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Complexes of Silicon and Phosphorus Chlorides with Nitrogen-Containing Bases as the Condensing Agents in the Synthesis of Amides

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Abstract—High effectiveness of new condensing agents on the basis of complexes of silicon and phosphorus chlorides with nitrogen-containing bases in the synthesis of amides from carboxylic acids and amines and also in heterocyclization is shown. Factors affecting the readiness of formation of the amide bond and the yields of the final products are established.

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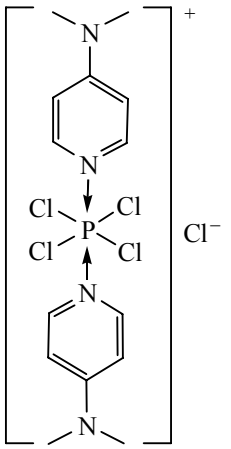
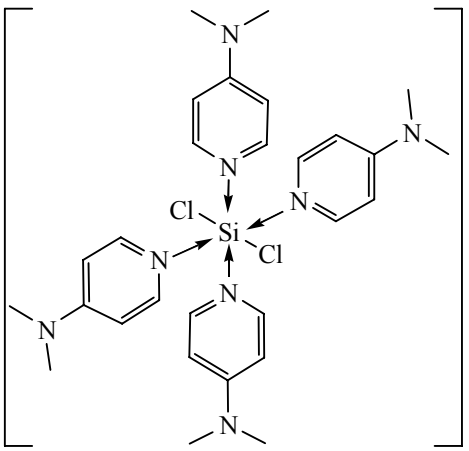
The formation of amides in the reaction of amines with carboxylic acids is of significant interest especially for the synthesis of peptides and lactams. The direct condensation of amines with carboxylic acids takes place at high temperatures (160–180°C) preventing the use of reagents with the labile functional groups. Therefore for performing the attack by amino group the activation of electrophilic component by means of different methods is necessary. The most part of these methods is based on converting carboxylic acids into more reactive compounds like acyl halides, anhydrides, acyl azides, and activated esters or on using condensing agents like carbodiimides, carbonyldiimidazole, *N,N*'-disuccinimidyl carbonate, etc. [1–4]. Since recently instead of carbodiimides and activated esters onium derivatives [3, 4] are often used. Most effective among them occurred to be ammonium and phosphonium salts.

In the series of the latter triamidophosphonium salts with dialkylamino- or pyrrolidine groups are the most widespread. It could be expected that analogous properties would be exhibited by the complexes of phosphorus and silicon with 4-dimethylaminopyridine and *N*-methylimidazole we formerly obtained.

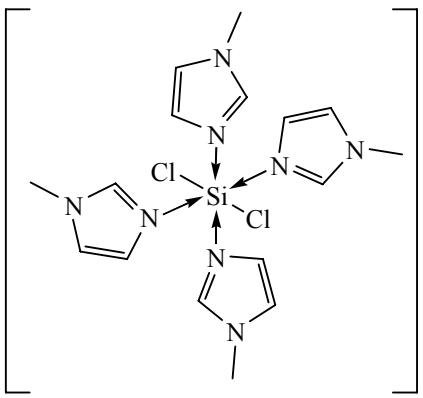
We carried out an investigation of factors affecting the amidation of carboxylic acids with aromatic



I



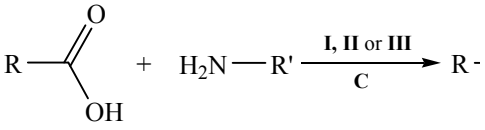
II



III

amines while using phosphorus **I** [5] and silicon complexes **II, III** as the condensing agents.

The reaction was carried out by heating in acetonitrile a mixture of acid **IV**, amine **V,** one of condensing agents **I–III**, and a base. Target amides **VI** can be easily obtained in a pure state by treating the reaction mixture with 10% aqueous alkali, and the products of hydrolysis of condensing agent are easily removed due to their solubility in water or alkali.



By the reaction of the derivatives of benzoic and phenoxyacetic acids with phenetidine in presence of complex **I** (method *a*) the corresponding amides **VIa**, **VIn** were prepared in high yields (Table 1). This method is more convenient for practical use than standard procedures with carbodiimides and carbonyldiimidazole. In the last case the reaction is carried out in two steps. In the first one the activated derivative of the acid is obtained, and in the second step the amine is added. The condensation effected by complex **I** permits heating together equimolar amounts of all three components.

