ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2010, *55*(2), 117-122

MICROWAVE-ASSISTED SYNTHESIS OF AROMATIC BIS-ESTERS IN LIQUID PHASE

Gheorghiţă N. ZBANCIOC,[a] Ana Maria V. ZBANCIOC[b] and Ionel I. MANGALAGIU[a*]

[a] "Al. I. Cuza" University of Iaşi, Faculty of Chemistry, Organic Chemistry Department, Bd. Carol I 11, 700506 Iaşi, Roumania
[b] "Gr.T.Popa" University of Iaşi, Faculty of Farmacy, Str. Universitatii 16, 700115 Iaşi, Roumania

Received June 11, 2009

A fast, general, environmentally friendly, and facile method for preparation of phenyl bis-esters under microwave irradiation in liquid phase is presented. Selective reaction pathways in order to get phenyl bis-esters only or phenyl monoesters only have been found. The microwave enhanced remarkably the rate of esterification, the reaction time decreasing dramatically, the reaction conditions were milder, the consumed energy decreased considerably and the amount of used solvents was reduced substantially. Consequently, the microwave-assisted esterification reaction could be considered eco-friendly. In the most cases, under MW irradiation the yields were higher than those in ordinary conditions, in some cases substantially (at least 75%). A feasible explanation for the MW efficiency is presented, ionic conduction mechanism having the higher contribution. A comparative study, microwave-conventional conditions was done.

INTRODUCTION

During the last decades microwave (MW) irradiation has became an increasingly valuable tool in organic chemistry, since it offers a versatile and facile pathway in a large variety of syntheses.[1-7] Thus, a large number of organic reactions can be carried out under MW irradiation in higher yields, shorter reaction time and milder conditions. Furthermore, reactions under MW have the great advantage of using small amounts of or no organic solvents ('solvent free'), thus such reactions are more environmentally friendly and generate less side products. Among these reactions, esterification[1-6] pays enough attention, especially in the case of fatty acids. However, under classical heating, esterification reaction of aromatic diols with chloroacyl chloride was extremely poorly studied, only in the case of benzene 1,2-diol with 2-chloroethanoyl chloride.[8] Moreover, under MW irradiation these reactions were not studied at all. In a preliminary communication we reported the synthesis and biological activity of such compounds in benzene.[9]

The aim of this work was to develop a efficient, general and eco-friendly method for preparation of phenyl bis-esters using MW irradiation in liquid phase and to bring contribution to the elucidation of the mechanism of MW action.

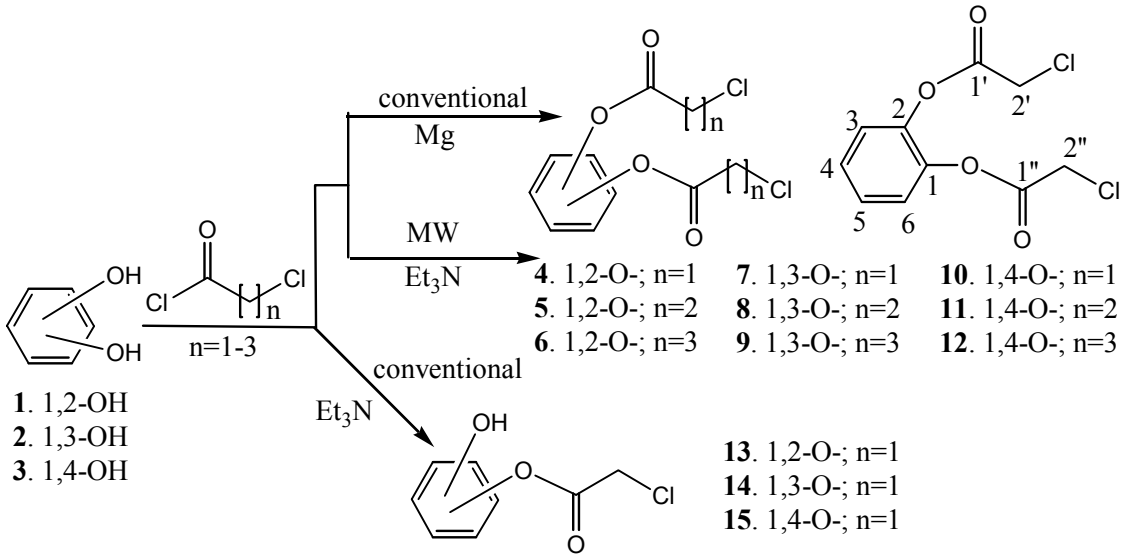
RESULTS AND DISCUSSION

In order to obtain the phenyl bis-esters bearing alkylating groups, we perform the esterification reaction of benzene diols (1,2-; 1,3- and 1,4-) with chloroacyl chloride (2-chloroethanoyl chloride, 3-chloropropanoyl chloride, 4-chlorobutanoyl chloride), under both conventional heating and MW irradiation (Scheme 1).

