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Synthesis and Reactions of Azomethines Containing a *m*-Phenoxyphenyl Group: II.* Chemical Transformations of *N*-Aryl-*m*-phenoxyphenylmethanimines and Arylhydrazones of *m*-Phenoxybenzaldehyde

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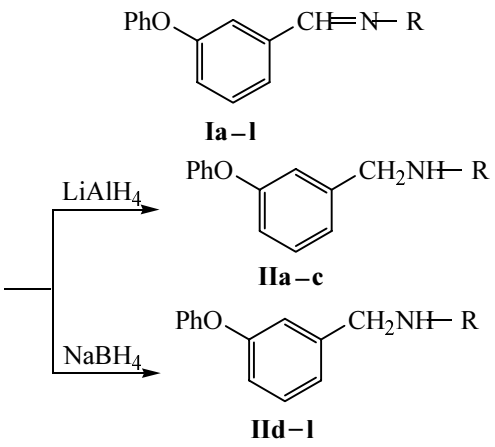
Abstract—Chemical transformations of *N*-aryl-*m*-phenoxyphenylmethanimines and *m*-phenoxybenzaldehyde arylhydrazones were studied by examples of reduction thereof with complex metal hydrides and reactions with dialkyl phosphates and dialkyl phosphites.

In the preceding paper [1] a synthesis of azomethines was described consisting in condensation of *m*-phenoxybenzaldehyde with aromatic amines and hydrazines. In extension of this research we studied the chemical properties of obtained azomethines (imines and hydrazones).

Bipolar character of the double bond between carbon and nitrogen in azomethines underlies their capability of reactions both with electrophilic and nucleophilic reagents. Reagents of metal–proton donor type (sodium, sodium amalgam, magnesium or aluminum in ethanol etc.) cleanly reduce azomethines into the corresponding amines. Treating with alkali metals in inert solvents, like ether or toluene, may result in reductive dimerization affording diamino compounds. Apparently the most efficient and convenient procedure for conversion of azometines into amines is their reduction with complex metal hydrides [2].



I, II, R= C_6H_5 (**a**), NHC_6H_5 (**b**), $NHCOC_6H_5$ (**c**), *o*, *m*-$NO_2C_6H_4$ (**d, e**), *p*-ClC_6H_4 (**f**), *p*-$OCH_3C_6H_4$ (**g**), *p*-OHC_6H_4 (**h**), *p*-BrC_6H_4 (**i**), *m, p*-$CH_3C_6H_4$ (**j, k**), 2,5-$(CH_3)_2C_6H_4$ (**l**).

We studied the reduction of the double carbon–nitrogen bond in the azomethines containing the *m*-phenoxyphenyl group with the use of lithium aluminum hydride as reductant. The reduction was carried out in anhydrous THF at the molar ratio of reagents azomethine–$AlLiH_4$ 1:1.2, at 66°C for 5 h. This procedure was plausible only for reducing N-phenyl-*m*-phenoxyphenylmethan-imine, and also for phenyl- and benzoylhydrazones of *m*-phenoxybenzaldehyde. At the attempt to reduce azomethines with functional groups, like bromine, chlorine, nitro, and hydroxy groups, simultaneously with the carbon–nitrogen bond the substituents in the benzene ring were also reduced providing a product mixture that we failed to separate by common procedures.

To conserve the functional groups that considerably affect the properties of azomethines we tested another reductant, sodium borohydride. The reaction was carried out in anhydrous methanol at equivalent reagents ratio within 2 h at 0°C.

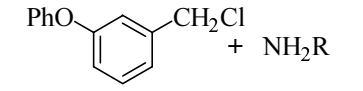
The amines obtained are crystalline substances or viscous fluids that were purified by recrystallization or vacuum distillation. The structure and composition of the new secondary amined were confirmed by IR, ^1H NMR spectroscopy, and elemental analysis. The presence in the IR spectra of a characteristic absorption band in the region 3350–3430 cm^{-1} corresponds to the stretching vibrations of the NH bond. In the ^1H NMR spectra of the

* For communication I see [1].

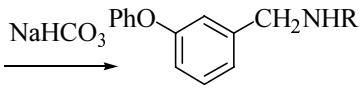
secondary amines the proton attached to nitrogen was revealed as a signal in the region δ 6.32–6.40 ppm.

Thus the azomethines reduction occurs in the best way under the treatment with sodium borohydride for the process is carried out under mild conditions, and although this reagent proper is a reductunt it also afforded a reductive complex in methanol.

