04. $C_{38}H_{28}N_2O_3$. Calculated, %: C 81.40; H 5.00; N 5.00.

***p,p′*-Bis(*m*-phenoxybenzylideneamino)diphenyl (IIIe).** Yield 76%, mp 158–159°C (from $C_6H_5CH_3$). IR spectrum, cm^{-1}: 1630 (C=N), 1250 (C–O–C), 3060, 1580 (C–H). ^1H NMR spectrum (CCl_4), δ, ppm: 8.29 s (C–H), 7.11–7.45 m (Ar). Found, %: C 83.80; H 5.17; N 4.94. $C_{38}H_{28}N_2O_2$. Calculated, %: C 83.82; H 5.15; N 5.15.

1,8-Bis(4-(*m*-phenoxybenzylideneamino)-phenyl]fluorene (IIIf). Yield 80%, mp 162–164°C [from$(C_2H_5)_2O$]. IR spectrum, cm^{-1}: 1635 (C=N), 1265 (C–O–C), 3060, 1575 (C–H). ^1H NMR spectrum (CCl_4), δ, ppm: 8.42 s (C–H), 6.50–7.68 m (Ar). Found, %: C 85.92; H 4.97; N 3.33. $C_{51}H_{36}N_2O_2$. Calculated, %: C 86.40; H 5.08; N 3.95.

1,4-[Bis(4-*m*-phenoxybenzylideneamino)phenyl]-cyclohexane (IIIg). Yield 75%, mp 141–143°C (from CCl_4). IR spectrum, cm^{-1}: 1630 (C=N), 1260 (C–O–C), 3060, 1580 (C–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.35 s (C–H), 6.87–7.45 m (Ar). Found, %: C 84.16; H 6.19; N 4.54. $C_{44}H_{38}N_2O_2$. Calculated, %: C 84.34; H 6.23; N 4.51.

Bis(*m*-phenoxybenzylideneamino)hexamethylene (IIIh). Yield 93%, mp 54–56°C (from EtOH). IR spectrum, cm^{-1}: 1650 (C=N), 1250 (C–O–C), 3060, 1540 (C–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.09 s (C–H), 6.97–7.50 m (Ar), 3.45 t (N–CH_2), 1.33–1.59 m [$(CH_2)_4$)] Found, %: C 80.03; H 7.24; N 6.27. $C_{32}H_{32}N_2O_2$. Calculated, %: C 80.67; H 6.72; N 5.18.

1,2-Bis(*m*-phenoxybenzylideneamino)ethane (IIIi). Yield 94%, bp 250–252°C (2 mm Hg). IR spectrum, cm^{-1}: 1650 (C=N), 1250 (C–O–C), 2930, 1580 (C–H). ^1H NMR spectrum (CCl_4), δ, ppm: 8.05 s (C–H), 6.98–7.45 m (Ar), 3.42 t (N–CH_2). Found, %: C 79.30; H 5.63; N 6.31. $C_{28}H_{24}N_2O_2$. Calculated, %: C 80.00; H 5.71; N 6.67.

Bis(*m*-phenoxybenzyl)amines IVa–IVf were prepared by procedure [1].

1,2-Bis(*m*-phenoxybenzylamino)benzene (IVa). Yield 96%, mp 179–180°C (from $CHCl_3$). IR spectrum, cm^{-1}: 3345 (NH), 1250 (C–O–C), 3055, 1540 (C–H). ^1H NMR spectrum [$(CH_3)_2CO$], δ, ppm: 2.63 s (NH), 7.05–7.20 m (Ar), 4.58 s (CH_2). Found, %: C 80.89; H 5.39; N 5.91. $C_{32}H_{28}N_2O_2$. Calculated, %: C 81.39; H 5.93; N 5.93.

***p*-Bis(*m*-phenoxybenzylamino)benzene (IVb).** Yield 84%, mp 223–225°C (from EtOH). IR spectrum, cm^{-1}: 3350 (NH), 1250 (C–O–C), 3060, 1540 (C–H). ^1H NMR spectrum ($CHCl_3$), δ, ppm: 2.59 s (NH), 7.11–7.25 m (Ar), 4.58 s (CH_2). Found, %: C 81.24; H 5.49; N 5.57. $C_{32}H_{28}N_2O_2$. Calculated, %: C 81.39; H 5.93; N 5.93.

***p,p′*-Bis(*m*-phenoxybenzylamino)diphenyl oxide (IVc).** Yield 80%, mp 64–66°C (from EtOH). IR spectrum, cm^{-1}: 3380 (NH), 1260 (C–O–C), 2930, 1585 (C–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.71 s (NH), 7.15–7.45 m (Ar), 4.67 s (CH_2). Found, %: C 79.19; H 5.60; N 4.97. $C_{32}H_{28}N_2O_3$. Calculated, %: C 80.85; H 5.85; N 4.96.

***p,p′*-Bis(*m*-phenoxybenzylamino)diphenyl (IVd).** Yield 80%, mp 138–140°C (from CCl_4). IR spectrum, cm^{-1}: 3390 (NH), 1260 (C–O–C), 3060, 1580 (C–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.70 s (NH), 7.15–7.47 m (Ar), 4.66 s (CH_2). Found, %: C 83.34; H 5.45; N 5.13. $C_{32}H_{28}N_2O_2$. Calculated, %: C 83.21; H 5.84; N 5.11.

