

Synthesis and Reactions of Schiff Bases Containing an *m*-Phenoxyphenyl Group: I. *N*-Aryl-*m*-phenoxybenzylideneamines and *N*-Aryl-*N'*-(*m*-phenoxybenzylidene)hydrazines

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Abstract—Condensation of *m*-phenoxybenzaldehyde with aromatic amines and hydrazines gave the corresponding Schiff bases and *m*-phenoxybenzaldehyde arylhydrazones. The products are promising as biologically active substances, polyfunctional additives to rubber compounds, and inhibitors of acid corrosion.

Schiff bases, i.e., compounds having a double C=N bond, are used as starting materials in the synthesis of important drugs, such as antibiotics and anti-allergic, antiphlogistic, and antitumor substances [1, 2, 3]. They are also used as components of rubber compounds [4]. Hydrazones have found application in synthetic and analytical chemistry, but their most valuable property is high physiological activity [5].

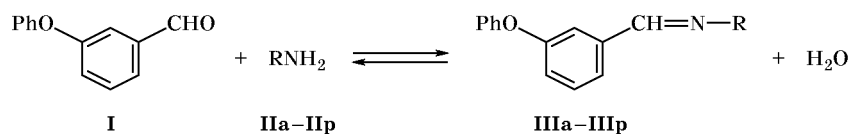
The goal of the present study was to develop procedures for synthesizing a series of new Schiff bases and hydrazones containing an *m*-phenoxyphenyl group and to find ways for their practical utilization. *m*-Phenoxybenzaldehyde (**I**) readily reacted with aromatic amines **IIa–IIp** to afford the corresponding *N*-aryl-*m*-phenoxybenzylideneamines **IIIa–IIIp**. The reactions started even at room temperature and were accompanied by appreciable heat evolution: the mixtures warmed up by 10–15°C. However, the rate of the condensation was low, and in 1.5–2 h the products were formed in 60–80% yield (Scheme 1). The reactant molar ratio **I**:**II** was 1:1. Raising the temperature to 60–80°C strongly accelerated the process, and the reaction was complete in 10–15 min, but the yields of products **II** did not change. Analysis of the reaction

mixtures by GLC did not reveal appreciable amounts of by-products. By the end of the process the mixture contained Schiff base **II**, water, and small amounts of the initial reactants.

A possible reason for relatively low yields of the condensation products in reactions of aldehyde **I** with aromatic amines is equilibrium character of the process. It is known that condensation of aldehydes with amines is reversible [2]. We performed a series of experiments with continuous removal of water as azeotropic mixture with benzene. In the reactions of **I** with aniline, *p*-anisidine, and *p*-bromoaniline the theoretical amount of water separated in 50 min, but the yields of the products slightly differed from those obtained in the previous experiments. The yield of *N*-phenyl-*m*-phenoxybenzylideneamine increased by 1.5%, of *N*-*p*-methoxyphenyl-*m*-phenoxybenzylideneamine, by 2%, and of *N*-*p*-bromophenyl-*m*-phenoxybenzylideneamine, by 3%. Therefore, we can conclude that reactions of aldehyde **I** with aromatic amines are almost irreversible.

Aromatic hydrazines turned out to be more reactive toward aldehyde **I**, as compared with aromatic amines [6]. The reactions readily occurred at room tempera-

Scheme 1.



R = C₆H₅ (**a**), *o*-O₂NC₆H₄ (**b**), *m*-O₂NC₆H₄ (**c**), *p*-O₂NC₆H₄ (**d**), *o*-CH₃OC₆H₄ (**e**), *p*-CH₃OC₆H₄ (**f**), *o*-HOC₆H₄ (**g**), *p*-HOC₆H₄ (**h**), *o*-CH₃C₆H₄ (**i**), *p*-CH₃C₆H₄ (**j**), *p*-ClC₆H₄ (**k**), *p*-BrC₆H₄ (**l**), 2,5-(CH₃)₂C₆H₃ (**m**), C₆H₅CH₂ (**n**), α -naphthyl (**o**), 2-thiazolyl (**p**).

EXPERIMENTAL

The IR spectra were recorded on a Specord M82 instrument (NaCl or KBr prism) from samples prepared as thin films (liquid products) or dispersions in mineral oil (crystalline products). The ^1H NMR spectra were obtained on a Tesla BS-487 spectrometer (100 MHz) relative to hexamethyldisiloxane as internal reference; the solvents were CCl_4 , CDCl_3 , and acetone- d_6 .

N-Phenyl-*m*-phenoxybenzylideneamine (IIIa). A four-necked reactor equipped with a stirrer, reflux condenser, and thermometer was charged with 15 g (0.076 mol) of *m*-phenoxybenzaldehyde (**I**), and 7.05 g (0.076 mol) of aniline was added under vigorous stirring and cooling with water. The mixture was then heated for 1.5–2 h at 100–110°C. It crystallized on cooling. The product was recrystallized from ethanol. Yield 88%, mp 58–60°C. Found, %: C 82.97; H 5.73; N 5.80. $\text{C}_{13}\text{H}_{15}\text{NO}$. Calculated, %: C 83.50; H 5.49; N 5.13.

Compounds **IIIb–IIIp** were synthesized following a similar procedure (see table).

N-Benzoyl-*N'*-(*m*-phenoxybenzylidene)hydrazine (Vb). A four-necked reactor equipped with a stirrer, reflux condenser, and thermometer was charged with 15 g (0.076 mol) of *m*-phenoxybenzaldehyde and 50 ml of chloroform. Benzoylhydrazine, 10.3 g (0.076 mol), was added under vigorous stirring and cooling with water, the mixture was heated for 1 h at

60–65°C, and the solvent was removed. The product was recrystallized from ethanol. Yield 23 g (96%), mp 158–160°C. Found, %: C 75.49; H 5.91; N 7.84. $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}$. Calculated, %: C 75.90; H 5.86; N 8.46.

Hydrazones **Va** and **Vc** were synthesized in a similar way (see table).

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