We also synthesized the secondary amines by a one-pot procedure consisting in reaction of *m*- phenoxybenzyl chloride with excess aromatic amine in the presence of sodium hydrogen carbonate. The reaction occurred along the following scheme:



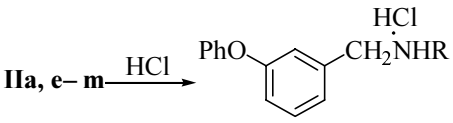
III **IVa–d**



IIa, j–l

R = C_6H_5 (**a**), *o,m,p*-$C_6H_4CH_3$ (**b, c**), 2,5-$C_6H_4(CH_3)_2$ (**d**).

The reaction of ammonia, primary and secondary amines with alkyl halides is known [3] to afford a mixture of products of different alkylation degree. In order the process to occur in more selective fashion to give secondary amines we used 10-fold molar excess of amine. The structure and composition of the secondary amines synthesized were confirmed by IR, ^{1}H NMR spectroscopy, and elemental analysis. The analytical data for secondary amines prepared by two-stage and one-stage methods were identical.

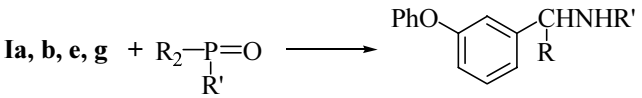


Va, e–l

The secondary amines synthesized easily form hydrochlorides when treated with hydrogen chloride in anhydrous solvents (ethyl ether, dioxane, chloroform) at 0–5°C. The reaction completion was determined by the weight gain of the reaction mixture. The structure of hydrochlorides was proved by IR spectra and elemental analyses. The formation of NH_2^+ moiety is indicated by the presence in the IR spectra of characteristic absorption bands in the 2760–2690 cm^{-1} region. The lack of absorption in the region 3300 cm^{-1} showed the disappearence of the NH bond.

Phosphorus-containing compounds are indispensable components of a number of medical and biological agents. Recent studied showed that introducing a phosphoryl fragment frequently improved the properties of preparations, and in some instances reduced the range of their activity and their toxicity. It was presumable that combination in the azomethine structure of a *m*-phenoxyphenyl and phosphoryl fragments would provide a possibility to develop new compounds possessing pharmaceutical and biological activity.

Aiming at preparation of new phosphorus-containing amines we studied the addition to azomethines of dialkyl phosphates and dialkyl phosphites. To this end the azomethines synthesized containing the *m*-phenoxyphenyl moiety were brought into reaction with di-2-ethylhexyl phosphate and dimethyl phosphite.



VIa, b **VIIa–h**

VI, R = $OCH_2CH(C_2H_5)(CH_2)_3CH_3$, R' = OH (**a**); R = OCH_3, R' = H (**b**); **VII**, R = OP(O)[$OCH_2CH(C_2H_5)(CH_2)_3CH_3$]$_2$, R' = C_6H_5 (**a**); R = OP–(O)[$OCH_2CH(C_2H_5)(CH_2)_3CH_3$]$_2$, R'= *m*-$C_6H_4NO_2$ (**b**); R = OP(O)– [$OCH_2CH(C_2H_5)$-$(CH_2)_3CH_3$]$_2$, R' = *p*-$C_6H_4OCH_3$ (**c**); R = OP(O)– [$OCH_2CH(C_2H_5)(CH_2)_3CH_3$]$_2$, R' = NHC_6H_5 (d); R = $P(O)(OCH_3)_2$, R' = C_6H_5 (**e**); R = $P(O)(OCH_3)_2$, R' = *m*-$C_6H_4NO_2$ (**f**); R = P(O)–$(OCH_3)_2$, R' = *p*-$C_6H_4OCH_3$ (**g**); R= $P(O)(OCH_3)_2$, R'=NHC_6H_5 (**h**).

The reactions were performed in ethanol as solvent at molar reagents ratio 1:1, at 78–80°C, within 1 h with di-2-ethylhexyl posphate , and within 2 h with dimethyl phosphite.

Dialkyl derivatives of phosphates and phosphites are known to show low reactivity towards addition to azomethines [4]. Therefore these reactions were carried out in the presence of catalyst (concn. sulfuric acid). It should be remarked that all phosphorus-containing compounds were obtained in relatively low yields (58–65%) even when the reaction time was doubled. This fact is probably due to the low reactivity of applied dialkyl phosphate and dialkyl phosphite, and to the pronounced sterical effects.