Yet at the use of phosphorus complexes a competing phosphorylation of starting amines sometimes takes place which decreases the yields of amides though this decrease in insignificant. At the same time the silicon complexes do not form by-products and their use is preferred.

The investigation of the condensing ability of complexes of silicon tetrachloride with 4-dimethylaminopyridine **II** (method *b*) and *N*-methylimidazole **III** (method *c*) showed the preparative preferability of complex **III** due to its higher hydrolytic stability.

In the amidation reaction under study a broad range of aromatic and heterocyclic amines and acids of various nature was used. The process is also applicable to the poorly nucleophilic nitoanilines and heterylamines which are difficultly acylated by means of usual condensing reagents. Yields of the amidation products (25–90%) depend significantly on the nature of substituents in the aromatic or heterocyclic ring of the amine. Aromatic amines containing bulky and especially electron-acceptor groups in the *ortho*-position to the amino group significantly more difficultly enter the reaction. For example, *o*-nitroaniline forms amide **VIb** in 50% yield, and 2,4,6-trichloroaniline under the analogous conditions practically gives no amide **VIe** (see Table 1).

Acylation conditions are sufficiently mild which permits to obtain amides **VIm, VIp** of the acids that often form tar under the another acylation conditions.

Nature of the carboxylic acid weakly affects the reaction time and the yields of the reaction products **VIl–VIq** (Table 1). In the majority of cases the yields of amides are high. Low yield of amide **VIp** is due to the partial decomposition of the indolylacetic acid under the reaction conditions.

While using diisopropylethylamine as a base (methods *a–c*) the target amides often primarily form oils which complicates their isolation. Due to that the use of *N*-methylimidazole is preparatively more convenient (method *d*).

The application of phosphorus **I** and silicon **II, III** complexes is not limited only to the synthesis of acyclic amides. Complex **III** was used also in amidation leading to different types of heterocycles (method *e*, Table 2).

For example, the reaction of thiosemicarbazides **VII** with carboxylic acids gave the derivatives of thiadiazole **VIIIa–VIIIc** in satisfactory yields. Yet with hydrazines no cyclization takes place. Instead the corresponding acylation products **Xa, Xb** are formed.

o-Aminothiophenol and *o*-phenylenediamine (compounds **XIIa, XIIb**) were used in heterocyclization. In the last case the yield of the cyclic product decreases due to competing acylation of both amino groups of o-phenylenediamine.

The reactions we have investigated show that the obtained condensing agents may be widely used in the synthesis of amides and in the heterocyclization. In many cases this method can successively supplement the other methods of synthesis of compounds containing the amido group.

EXPERIMENTAL

^{1}H NMR spectra were registered on a Varian VXR-300 spectrometer (299.95 MHz) in $CDCl_3$ and DMSO-d_6.