Under conventional heating, the reactions have some major disadvantages: long reaction time (15-56 h), high energy consumption, variable yields (from 15% to 85%), great amounts of solvents, etc. Moreover, phenyl bis-esters **4–12** could be obtained only when we use magnesium as a catalyst, which is another inconvenient (when we used triethylamine, we got phenyl monoesters **13-15** only, no mater the conditions employed). This is why we decided to use

* Corresponding author: Tel.: +40 232 201343; fax: +40 232 201313. E-mail address: ionelm@uaic.ro

nonconventional methods (*i.e.*, microwave technology). The MW assisted reactions were carried out using a monomod reactor, a constant irradiation power and varying the temperature. Table 1 lists the optimized conditions we employed under MW irradiation, as well as under conventional heating.



Scheme 1 – Reaction pathways used to obtain aromatic bis- and mono- esters.

Table 1

Syntheses of phenyl bis-esters under MW and conventional heating conditions, in liquid phase

Compound	Microwaves						Conventional	
	Reaction time, min.	Yield, % (benzene)	Yield, % (acetone)	Yield, % (toluene)	Reaction time, min.	Yield, % (toluene)	Reaction time, hours	Yield, % (toluene)
4 (1,2-OH)	5	96	54	93	15	89	17	72
5 (1,2-OH)	5	67	64	67	15	56	56	74
6 (1,2-OH)	5	95	93	96	15	88	28	85
7 (1,3-OH)	5	94	61	91	15	87	30	50
8 (1,3-OH)	5	60	57	60	15	49	53	78
9 (1,3-OH)	5	97	92	97	15	86	15	83
10 (1,4-OH)	5	90	58	90	15	79	55	18
11 (1,4-OH)	5	45	29	48	15	36	58	75
12 (1,4-OH)	5	85	86	87	15	72	45	55

Figure 1 presents the temperature variation under MW irradiation (in toluene) in the case of compounds **6** and **12**, as being representative for the series.

Analysing the data from table and graphics, the following important conclusions can be advanced:
MW induced a remarkable acceleration of reactions, the reaction time decreasing dramatically, from hours to minutes (5 min.). Consequently, the consumed energy decreases considerably. Moreover, the amount of used solvents is five times less (see experimental), these type of reactions being considered as environmentally friendly;

Under MW irradiation the reaction became highly selective, only phenyl bis-esters **4**–**12** being obtained. In the most cases, under MW irradiation the yields are higher, in some cases substantially (at least 75%);

During a cycle, the temperature rises up from the room temperature closely to the boiling point of solvents, then remain almost constant no matter the time were used [initially we used for MW heating different time (30, 15, 10, 5 min.), but the best results were obtained at 5 min.]. Moreover, time increasing has no beneficial effect, the yields being lower [in Table 1 are presented the yields on 5 and 15 min., and in Figure 1, up, the graphics for 5 and 15 min. in the case of compound **12**, in order to allow comparison]. The most reasonable explanation for this behaviour of compounds **4-12** could be the beginning of their decomposition when exposed for longer time to MW;