The structure and composition of the compounds synthesized were confirmed by IR, ^{1}H NMR spectroscopy, and elemental analysis. The appearance in the IR spectra of phosphates and phosphonates obtained of a characteristic absorption band in the region 3300–3500 cm^{-1} proves the presence of the NH bond. To the P=O and P–

O–C bonds belong absorption bands in the regions 1340–1360 and 1130–1150 cm^{-1} respectively. The lack of absorption bands in the region 1633–1640 cm^{-1} reveals the disappearance of >C=N–bonds. In the upfield region of ^1H NMR spectrum a singlet observed at 4.18–4.50 ppm (6H) belongs to two methoxy groups attached to phosphorus. The aromatic ring protons give rise to a multiplet at δ 6.58–7.50 ppm. The singlet belonging to the proton of the amino group is observed in the region δ 5.02–5.28 ppm. The singlet of the chemical shift δ 8.10–8.25 ppm corresponds to the methine group of phosphates and phosphites.

The reduction of imino group in the basic structure to amino group according to prediction significantly affects the range of the compound activity: amine **IIa** lacks fungicidal property and demonstrates pronounced psychopharmacological activity, first of all antidepressant and antiamnestic qualities that are modulated by substituents attached to the nitrogen atom in contrast to compounds from the imine series. From this viewpoint the amine class may be regarded as most promising for pharmacological testing also taking into account high solubility of amine hydrochlorides in water in contrast to imines, for the latter property is crucial for practical application.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord M82 from thin films for liquids and mulls in mineral oil for solids, prisms of NaCl or KBr. ^1H NMR spectra were registered on spectrometer Tesla BS487, operating frequency 100 MHz, internal reference HMDS, solvents carbon tetrachloride, deuterochloroform, deuteroacetone..

N-Aryl-*m*-phenoxyphenylmethanimins and arylhydrazones of *m*-phenoxybenzaldehyde were obtained by procedures from [1].

***N*-Aryl-*m*-phenoxybenzylamines.** (a) Into a four-neck flask equipped with a stirrer, thermometer, and reflux condenser with attached drying tube was charged 50 ml of THF and 0.54 g of lithium aluminum hydride. The flask was cooled on an ice bath, and at vigorous stirring a solution of 5 g of an appropriate *N*-aryl-*m*-phenoxyphenylmethanimide **I** in 15 ml of THF was added thereto. The reaction was carried out for 5 h at heating to 66°C. On completion of the process the reaction mixture was treated with weakly alkaline water solution, filtered, and the solvent was evaporated. The final reaction product was purified by recrystallization from ethanol.

(b) Into a four-neck flask equipped with a stirrer, thermometer, and reflux condenser was charged 1.44 g of sodium hydrogen carbonate, 12 g of an appropriate amine **IV**, and 3 g of *m*-phenoxybenzyl chloride **III**. The reaction was carried out at heating to 150–160°C for 5 h. The reaction mixture crystallized on cooling. The excess amine was distilled off, and the product was purified by recrystallization from ethanol.

***N*-Aryl-*m*-phenoxybenzylhydrazines.** General procedure. Into a four-neck flask equipped with a stirrer, thermometer, and reflux condenser with a drying tube was charged 0.80 g of lithium aluminum hydride and 40 ml of THF. The flask was cooled on an ice bath, and at vigorous stirring a solution of 5 g of an appropriate *m*-phenoxybenzaldehyde hydrazone **Ib** was added. The reaction was carried out for 2 h at heating to 66°C. On completion of the process the reaction mixture was treated with weakly alkaline water solution, filtered, and the solvent was evaporated. The final reaction product was purified by recrystallization from ethanol.

***N*-Phenyl-*m*-phenoxybenzylamine (IIa)**. Along procedure *a* compound **IIa** was obtained in 80% yield, by procedure *b* the yield reached 75%, mp 56–58°C. IR spectrum, cm^{-1}: 1310 (C–N), 1250 (C–O–C), 3410 (NH), 3000, 1560 (CH). ^1H NMR spectrum, δ, ppm: 4.52 s (NH), 4.12 s (CH_2), 6.86–7.02 m (Ar). Found, %: C 83.22; H 5.70; N 5.01. $C_{19}H_{15}NO$. Calculated, %: C 82.90; H 6.18; N 5.09.