Table 1. Yields and some parameters of synthesis of amides **VIa–VIq**

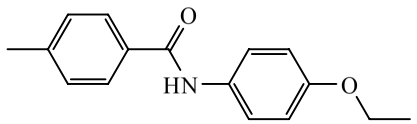
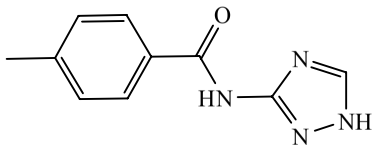
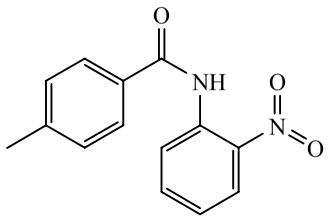
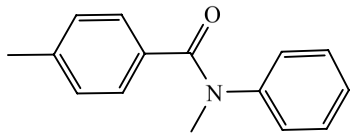
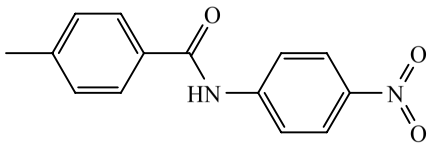
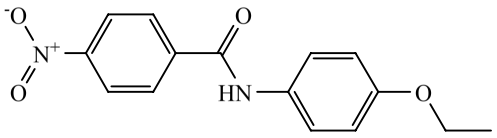
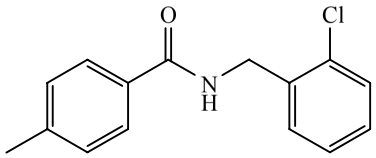
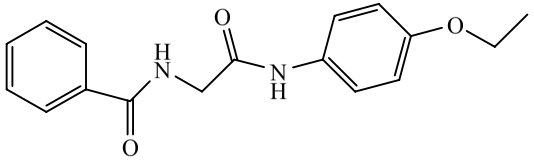
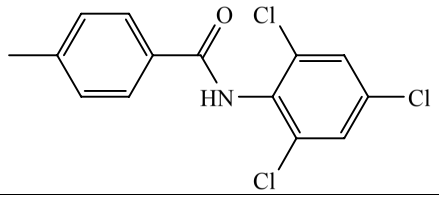
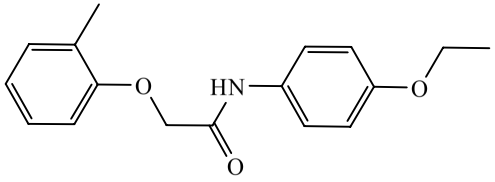
Comp. no.	Amide	Yield, % (method)	Reaction time, h	Comp. no.	Amide	Yield, % (method)	Reaction time, h
VIa		71 (*a*) 60 (*b*) 76 (*c*) 94 (*d*)	3	**VIj**		70 (*c*)	11
VIb		30 (*c*) 50 (*d*)	10	**VIk**		20 (*c*)	15
VIc		70 (*c*)	7.5	**VIl**		65 (*c*)	8
VId		70 (*b*) 77 (*c*)	3	**VIm**		55 (*c*)	8
VIe		12 (*c*)	15	**VIn**		73 (*a*) 81 (*c*)	6.5

Table 1. (Contd.)