Bis(*m*-phenoxybenzylamino)hexamethylene (IVe). Yield 78%, bp 242–244°C (2 mm Hg). IR spectrum, cm^{-1}: 3350 (NH), 1250 (C–O–C), 3060, 1540 (C–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.48 s (NH), 6.79–7.25 m (Ar), 4.58 s (N–CH_2), 1.33–1.59 m [$(CH_2)_4$]. Found, %: C 80.70; H 6.59; N 5.66. $C_{32}H_{36}N_2O_2$. Calculated, %: C 80.33; H 7.11; N 5.86.

1,2-Bis(*m*-phenoxybenzylamino)ethane (IVf). To 6.9 g (0.016 mol) of compound **IIIi** in 40 ml of methanol was added at vigorous stirring and cooling 0.73 g (0.0192 mol) of sodium borohydride. The reaction proceeded for 2 h at –5 to 0°C. On completion of the process methanol was distilled off, distilled water and ethyl ether were added to the residue. The organic layer was separated, ethyl ether was distilled off, and the reaction product was subjected to vacuum distillation, yield 72%, bp 216–218°C (2 mm Hg). IR spectrum, cm^{-1}: 3410 (NH), 1250 (C–O–C), 2930, 1580 (C–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.24 s (NH), 6.88–7.14 m (Ar), 4.32 s (N–CH_2), 1.44–1.62 m [$(CH_2)_2$]. Found, %: C 79.19; H 6.97; N 6.18. $C_{32}H_{28}N_2O_2$. Calculated,%: C 79.25; H 6.60; N 6.60.

Hydrochlorides of bis(*m*-phenoxybenzyl)amines Va–Vc were obtained by procedure [1].

***p*-Bis(*m*-phenoxybenzylamino)benzene hydrochloride (Va).** Yield 98%, mp 152–153°C. IR spectrum, cm^{-1}: 1310 (C–N), 1240 (C–O–C), 2710 ($^+NH_2$), 3010, 1570 (C–H). ^1H NMR spectrum (CCl_4), δ, ppm: 2.62 s (NH), 7.11–7.22 m (Ar), 4.59 s (N–CH_2), 9.15 s ($^+NH_2$). Found, %: C 70.12; H 5.25; Cl 12.96; N 5.00. $C_{32}H_{30}Cl_2N_2O_2$. Calculated, %: C 70.46; H 5.50; Cl 13.03; N 5.14.

***p*,*p*′-Bis(*m*-phenoxybenzylamino)diphenyl oxide hydrochloride (Vb).** Yield 98%, mp 30–31°C. IR spectrum, cm^{-1}: 1310 (C–N), 1240 (C–O–C), 2750 ($^+NH_2$), 3040, 1580 (C–H). ^1H NMR spectrum (CCl_4), δ, ppm: 2.24 C (NH), 7.15–7.45 m (Ar), 4.65 c (N–CH_2), 9.30 C ($^+NH_2$). Found, %: C 71.26; H 5.21; Cl 11.02; N 4.12. $C_{32}H_{34}Cl_2N_2O_3$. Calculated, %: C 71.59; H 5.34; Cl 11.15; N 4.40.

***p*,*p*′-Bis(*m*-phenoxybenzylamino)diphenyl hydrochloride (Vc).** Yield 96%, mp 242–244°C. IR spectrum, cm^{-1}: 1310 (C–N), 1240 (C–O–C), 2710 ($^+NH_2$), 3020, 1570 (C–H). ^1H NMR spectrum (CCl_4), δ, ppm: 2.72 s (NH), 7.11–7.38 m (Ar), 4.70 s (N–CH_2), 9.32 s ($^+NH_2$). Found, %: C 74.14; H 5.13; Cl 11.07; N 4.24. $C_{32}H_{34}Cl_2N_2O_2$. Calculated, %: C 74.43; H 5.48; Cl 11.43; N 4.51.

REFERENCES

1. Popov, Yu.V., Korchagina, T.K., Chicherina, G.V., and Ermakova, T.A., *Zh. Org. Khim*., 2004, vol. 40, p. 718.
2. Mashkovskii, M.D., *Lekarstvennye sredstva* (Drugs), Moscow: OOO Novaya Volna, 2001, vol. 1, 540 p.
3. Novopol'tseva, O.M., *Cand. Sci. (Chem.) Dissertation,* Volgograd, 1994.
4. Novakov, I.A. and Novopol'tseva, O.M., *Collection of Scientific Materials of Volgograd. Gos. Techn. Univ.*, Volgograd, 2003, p. 3.
5. Tankov, D.Yu., *Cand. Sci. (Chem.) Dissertation,* Volgograd, 2003.
6. Popov, Yu.V., Korchagina, T.K., and Chicherina, G.V., *Zh. Org. Khim*., 2001, vol. 37, p. 716
7. *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 3; Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1982, vol. 3, p. 734.
8. Chicherina, G.V., *Cand. Sci. (Chem.) Dissertation,* Volgograd, 1998, 24 p.
9. Novakov, I.A., Popov, Yu.V., Korchagina, T.K., Chicherina, G.V., Novopol'tseva, O.M., and Ermakova, T.A., RF Patent 2174131, 2000; *Byull. Izobr*., 2001, no. 27.
10. Popov, Yu.V., Korchagina, T.K., Chicherina, G.V., and Uskach, Ya.L., RF Patent 2115766, 1997; *Byull. Izobr.,* 1998, no. 20.