CONDENSING REACTION BETWEEN ARYLALDEHYDES AND HYDRAZINE DERIVATIVED FROM AMINOSULPHONYL PHENOXYACETYLHYDRAZIDES

Anca M. Mocanu*, Corina Cernatescu

Technical University "Gh. Asachi", Faculty of Chemical Engineering, D. Mangeron Ave. no. 71A, 700050, Iasi, Romania.

*Corresponding author: ancamocanu2004@yahoo.com

Received: 27/06/2007
Accepted after revision: 11/01/2008

Abstract: By taking into account the important biological activity of the aminosulphonyl-phenoxyacetic acids, we considered useful to capitalize a series of seven previously syntetised hydrazides by their condensation with arylaldehydes. The reaction was carried out in ethanol medium using acetic acid as a catalyst. The obtained products were purified by recrystallisation in organic solvents (ethanol especially) and characterised by elemental analysis data, IR spectral measurements and melting points.

Keywords: *hydrazides of sulphonamidatedphenoxyacetic acids, condensing reactions with arylaldehydes, hydrazones, potential bioactivity.*

INTRODUCTION

Recently new biologically active products with potential applications in agriculture as herbicides, growing biostimulators, fungicides, acaricides have been obtained. The aryloxy-alkylcarboxylic acids and their derivatives are particularly important among various compounds studied lately, their herbicidal and auxinic actions being well known for a long time.

By introducing sulphonamidic groups in the molecules of the phenoxyacetic, chlorophenoxyacetic, cresoxyacetic, xylenoxyacetic, α-phenoxypropionic and γ-phenoxy-butiric acids, the auxinic and selective herbicidal properties of the phenoxyalkane carboxylic derivatives have been improved along with the lack of the toxic residues and toxicity towards human beings and animals.

The phenoxyalkane carboxylic derivatives include some of the most efficient and selective herbicidal agents, being used on annual and evergreen dicotyledonous plant in the haulm crops.

There are three main classes of phenoxyalkane acid type pesticides: phenoxyacetic acids (1), *α*-phenoxypropyonic acids (2), and *γ*-phenoxybutyric acids (3) (Figure 1).

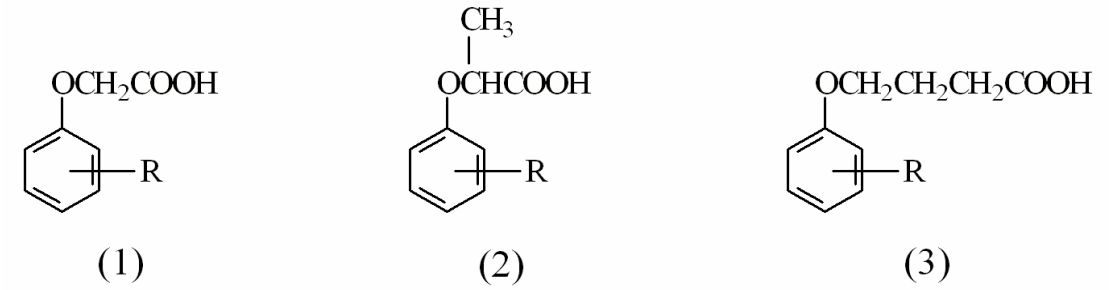


Figure 1. *The main classes of phenoxyalkane acid type pesticides*

These compounds as well as some of their derivatives (esters, amides, hydrazides) are also used as auxins, at low doses [1, 2]. By introducing a sulphonamidated moiety on the aromatic ring both herbicidal and growth regulatory actions of the compounds are improved, the toxicity toward human beings and mammalian becoming insignificant. For example, *Asfac*® induces an augmentation of the production of about 40 %, when applied on beet sugar crops, and does not produce toxic wastes [1, 3].

In order to obtain a new class of herbicides, we synthesized a series of derivatives with general formula (4) (Figure 2), in which the sulphonamidated phenoxyalcane carboxylic residue is linked to different benzylidene residues, through a hydrazine segment [6]. We anticipated that this kind of compounds might have synergic herbicidal actions due to both sulphonamidated phenoxyalkane carboxylic and benzaldehydes residues (also present in herbicides such as: *Dinoterb*® and *Medinoterb*®), and additionally, auxin actions [1].