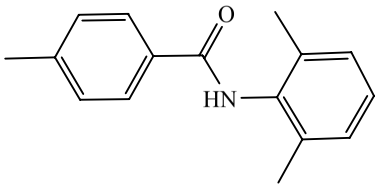
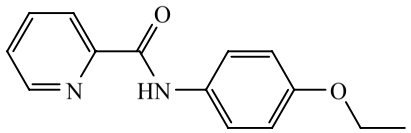
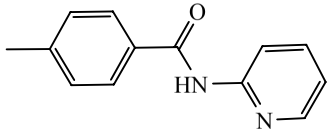
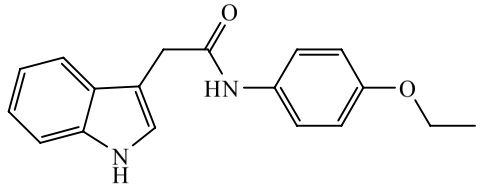
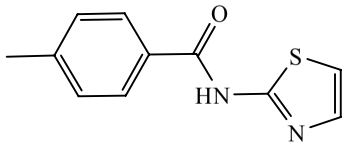
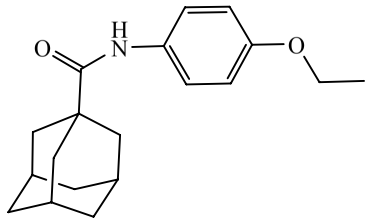
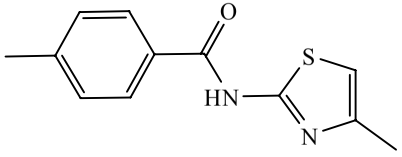
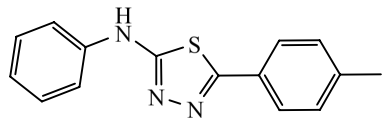
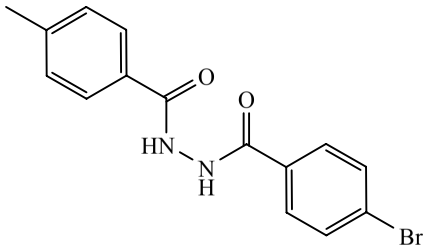
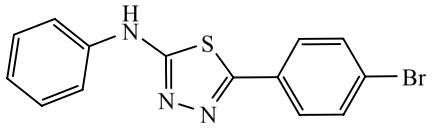
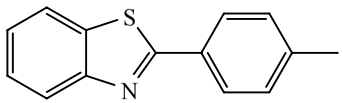
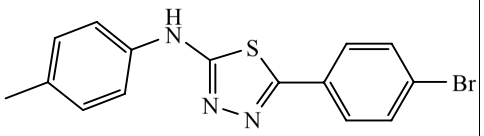
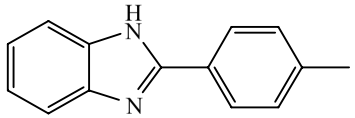
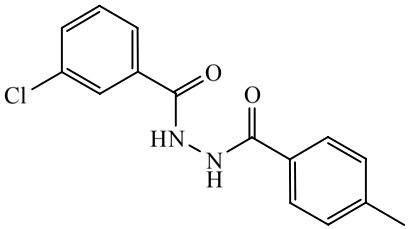
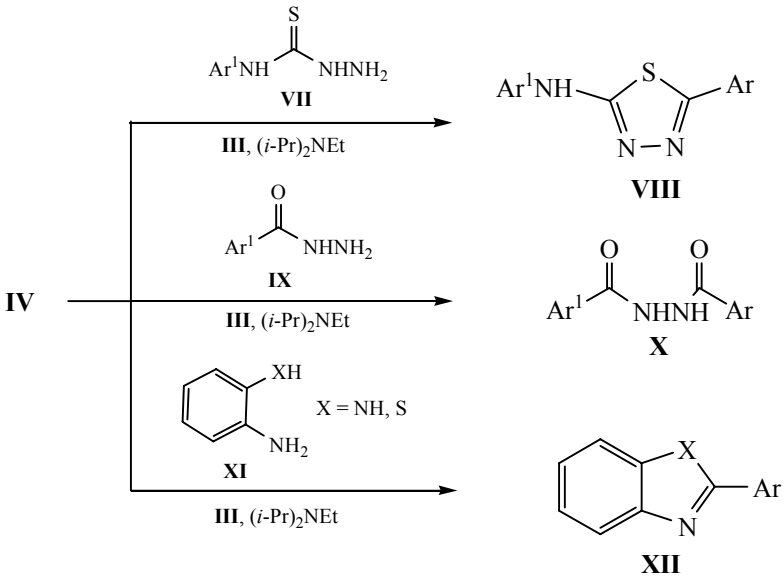
Comp. no.	Amide	Yield, % (method)	Reaction time, h	Comp. no.	Amide	Yield, % (method)	Reaction time, h
VIf		50 (*c*)	10	**VIk**		74 (*c*)	5
VIg		60 (*c*)	5	**VIp**		30 (*c*)	8
VIh		55 (*c*)	5	**VIq**		45 (*c*)	8
VIi		65 (*c*)	5				

Table 2. Yields of the compounds **VIII, X, XII**

Comp. no.	Compound	Yield, %	Reaction time, h	Comp. no.	Compound	Yield, %	Reaction time, h
VIIIa		70	9	**Xb**		70	8
VIIIb		60	9	**XIIa**		60	10
VIIIc		40	9	**XIIb**		40	8.5
Xa		80	6				



Chemical shifts were measured against internal TMS. Synthesis of compounds **II** and **III** was carried out under the anhydrous conditions in the flow of dry argon. Anhydrous solvents were prepared by distillation over phosphorus anhydride. The duration of reactions, methods of synthesis, and the yields of obtained amides are listed in Tables 1, 2. Greater part of the amides synthesized was analytically pure and required no additional purification.

Tetrakis(4-dimethylaminopyridine)dichlorosilicium dichloride (II). To a solution of 5 g of 4-dimethylaminopyridine in 30 ml of chloroform a solution of 1.07 g of tetrachlorosilane in 5 ml of chloroform was added dropwise with stirring. The obtained oil crystallized at the addition of 20 ml of diethyl ether. The obtained precipitate was filtered off, washed with diethyl ether, and dried in a vacuum. Yield 2.5 g (60%), decomposition point 250–260°C. IR spectrum (mull in mineral oil), ν, cm^{-1}: 1200 (C–N), 1350–1550 (C–C), 2900–2980 (C–H_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.21 s (24H, NCH_3), 6.83 d (8H_{arom}, J_{HH} 8.1), 7.89 d (8H_{arom}, J_{HH} 8.1). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 41.02 (NCH_3), 107.43 (arom), 138.37 (arom). Found, %: C 50.47; H 6.19; Cl 21.37; N 16.94; Si 4.16. $C_{28}H_{40}Cl_4N_8Si$. Calculated, %: C 51.07; H 6.12; Cl 21.53; N 17.01; Si 4.26.