***N*-Phenyl-*m*-phenoxybenzylhydrazine (IIb)**. Yield 94%, mp 71–75°C. IR spectrum, cm^{-1}: 3300 (NH), 3060, 1590 (CH). ^1H NMR spectrum, δ, ppm: 6.25–6.40 m (NH–NH), 4.12 d (CH_2), 6.70–7.05 m (Ar). Found, %: C 78.25; H 5.55; N 9.32. $C_{19}H_{16}N_2O$. Calculated, %: C 78.62; H 6.21; N 9.66.

***N*-Benzoyl-*m*-phenoxybenzylhydrazine (IIc)**. Yield 97%, mp 126–128°C. IR spectrum, cm^{-1}: 3400 (NH), 3040, 1570 (CH), 1710 (C=O). ^1H NMR spectrum δ, ppm: 6.30–6.55 m (NH–NH), 4.23 s (CH_2), 6.80–7.14 m (Ar). Found, %: C 74.24, H 5.60, N 8.76. $C_{20}H_{16}N_2O_2$. Calculated, %: C 75.47; H 5.66; N 8.81.

***N*-*o*-Nitrophenyl-*m*-phenoxybenzylamine (IId)**. Yield 74%, mp 69–71°C. IR spectrum, cm^{-1}: 1320 (C–N), 1250 (C–O–C), 3400 (NH), 3030, 1590 (CH). ^1H NMR spectrum, δ, ppm: 4.12 s (NH), 4.02 s (CH_2), 6.66–6.95 s (Ar). Found, %: C 78.52; H 5.15; N 4.12. $C_{19}H_{14}N_2O_3$. Calculated, %: C 78.83; H 5.55; N 4.57.

***N*- *m* -Nitrophenyl-*m*-phenoxybenzylamine (IIe)**. Yield 68%, mp 63–65°C. IR spectrum, cm^{-1}: 1310 (C–N), 1250 (C–O–C), 3410 (NH), 3000, 1560 (CH). ^1H NMR spectrum, δ, ppm: 4.15 s (NH), 4.09 s (CH_2), 6.69–6.98 m (Ar). Found, %: C 78.45; H 5.12; N 4.20. $C_{19}H_{14}N_2O_3$. Calculated, %: C 78.83; H 5.55; N 4.57.

***N*-*p*-Chlorohenyl-*m*-phenoxybenzylamine (IIf)**. Yield 78%, mp 75–78°C. IR spectrum, cm^{-1}: 1310 (C–N), 1250 (C–O–C), 3390 (NH), 3030, 1580 (CH). ^1H NMR spectrum NMR spectrum, δ, ppm: 4.21 s (NH), 4.10 s (CH_2), 6.85–7.06 m (Ar). Found, %: C 74.11; H 4.35; N 4.12. $C_{19}H_{14}NOCl$. Calculated, %: C 74.20; H 4.62; N 4.55.

N-*p*-Methoxyphenyl-*m*-phenoxybenzylamine (IIg). Yield 92%, mp 35–36°C. IR spectrum, cm^{-1}: 1310 (C–N), 1250 (C–O–C), 3410 (NH), 3370, 1580 (CH). ^1H NMR spectrum, δ, ppm: 3.78 s (NH), 3.56 s (CH_2), 3.28 s (OCH_3), 6.55–7.37 m (Ar).Found, %: C 72.09; H 5.60; N 4.62. $C_{20}H_{17}NO_2$. Calculated, %: C 78.83; H 5.55; N 4.57.

N-*p*-Hydroxyphenyl-*m*-phenoxybenzylamine (IIh). Yield 70%, mp 100–103°C. IR spectrum, cm^{-1}: 1310 (C–N), 1250 (C–O–C), 3410 (NH), 3010, 1570 (CH). ^1H NMR spectrum, δ, ppm: 4.58 s (NH), 3.42 s (CH_2), 2.52 s (OH), 6.80–7.32 m (Ar). Found, %: C 78.30; H 5.69; N 4.10. $C_{19}H_{15}NO_2$.Calculated, %: C 78.35; H 5.84; N 4.82.

N-*p*-Bromophenyl-*m*-phenoxybenzylamine (IIi). Yield 66%, mp 49–51°C. IR spectrum, cm^{-1}: 1320 (C–N), 1250 (C–O–C), 3400 (NH), 3030, 1590 (CH). ^1H NMR spectrum, δ, ppm: 4.42 s (NH), 3.87 s (CH_2), 6.65–7.00 m (Ar). Found, %: C 64.72; H 3.92; N 4.03. $C_{19}H_{14}NOBr$. Calculated, %: C 64.83; H 4.50; N 3.94.