Since the last step in the synthesis of compounds (4) is characterized by low yields, we carried out the reaction under different conditions by varying the main parameters influencing the process under study.

The sulphonamidic group was found to confer biologically active properties and low toxicity to the obtained products [3].

By taking the practical importance of these products into account we have continued the researches by studying the synthesis of hydrazones of the aminosulphonyl phenoxyacetic acids [4, 5].

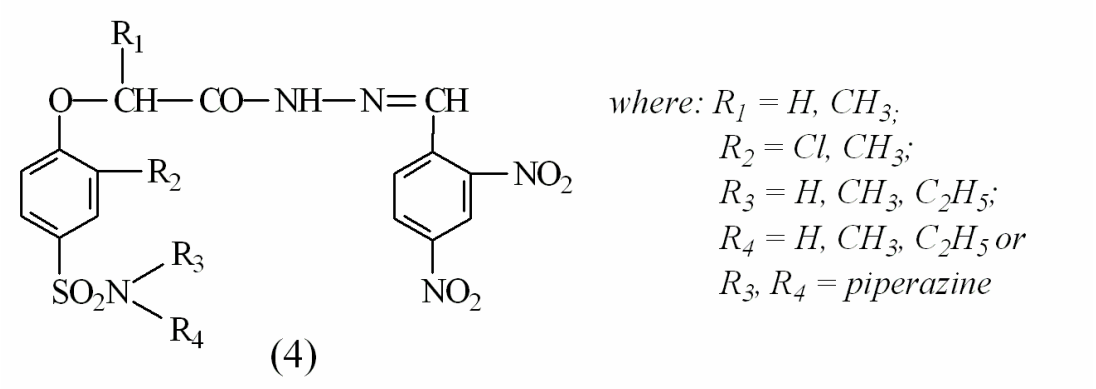


Figure 2. *A new class of herbicides*

MATHERIALS AND METHODS

General procedure

The corresponding hydrazide was solved in acetone, then a solution of aldehyde in warm ethanol and 3 drops of acetic acid were added. The reaction mixture was refluxed for 30 – 60 min, under vigorous stirring. The final product separated in time was then filtered and washed with ethanol on filter. The solid product was then purified by recrystallisation from ethanol.

4-dimethylaminobenzaldehyde{2-[4-(aminomethyl)-phenoxy]ethyl}-hydrazone

The hydrazide (0.5 g; 1.3 mmols) was solved in 15 mL acetone, then *p*-dimethylamino-benzaldehyde (0.230 g; 1.3 mmols) in 10 mL ethanol and 3 drops of acetic acid added. The reaction proceeded as described above. The product separated after 12 hours, was filtered and washed with ethanol on filter. The hydrazone was purified by recrystallisation from ethanol. A white-yellow amorphous powder finally separated, m.p. (melting point) = 196 – 200 ^{0}C.

4-nitrobenzaldehyde {2-[4-(aminomethyl)-phenoxy]ethyl}hydrazone

The hydrazide (0.5g; 1.3 mmols) and *p*-nitrobenzaldehyde (0.286 g; 1.3 mmols) were submitted to the general reaction procedure presented above. The solid separated in time, was subsequently filtered, washed on filter with ethanol and dried. The purification was made by recrystallisation from ethanol. The final hydrazone is an amorphous white yellow powder with m.p. = 220 – 224 °C.

2,4-dinitrobenzaldehyde {2-[4-(aminomethyl)-phenoxy]ethyl}hydrazone

The hydrazide (0.5 g; 1.1 mmols) solved in 15 mL acetone, reacted with 2,4-dinitro-benzaldehyde (0.372 g; 1.1 mmols) as described above. The product separated in a couple of days was filtered and washed with ethanol on filter. The solid was then recrystallised from ethanol. The final product separated as glittering white-yellow needles, m.p. = 225 – 229 ^{0}C.