Tetrakis(*N*-methylimidazol)dichlorosilicon(2^+) chloride (III). This compound was obtained analogously to **II** from 5.074 g of *N*-methylimidazole and 1.5 g of tetrachlorosilane. Yield 4.1 g (93%), decomposition point 225°C. IR spectrum (mull in mineral oil), ν, cm^{-1}: 1100 (C–N), 1300–1500 (C–C), 2900–2980 (C–H_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.78 s (12H, NCH_3), 7.1 s (4H_{arom}), 7.42 s (4H_{arom}), 8.59 (4H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 35.00 (NCH_3), 122.03 (arom.), 126.64 (arom), 142.05 (arom.). Found, %: C 38.25; H 4.82; Cl 28.48; N 22.45; Si 5.61. $C_{16}H_{24}Cl_4N_8Si$. Calculated, %: C 38.56; H 4.85, Cl 28.46; N 22.49; Si 5.64.

Synthesis of carboxamides *(general procedure).* To a mixture of 2.35 mmol of amine and 2.82 mmol of acid in 2 ml of acetonitrile 11.75 mmol of diisopropylethylamine was added with stirring. To the obtained homogenous solution 2.35 mmol of complex **I** was added, and the reaction mixture was refluxed for 1 h. After that it was treated with a solution of 1 g of potassium carbonate in 20 ml of water, and the mixture obtained was stirred for 0.5 h. The precipitate formed was filtered off, washed with 1:1 water–acetonitrile mixture, and dried in air.

To a mixture of 4 mmol of amine and 4.4 mmol of the acid in 8 ml of acetonitrile 3 ml of diisipropylethylamine was added with stirring. The obtained homogenous solution was treated with 4 mmol of complex **II**, and the reaction mixture was refluxed from 3 to 15 h depending on the nucleophilicity of the amine. The reaction progress was monitored by ^1H NMR spectroscopy of the reaction mixture. After the completion of the process the mixture obtained was added gradually with stirring to 50 ml of 10% NaOH. The product obtained precipitated from the homogenous solution formed. In the case of formation

of oil the reaction mixture was left until the complete evaporation of diisopropylethylamine, and gradual crystallization of the product took place. The crystals formed were filtered off, washed with water, and dried in air.

The reaction was carried out analogously to the procedure *b*. Complex **III,** 4 mmol, was used instead of complex **II**.

The reaction was carried out as described in the procedure *b*. Complex **III**, 4 mmol was used instead of complex **II**, and *N*-methylimidazole, 4 mmol, was used instead of diisopropylethylamine.

(4'-Ethoxy)-4-mehylbenzanilide (VIa) was prepared from 0.6 g of toluic acid and 0.548 g of *p*-phenetidine, mp 200–201°C (190–102°C [6]). Spectral data of the product agree with the reported in [5].

(2'-Nitro)-4-methylbenzanilide (VIb) was prepared from 0.6 g of toluic acid and 0.55 g *o*-nitroaniline, mp 101–102°C (110°C [7]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.41 s (3H, Ar-CH_3), 7.35 d (2H$_{arom}$, J_{HH} 8), 7.36 d.d (1H$_{arom}$, J_{HH} 7, J_{HH} 1), 7.73 d.d (1H$_{arom}$, J_{HH} 8.6, J_{HH} 1.5), 7.86 d (2H$_{arom}$, J_{HH} 8), 7.92 d.d (1H$_{arom}$, J_{HH} 8, J_{HH} 1.25), 8.02 d.d (1H$_{arom}$, J_{HH} 8, J_{HH} 1.25), 10.68 s (1H, NH).