N-*m*-Methylphenyl-*m*-phenoxybenzylamine (IIj). Along procedure *a* compound **IIj** was obtained in 72% yield, by procedure *b* the yield reached 65%, bp 289–291°C (2 mm Hg). IR spectrum, cm^{-1}: 1310 (C–N), 1250 (C–O–C), 3410 (NH), 3370, 1580 (CH). ^1H NMR spectrum, δ, ppm: 4.30 s (NH), 3.50 s (CH_2), 2.28 s (CH_3), 6.86–7.10 m (Ar). Found, %: C 69.02; H 6.87; N 5.54. $C_{20}H_{17}NO$. Calculated, %: C 69.14; H 6.99; N 5.76.

***N*-*p*-Methylphenyl-*m*-phenoxybenzylamine (IIk)**. Yield 78%, mp 22–23°C. IR spectrum, cm^{-1}: 1300 (C–N), 1250 (C–O–C), 3430 (NH), 3040, 1580 (CH). ^1H NMR spectrum, δ, ppm: 4.32 s (NH), 3.48 s (CH_2), 2.28 s (CH_3), 6.88–7.00 m (Ar). Found, %: C 68.90; H 6.52; N 5.43. $C_{20}H_{17}NO$. Calculated, %: C 69.14; H 6.99; N 5.76.

N-2,5-Dimethylphenyl-*m*-phenoxybenzylamine (IIl). Along procedure *a* compound **IIl** was obtained in 68% yield, by procedure *b* the yield reached 62%, bp 280–282°C (2 mm Hg. IR spectrum, cm^{-1}: 1310 (C–N), 1250 (C–O–C), 3440 (NH), 3020, 1580 (CH). ^1H NMR spectrum, δ, ppm: 3.48 s (NH), 2.78 s (CH_2), 1,48, 1.25 s ($2CH_3$), 6.16–6.92 m (Ar). Found, %: C 82.40; H 6.12; N 4.28. $C_{21}H_{20}NO$. Calculated, %: C 82.62; H 6.88; N 4.59.

***N*-Aryl-*m*-phenoxybenzylamines hydrochlorides.** General procedure. Into a weighed flask was charged 0.5 g of an appropriate N-aryl-*m-phenoxybenzyl*amine and 20 ml of ethyl ether. At cooling with ice the reaction mixture was saturated with hydrogen chloride. The reaction completion was determined by weight gain and separation of a precipitate that was filtered off and washed with pure ethyl ether.

N-Phenyl-*m*-phenoxybenzylaminea hydrochloride (Va). Yield 88%, mp 140–141°C. IR spectrum, cm^{-1}: 1310 (C–N), 1250 (C–O–C), 2720 ($^+NH_2$), 3000, 1560 (CH). Found, %: C 2.96; H 5.11; Cl 11.09; N 4.19. $C_{19}H_{16}ClNO$. Calculated, %: C 73.19; H 5.13; Cl 11.39; N 4.49.

***N*-*m*-nitrophenyl-*m*-phenoxybenzyl-amine hydrochloride (Ve).** Yield 91%, mp 132–133°C. IR spectrum, cm^{-1}: 1310 (C–N), 1240 (C–O–C), 2750 ($^+NH_2$), 3045, 1570 (CH). Found, %: C 63.43; H 4.52; Cl 10.10; N 7.56. $C_{19}H_{15}ClN_2O_3$. Calculated, %: C 36.78; H 4.76; Cl 10.21; N 7.83.

***N*-*p*-Methoxyphenyl-*m*-phenoxybenzylamine hydrochloride (Vg).** Yield 81%, mp 120–121°C. IR spectrum, cm^{-1}: 1320 (C–N), 1240 (C–O–C), 2720 ($^+NH_2$), 3020, 1580 (CH). Found, %: C 70.01; H 5.68; Cl 11.09; N 4.19. $C_{20}H_{18}ClNO_2$. Calculated, %: C 70.07; H 5.84; Cl 10.36; N 4.49.