4-hydroxybenzaldehyde {2-[4-(aminomethyl)-phenoxy]ethyl}hydrazone

The hydrazide (0.5 g; 1.4 mmols) was solved in 15 mL acetone, then *p*-hidroxy-benzaldehyde (0.247 g; 1.4 mmols) in 10 mL ethanol and 3 drops of acetic acid added. The reaction proceeded such as presented above. The solid separated over night was filtered and washed on filter and purified by recrystallisation from ethanol. The final product is a creamy powder, m.p. = 234 – 238 °C.

4-methoxybenzaldehyde {2-[4-(aminomethyl)-phenoxy]ethyl}hydrazone

The hydrazide (0.5 g; 1.3 mmols) and anisaldehyde (0.228 g; 1.3 mmols) reacted as presented in general reaction procedure. The solid separated in time was filtered, washed on filter with ethanol and recrystallised from ethanol. The final hydrazone is an amorphous white powder, m.p. = 233 – 235 °C.

4-methylbenzaldehyde {2-[4-(aminomethyl)-phenoxy]ethyl}hydrazone

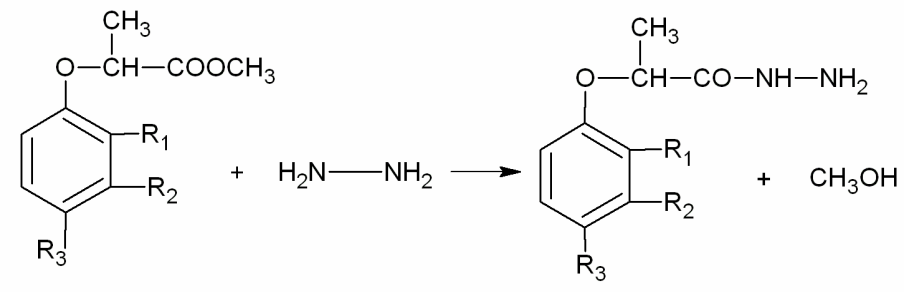
The hydrazide (0.5 g; 1.4 mmols) and *p*-tolylaldehyde (0.200 g; 1.4 mmols) reacted as presented in general reaction procedure. The solid separated in time was filtered, washed on filter with ethanol and recrystallised from ethanol. The final hydrazone is an amorphous white powder, m.p. = 228 – 232 °C.

4-chlorobenzaldehyde {2-[4-(aminomethyl)-phenoxy]ethyl}hydrazone

The hydrazide (0.5 g; 1.3 mmols) and *p*-clorbenzaldehyde (0.238 g; 1.3 mmols) reacted as presented in general reaction procedure. The solid separated in time was filtered, washed on filter with ethanol and recrystallised from ethanol. The final hydrazone is an amorphous white powder with m.p. = 200 – 205 ^{0}C.

RESULTS AND DISCUSSION

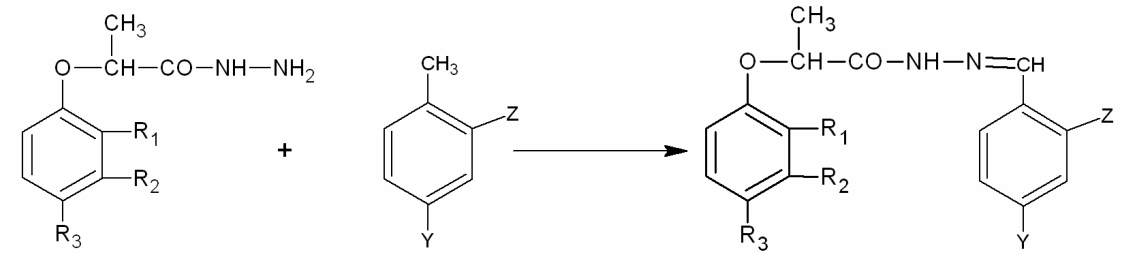
Based on the above considerations we have taken the hydrazides of the sulphonamidated phenoxyacetic acids, previously synthesized [4, 5] and submitted then to chemical reactions according to the reaction presented in figure 3.



where: R1=H, Cl, CH3,
R2=H, CH3;
R3=aminosulphonyl;

Figure 3. *Synthesis of hydrazides from sulphonamidated phenoxyacetic acids*

Due to the biological actions of the obtained compounds (4), we started from the above mentioned hydrazides to synthesize the corresponding hydrazones by condensing them with: *p*-dimethylaminobenzaldehyde, *p*-nitrobenzaldehyde, 2,4-dinitrobenzaldehyde, *p*-hidroxy-benzaldehyde, anisaldehyde, *p*-tolylaldehyde, *p*-clorbenzaldehyde (figure 4).



where: R1=H, Cl, CH3,
R2=H, Cl, CH3;
R3=aminosulphonyl;
Y= N(CH3)2, NO2, OH, OCH3, CH3, Cl.
Z= H, NO2.