(4'-Nitro)-4-methylbenzanilide (Vic) was prepared from 0.6 g of toluic acid and 0.55 g of *p*-nitroaniline, mp 200°C (207°C[8]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.45 s (3H, ArCH$_3$), 7.32 d (2H$_{arom}$, J_{HH} 8), 7.80 d (2H$_{arom}$ J_{HH} 8 Hz), 7.84 d (2H$_{arom}$, J_{HH} 9), 8.14 s (1H, NH), 8.25 d (2H$_{arom}$, J_{HH} 9).

***N*-2'-Chlorobenzyl-4-methylbenzamide (VId)** was prepared from 0.6 g of toluic acid and 0.56 g of 2-chlorobenxylamine, mp 130–132°C (128–129°C [9]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.39 s (3H, Ar-CH_3), 4.72 d (2H, NH-CH_2, J_{HH} 6), 6.60 s (1H, NH), 7.24 m (4H$_{arom}$), 7.39 d.d (1H$_{arom}$, J_{HH} 5, J_{HH} 7), 7.47 d.d (1H$_{arom}$, J_{HH} 5, J_{HH} 7), 7.69 d (2H$_{arom}$, J_{HH} 8).

(2',4',6'-Trichloro)-4-methylbenzanilide (VIe) was prepared from 0.6 g of toluic acid and 0.785 g of 2,4,6-trichloroaniline, mp 220°C (233°C [10]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.38 s (3H, Ar-CH_3), 7.24 d (2H$_{arom}$, J_{HH} 8), 7.60 d (2H$_{arom}$, J_{HH} 8), 7.78 s (2H$_{arom}$), 10.23 s (1H, NH).

(2',6'-Dimethyl)4-methylbenzanilide (VIf) was prepared from 0.6 g of toluic acid and 0.484 g of 2,6-dimethylaniline, mp 230°C (235°C [11]). ^{1}H NMR spectrum ($CDCl_3$)), δ, ppm (*J*, Hz): 2.27 s 6H, Ar'-CH_3), 2.44 s (3H, Ar-CH_3), 7.12 m (3H$_{arom}$), 7.30 d (3H$_{arom}$, J_{HH} 8), 7.38 s (1H, NH), 7.80 d (2H$_{arom}$, J_{HH} 8).

4-Methyl-*N*-pyridin-2-ylbenzamide (VIg) was prepared from 0.6 g of toluic acid and 0.376 g of 2-aminopyridine, mp 105°C (105–106°C [12]). Spectral data are consistent with the reported parameters [13].

4-Methyl-*N*-thiazol-2-ylbenzamide (VIh) was prepared from 0.6 g of toluic acid and 0.4 g of 2-amino-1,3-thiazole. The product was extracted from alkaline solution with chloroform (3×10 ml), the solvent was removed in a vacuum, and the residue was crystallized from chloroform, mp 210°C (211–214°C [14]). Spectral characteristics of the product are consistent with the reported parameters [14].

4-Methyl-*N*-(4'methyl)thiazol-2-ylbenzamide (VIi) was prepared from 0.6 g of toluic acid and 0.456 g of 2-amino-4-methyl-1,3-thiazole. The product was extracted from alkaline solution with chloroform (3×10 ml), the solvent was removed in a vacuum, and the residue was crystallized from chloroform, mp above 250°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.16 s (3H, Het-CH_3), 2.31 s (3H, Ar-CH_3), 6.19 s (1H$_{arom}$), 7.13 d (2H$_{arom}$, J_{HH} 8), 8.0 d (2H$_{arom}$, J_{HH} 8), 9.8 s (1H, NH). Found, %: C 62.06; H 5.15; N 11.98; S 13.75. $C_{12}H_{12}N_2OS$. Calculated, %: C 62.04; H 5.21; N 12.06; O 6.89; S 13.80.

4-Methyl-*N*-triazol-3-yl1,2,4-benzamide (VIj) was prepared from 0.6 g of toluic acid and 0.336 g of 3-amino-1,2,4-triazole. The product was extracted with butanol (3×10 ml), the solvent was removed in a vacuum, and the residue was crystallized from ethanol, mp 230–235°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.37 s (3H, Ar-CH_3), 7.33 d (2H$_{arom}$, J_{HH} 8), 7.80 s (1H$_{arom}$), 7.95 d (2H$_{arom}$, J_{HH} 7), 11.83 s (1H, NH), 13.56 s (1H, NH). Found, %: C 59.30; H 4.95; N 27.75. $C_{10}H_{10}N_4O$. Calculated, %: C 59.40; H 4.98; N 27.71; O 7.91.