***N*-*p*-Hydroxyphenyl-*m*-phenoxybenzylamine hydrochloride (Vh).** Yield 90%, mp 175–177°C. IR spectrum, cm^{-1}: 1310 (C–N), 1240 (C–O–C), 2710 ($^+NH_2$), 3010, 1570 (CH). Found, %: C 68.96; H 5.22; Cl 11.01; N 4.10. $C_{19}H_{16}ClNO_2$. Calculated, %: C 69.41; H 5.48; Cl 11.11; N 4.26.

***N*-*p*-Bromophenyl-*m*-phenoxybenzylamine hydrochloride (Vi).** Yield 92%, mp 134–136°C. IR spectrum, cm^{-1}: 1320 (C–N), 1250 (C–O–C), 2750 ($^+NH_2$), 3030, 1590 (CH). Found, %: C 57.93; H 4.22; Cl 28.95; N 3.42. $C_{19}H_{15}BrClNO$. Calculated, %: C 58.24; H 4.34; Cl 29.76; N 3.58.

***N*-*m*-Methylphenyl-*m*-phenoxybenzylamine hydrochloride (Vj).** Yield 84%, mp 135–136°C. IR spectrum, cm^{-1}: 1300 (C–N), 1240 (C–O–C), 2750 ($^+NH_2$), 3040, 1580 (CH). Found, %: C 73.01; H 5.17; Cl 10.44; N 4.21. $C_{20}H_{18}ClNO$. Calculated, %: C 73.50; H 5.51; Cl 10.87; N 4.28.

***N*-*p*-Methylphenyl-*m*-phenoxybenzylamine hydrochloride (Vk).** Yield 94%, mp 101–103°C. IR spectrum, cm^{-1}: 1305 (C–N), 1240 (C–O–C), 2750 ($^+NH_2$),

3042, 1580 (CH). Found, %: C 73.20; H 5.30; Cl 10.35; N 4.18. $C_{20}H_{18}ClNO$. Calculated, %: C 73.50; H 5.51; Cl 10.87; N 4.28.

***N*-2,5-Dimethylphenyl-*m*-phenoxybenzylamine hydrochloride (VI).** Yield 82%, mp 155–156°C. IR spectrum, cm^{-1}: 1300 (C–N), 1235 (C–O–C), 2710 ($^+NH_2$), 3040, 1570 (CH). Found, %: C 73.55; H 4.36; Cl 10.32; N 4.07. $C_{21}H_{21}ClNO$. Calculated, %: C 73.78; H 4.97; Cl 10.39; N 4.09.

Dimethyl (*m*-phenoxyphenyl-*N*-arylphenylaminomethyl) phosphonates and di-2-ethylhexyl (*m*-phenoxyphenyl-*N*-arylphenylaminomethyl) phosphates. General procedure. Into a one-neck flask was charged 3 g of an appropriate *N*-aryl-*m*-phenoxyphenylmethanimine **I**, 8 ml of ethanol, 2–3 drops of concn. hydrochloric acid, and 1.1 g of the corresponding phosphorus-containing compound **VI**. The reaction mixture was heated to 75–80°C for 2 h. On completion of the reaction the final product was purified by recrystallization.

Di-2-ethylhexyl (*m*-phenoxyphenyl-*N*-phenylaminomethyl) phosphate (VIIa). Yield 60%, mp 48–49°C. IR spectrum, cm^{-1}: 1150 (P–O–P), 1345 (P=O), 3300 (NH), 3040, 1580 (CH). ^1H NMR spectrum, δ, ppm: 5.30 s (NH), 1.78 m (CH_2), 4.50 t (OCH_2), 5.10 s (ArCH), 6.96–7.52 (Ar), 0.86 s (CH_3). Found, %: C 70.08; H 7.93; N 2.45; P 5.12. $C_{35}H_{48}NO_5P$. Calculated, %: C 70.83; H 8.09; N 2.36; P 5.23.

Di-2-ethylhexyl (*m*-phenoxyphenyl-*N*-*m*-nitrophenylaminOmethyl) phosphate (VIIb). Yield 62%, mp 60–61°C. IR spectrum, cm^{-1}: 1130 (P–O–P), 1360 (P=O), 3340 (NH), 3000, 1560 (CH). ^1H NMR spectrum, δ, ppm: 5.35 s (NH), 1.86 m (CH_2), 4.52 t (OCH_2), 5.17 s (ArCH), 6.94–7.60 m (Ar), 0.89 s (CH_3).Found, %: C 64.96; H 7.12; N 4.05; P 4.51. $C_{35}H_{47}N_2O_7P$. Calculated, %: C 65.83; H 7.37; N 4.39; P 4.86.