Figure 4. *Synthesis of hydrazones*

Table 1. *Physical-chemical characteristics of the obtained hydrazones*

Nr	Z	Y	Formula	M [g/mol]	Melting point [°C]	Color
1	-H	$-N(CH_3)_2$	$C_{17}H_{20}N_4O_4S$	376	196-200	white-yellow powder
2	-H	$-NO_2$	$C_{15}H_{14}N_4O_6S$	378	220-224	white-yellow powder
3	$-NO_2$	$-NO_2$	$C_{15}H_{13}N_5O_8S$	423	225-229	white-yellow powder
4	-H	-OH	$C_{15}H_{14}N_3O_5S$	349	234-238	cream powder
5	-H	$-OCH_3$	$C_{16}H_{17}N_3O_5S$	363	233-235	white powder
6	-H	$-CH_3$	$C_{16}H_{15}N_3O_4S$	347	228-232	white powder
7	-H	-Cl	$C_{15}H_{14}N_3O_4SCl$	367.5	200-205	white powder
R_1=R_2= -H; $R_{3=}$ aminosulphonyl;						

The products were finally purified by recrystallization from organic solvents and then submitted to UV, IR (table 3) and NMR spectral measurements.
Physical-chemical characteristics and elemental analysis data of the obtained hydrazones are listed in tables 1 and 2.

Table 2. *Elemental analysis data of the obtained hydrazones*

Comp.	Elemental analysis					
	C%		H%		N%	
	Calc.	Found	Calc.	Found	Calc.	Found
1	54.25	54.17	5.31	5.40	14.89	14.97
2	47.61	47.50	3.70	3.74	14.81	14.93
3	42.55	42.44	3.07	3.14	16.54	16.56
4	51.57	51.46	4.01	4.09	12.03	12.11
5	52.89	52.77	4.68	4.72	11.57	11.48
6	55.33	55.27	4.32	4.42	12.10	12.16
7	48.97	48.88	3.80	3.86	11.42	11.57

Table 3. *IR characteristic absorptions of the obtained hydrazones*

Comp.	Characteristic bands (cm^{-1}) and their intensity (VS = very strong, S = strong, M = medium, W = weak, VW = very weak)
1	667.37 S, 698.23 S, 729.09 S, 815.89 M, 893.04 M, 910.40 S, 1105.21 S, 1136.07 S, 1153.43 VS, 1207.44 M, 1251.80 VS, 1498.69 S, 1583.55 M, 1597.06 M, 1679.99 VS, 3076.45 M, 3323.34 S.
2	686.66 S, 717.52 S, 746.45 S, 792.74 S, 825.53 S, 839.03 S, 883.40 M, 916.19 S, 1099.42 VS, 1138.00 VS, 1157.29 VS, 1205.51 S, 1257.59 VS, 1317.38 VS, 1342.45 VS, 1492.90 S, 1517.97 VS, 1585.48 S, 1689.64 VS, 3082.24 M, 3352.27 S.
3	667.37 M, 698.30 M, 725.23 M, 817.82 M, 831.32, 856.39 W, 912.33 M, 1101.35 S, 1136.07 VS, 1155.36 S, 1207.44 M, 1255.66 VS,1338.60, 1496.76 S, 1535.33 S, 1566.19 M, 1693.50 VS, 3381.21 M.
4	678.94 M, 717.52 W, 804.31 M, 825.53 VW, 875.68 W, 912.33 M, 1018.41 W, 1093.64 M, 1109.07 W, 1159.22 S, 1251.80 S, 1583.55 M, 1672.28 VS, 3072.60 W, 3383.14 M.
5	667.37 S, 698.23 S, 729.09 S, 815.89 M, 893.04 M, 910.40 S, 1060.85 M, 1105.21 S, 1136.07 S, 1153.43 S, 1207.44 M, 1251.80 VS, 1498.69 S, 1583.55 M, 1598.98 M, 1678.07 VS, 3076.53 M, 3323.34 M.
6	669.30 S, 698.23 S, 729.09 S, 815.89 M, 893.04 M, 910.40 S, 1105.21 S, 1136.07 S, 1153.43 VS, 1207.44 M, 1251.80 VS, 1597.06 S,1679.99 VS, 3076.45 M,3323.34 S.
7	457.13 M, 514.99 M, 586.36 S, 727.16 M, 914.26 M, 1010.70 M, 1101.35 S, 1138.00 VS, 1253.73 VS, 1591.27S, 1685.78 VS, 3093.81 S, 3529.73 M.