***N*-Methyl-(4-methyl)benzanilide (VIk)** was prepared from 0.6 g of toluic acid and 0.428 g of *N*-methylaniline, mp 70–72°C (69.5–71°C [15]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.21 s (3H, Ar-CH_3), 3.33 s (3H, NCH_3), 6.99 d (2H$_{arom}$, J_{HH} 8), 7.13 m (5H$_{arom}$), 7.25 d (2H$_{arom}$, J_{HH} 8), 7.27 s (1H, NH).

(4'-Ethoxy)-4-nitrobenzanilide (VIl) was prepared from 0.54 g of *p*-nitrobenzoic acid and 0.55 g of *p*-phenetidine, mp 185–187°C (186–186°C [16]). ^{1}H

NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.43 t (3H, OCH_2CH_3, J_{HH} 7), 4.03 q (2H, OCH_2CH_3, J_{HH} 7), 6.92 d ($2H_{arom}$, J_{HH} 9), 7.52 d ($2H_{arom}$, J_{HH} 9), 7.82 s (1H, NH), 8.04 d ($2H_{arom}$, J_{HH} 7), 8.33 d ($2H_{arom}$, J_{HH} 8).

(4'-Ethoxy)-*N*-benzoylaminoacetanilide (VIm) was prepared from 0.78 g of hyppuric acid 0.548 g of *p*-phenetidine, mp 205°C (203°C [17]). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.40 t (3H, OCH_2CH_3, J_{HH} 7), 4.03 q (2H, OCH_2CH_3, J_{HH} 7), 4.34 d (2H, $NHCH_2$, J_{HH} 5.4), 6.85 d ($2H_{arom}$, J_{HH} 9), 7.32 br.s (1H, CH_{arom}), 7.46 d ($2H_{arom}$, J_{HH} 9), 7.47 t ($2H_{arom}$, J_{HH} 7.5), 7.54 t (1H, $NHCH_2$, J_{HH} 5.4), 7.87 d ($2H_{arom}$, J_{HH} 8), 8.6 s (1H,NH).

(4'-Ethoxy)-2-methylphenoxyacetanilide (VIn) was prepared from 0.73 g of 2-methylphenoxyacetic acid and 0.584 g of *p*-phenetidine, mp 112°C (112–113°C [18]). Spectral data agree with the reported one [5].

(4'-Ethoxy)pyridin-2-yl-carboxyanilide (VIo) was prepared from 0.73 g of pyridine-2-carboxylic acid and 0.548 g of *p*-phenetidine, mp 118°C (120–122°C [19]). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.43 t (3H, OCH_2CH_3, J_{HH} 7), 4.03 q (2H, OCH_2CH_3, J_{HH} 7), 6.66 d ($2H_{arom}$, J_{HH} 9), 6.74 m (2H-pyridine), 6.85 d ($2H_{arom}$, J_{HH} 9), 7.75 s (!H, NH).

(4'-Ethoxy)-1H-indol-3-ylacetanilide (VIp) was prepared from 0.77 g of 1*H*-indol-3-ylacetic acid and 0.548 g of *p*-phenetidine, mp 153°C (154–155°C [20]). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.37 t (3H, OCH_2CH_3, J_{HH} 7). 3.88 s (2H, CH_2CO), 3.96 q (2H, OCH_2CH_3, J_{HH} 7), 6.76 d ($2H_{arom}$, J_{HH} 9), 7.24 m ($6H_{arom}$, indol), 7.43 d (1H indol, J_{HH} 8.4), 7.63 d (1H indol, J_{HH} 8.4), 8.34 s (1H, NH), 10.58 s (1H, NH indol).

(4'-Ethoxy)-adamantylcarboxanilide (VIq) was prepared from 0.79 g of adamant-1-ylcarboxylic acid and 0.548 g of *p*-phenetidine, mp 208–210°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.40 t (3H, OCH_2CH_3, J_{HH} 7), 1.76 s (6H adamantine), 1.96 s (6H adamantame), 2.10 s (3H adamantane), 4.02 q (2H, OCH_2CH_3, J_{HH} 7), 6.86 d ($2H_{arom}$, J_{HH} 9), 7.19 s (1H, NH), 7.40 d ($2H_{arom}$, J_{HH} 9). Found, %: C 76.10, H 8.45. N 4.65. $C_{19}H_{25}NO_2$. Calculated, %: C 76.22, H 8.42, N 4.68, O 10.69.