Di-2-ethylhexyl (*m*-phenoxyphenyl-*N*-*p*-methoxyphenylaminomethyl) phosphate (VIIc). Yield 65%, mp 45–49°C. IR spectrum, cm^{-1}: 1140 (P–O–P), 1360 (P=O), 3330 (NH), 3030, 1560 (CH). ^1H NMR spectrum, δ, ppm: 5.24 s (NH), 1.56 m (CH_2), 4.12 t (OCH_2), 5.00 s (ArCH), 6.55–7.45 m (Ar), 0.74 s (CH_3), 5.00 s (OCH_3). Found, %: C 70.96; H 8.03; N 2.41; P 5.00. $C_{36}H_{50}NO_6P$. Calculated, %: C 71.17; H 8.24; N 2.31; P 5.11.

Di-2-ethylhexyl (*m*-phenoxyphenyl-*N*-phenylhydrazinomethyl) phosphate (VIId). Yield 58%, mp 50–52°C. IR spectrum, cm^{-1}: 1150 (P–O–P), 1355 (P=O), 3300 (NH), 3010, 1570 (CH). ^1H NMR spectrum, δ, ppm: 5.12 s (NH–NH), 2.12 m (CH_2), 4.50 t (OCH_2), 4.85 s (ArCH), 6.58–7.02 m (Ar), 0.92 s (CH_3). Found, %: C 68.12; H 8.25; N 4.18; P 4.96. $C_{35}H_{49}N_2O_5P$. Calculated, %: C 68.90; H 8.40; N 4.60; P 5.10.

Dimethyl (*m*-phenoxyphenyl-*N*-phenylaminomethyl) phosphonate (VIIe). Yield 62%, mp 105–106°C. IR spectrum, cm^{-1}: 1150 (P–O–P), 1350 (P=O), 3340 (NH), 3020, 1560 (CH). ^1H NMR spectrum, δ, ppm: 5.05 s (NH), 4.42 s (OCH_3), 4.27 s (ArCH), 6.84–7.20 m (Ar). Found, %: C 65.48; H 5.35; N 3.21; P 7.98. Calculated, %: C 65.79; H 5.74; N 3.66; P 8.09. $C_{21}H_{20}NO_4P$.

Dimethyl (*m*-phenoxyphenyl-*N*-*m*-nitrophenylaminomethyl) phosphonate (VIIf). Yield 58%, mp 112–114°C. IR spectrum, cm^{-1}: 1130 (P–O–P), 1360 (P=O), 3380 (NH), 3000, 1560 (CH). ^1H NMR spectrum, δ, ppm: 4.88 s (NH), 4.34 s (OCH_3), 4.12 s (ArCH), 6.64–6.90 m (Ar). Found, %: C 61.98; H 5.12; N 6.45; P 7.38. $C_{21}H_{19}N_2O_6P$. Calculated, %: C 62.38; H 5.20; N 6.93; P 7.67.

Dimethyl (*m*-phenoxyphenyl-*N*-*p*-methoxyphenylaminomethyl) phosphonate (VIIg). Yield 63%, mp 108–109°C. IR spectrum, cm^{-1}: 1140 (P–O–P), 1350 (P=O), 3350 (NH), 3020, 1560 (CH). ^1H NMR spectrum, δ, ppm: 4.94 s (NH), 4.53 s (ArCH), 6.88–7.25 m (Ar), 4.75 s (OCH_3). Found, %: C 63.45; H 5.28; N 3.12; P 7.05. $C_{22}H_{21}NO_5P$. Calculated, %: C 63.92; H 5.81; N 3.39; P 7.51.

Dimethyl (*m*-phenoxyphenyl-*N*-phenylhydrazinomethyl) phosphonate (VIIh). Yield 64%, mp 100–103°C. IR spectrum, cm^{-1}: 1160 (P–O–P), 1350 (P=O), 3300 (NH), 3020, 1560 (CH). ^1H NMR spectrum, δ, ppm: 5.26 s (NH–NH), 3.85 s (ArCH), 6.88–7.45 m (Ar), 4.18 s (CH_3). Found, %: C 62.96; H 5.13; N 6.82; P 7.15. $C_{21}H_{21}N_2O_4P$. Calculated, %: C 63.30; H 5.80; N 7.10; P 7.80.

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