Thus, the stretching vibration bands for C=C were found in the 1566.19-1597.06 cm^{-1} range, as a strong or very strong band. Vibrations bands for C=O, C=N bonds were found in the 1672.07-1693.50 cm^{-1} range, as a very strong band. The C=S bands were found between 1099.42 and 1109.07 cm^{-1}.

The peaks corresponding to the $–SO_2–NH–$ group, appeared at 1153.43-1159.22 cm^{-1}, and those for Ar–O at 1251.80-1253.73 cm^{-1}. The S=O and S–N bonds were found between 1060.85 and 1105.21cm^{-1}.
The deformation ring vibration bands were present at 418.55 - 601.79 cm^{-1} and between 910.40 - 916.19 cm^{-1}. Vibration bands for νNO_2 sym. were found within the 1317.38 and 1342.45 cm^{-1} range, as a very strong band. The valence vibration bands for C–N appeared at 1136.07 - 1138.00 cm^{-1} and for C–OH bonds at 1018.41 cm^{-1}.
The deformation vibration bands for δCH_3 sym. and δCH_3 asym., have medium and strong absorptions around 1317.38 cm^{-1} and 1498.69 cm^{-1}, respectively.

CONCLUSIONS

By taking into account the biological activity of the aminosulphonyl phenoxyacetic acids we considered useful to capitalize a series of seven hydrazides by their condensation with aldehydes.
The reactions were carried out in ethanol medium using acetic acid as a catalyst.
The obtained products were purified by recrystallisation in organic solvents (ethanol especially). The final products were characterized by spectral measurements.

REFERENCES

1. Comanita, E., Soldea, C., Dumitrescu, E.: *Chimia si tehnologia pesticidelor* (*Chemistry and Technology of Pesticides* – in Romanian), Ed. Tehnica, Bucuresti, **1986**, 30-150;
2. Dinoiu, V., Caproiu, M.: Reactions of benzylhydrazine derivatives with carbonyl compounds, *Revista de Chimie*, **2004**, **55**(4), 240-243;
3. Botez, Gh., Tutoveanu, M., Comanita, E.: Sulfanidele acizilor fenoxiacetici, *Bul. IPI*, **1962**, Tom **VIII**(**XII**), Fasc. 3-4;
4. Oniscu, C., Dumitrascu, A., Cascaval, D., Radu, I.: Synthesis of some hydrazides derived from sulphonamidated aryloxyalkylcarboxylic acids, *Roum. Biotechnol. Lett*, **1997**, **2**(5), 373-378;
5. Dumitrascu, A.: *Studies on synthesis of new sulphamoyl-R-phenoxyacetic acids derivatives having potential biological activity,* Doctoral thesis, Technical University "Gh. Asachi" Iaşi, **1998**, 70-180;
6. Mocanu, A., Dumitrascu, A., Cernatescu, C.: Hydrazone derivatives of pyperazino-sulphonyl and pyperydinosulphonyl-phenoxyacetylhydrazides, *The 12th ICIT International Conference, Progress in Cryogenics and Isotopes Separation, Section 3 Science and Materials Engineering*, 25-27 oct., Ramnicu Valcea, **2006**, 80-82.