5-(4-Methylphenyl)-*N*-phenyl-2-amino-1,3,4-thiadiazole (VIIIa) was prepared from 0.6 g of toluic acid and 0.67 g of phenylthiosemicarbazide, mp 205°C (208–209°C [21]). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.23 s (3H, Ar-CH_3), 7.07 d ($2H_{arom}$, J_{HH} 8), 7.11 d ($2H_{arom}$, J_{HH} 5), 7.23 d ($2H_{arom}$, J_{HH} 7.5), 7.42 t ($3H_{arom}$, J_{HH} 7), 7.93 s (1H, NH).

5-(4-Bromophenyl)-*N*-phenyl-2-amino-1,3,4-thiadiazole (VIIIb) was prepared from 0.884 g of p-bromobenzoic acid and 0.67 g of phenylthiosemicarbazide, mp 250°C (320–323°C [22]). Spectral characteristics of the product agree with the reported data [22].

5-(4-Bromophenyl)-*N*-(4-methylphenyl)-2-amino-1,3,4-thiadiazole (VIIIc) was prepared from 0.88 g of *p*-bromobenzoic acid and 0.725 g of *p*-tolylthiosemicarbazide. The product was purified by column chromatography, elution with 8:1 hexane–ethyl acetate, mp above 250°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz):2.25 s (3H, Ar-CH_3), 7.11 d ($2H_{arom}$, J_{HH} 8), 7.21 d ($2H_{arom}$, J_{HH} 8), 7.35 d ($2H_{arom}$, J_{HH} 8), 7.52 d ($2H_{arom}$, J_{HH} 8), 7.93 s (1H, NH). Found, %: C 52.06, H 3.45, Br 23.07, N 12.10, S 9.32. $C_{15}H_{12}BrN_3S$. Calculated, %: C 52.03, H 3.49, Br 23.08, N 12.14, S 9.26.

***N*'-(4-Methylbenzoyl)-3-chlorobenzylhydrazide (Xa)** was prepared from 0.6 g of toluic acid and 0.682 g of *m*-chlorophenylhydrazine, mp above 250°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.36 s (3H, Ar-CH_3), 7.23 d ($2H_{arom}$, J_{HH} 8), 7.33 d ($2H_{arom}$, J_{HH} 5), 7.72 d ($2H_{arom}$, J_{HH} 8), 7.85 m ($1H_{arom}$), 7.90 m ($1H_{arom}$). Found, %: C 66.50, H 4.15, Cl 13.12, N 10.32. $C_{15}H_{11}ClN_2O$. Calculated, %: C 66.55, H 4.10, Cl 13.10, N 10.35, O 5.91.

***N*'-(4-Bromobenzoyl)-4-methylbenzylhydrazide (Xb)** was prepared from 0.88 g of *p*-bromobenzoic acid and 0.6 g of *p*-tolylhydrazine, mp above 250°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.37 s (3H, Ar-CH_3), 7.25 d ($2H_{arom}$, J_{HH} 8), 7.54 d (2Harom, J_{HH} 8.4), 7.76 d ($2H_{arom}$, J_{HH} 8), 7.85 d ($2H_{arom}$, J_{HH} 8.4), 10.55 s (2H, NH).

2-(4-Methylphenyl)benzothiazole (XIIa) was prepared from 0.6 g of toluic acid and 0.5 g of 2-aminothiophenol. The product was purified by column chromatography, elution with 9:1 hexane–ethyl acetate, mp 85°C (82–84°C [23]). Spectral characteristics of the product are consistent with the reported parameters [23].

2-(4-Methylphenyl)benzimidazole (XIIb) was prepared from 0.6 g of toluic acid and 9.432 g of 1,2-phenylenediamine. According to ^1H NMR data the product contained about 20% of acyclic product of acylation of phenylenediamine at both amino groups.

Spectral characteristics of the product agree with the reported data [24].

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