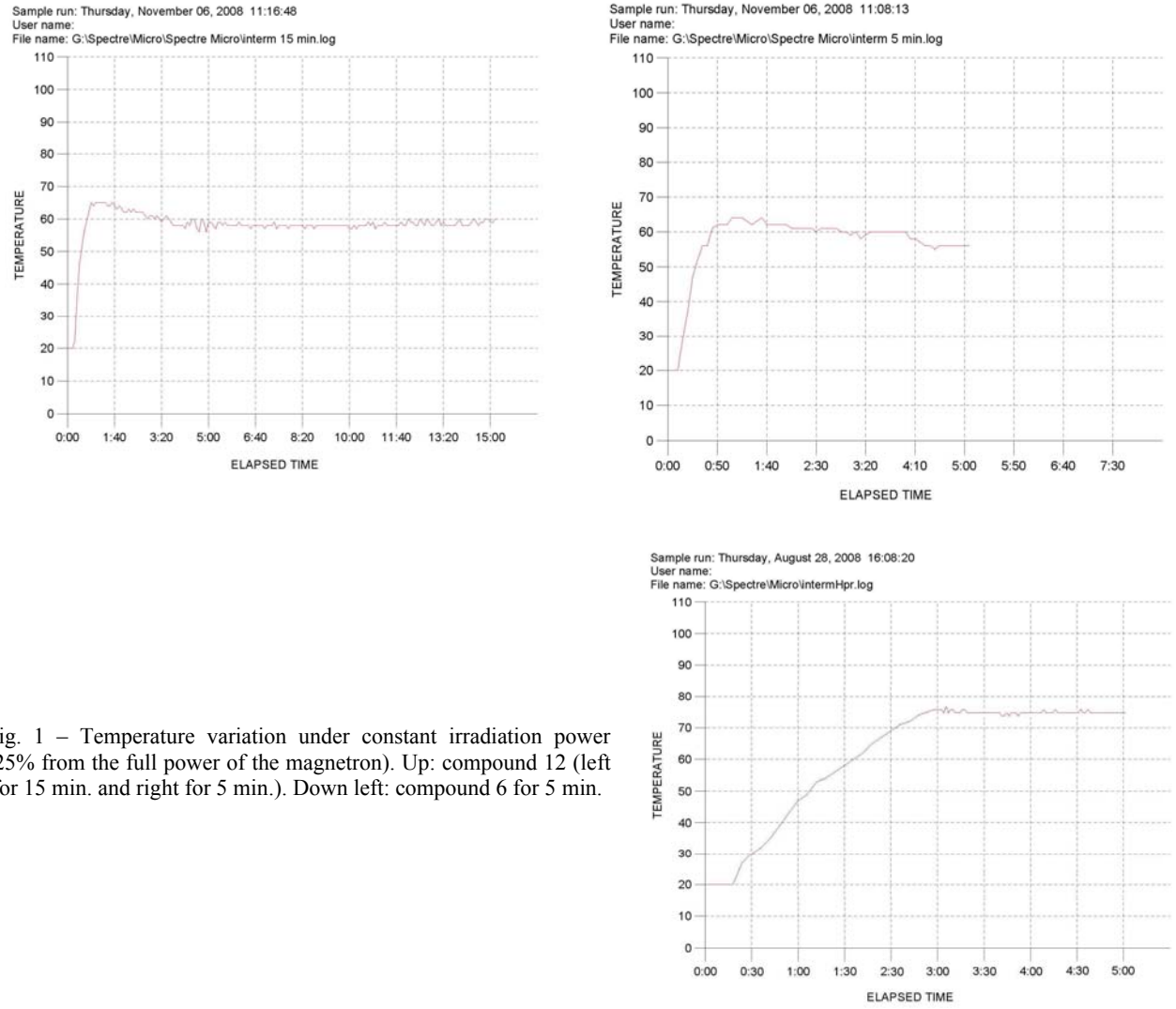


Fig. 1 – Temperature variation under constant irradiation power (25% from the full power of the magnetron). Up: compound 12 (left for 15 min. and right for 5 min.). Down left: compound 6 for 5 min.

Under MW irradiation and conventional heating, there is a difference of reactivity for benzene diols: benzene-1,4-diol is less reactive than benzene-1,2- and 1,3- diols. This is proved under conventional heating by the shorter reaction time for the last two diols and, under MW irradiation by the appearance of curves: while for the esterification of benzene-1,2-diol and 1,3-diols there could be notice a powerful exothermic effect during a period of about 150 seconds (down right, Fig. 1), in the case of 1,4-diol the same effect are over a much shorter period, about 30 seconds (up right, Fig. 1). This could be inferred to the ionic conduction mechanism for MW (dipolar polarization mechanism is less probable because the dipole moment of 1,4-diol is zero and for 1,2- and 1,3-diols it is small).

There is also a certain difference of reactivity for chloroacyl chloride in the esterification reaction: under conventional heating, the reaction time for 3-chloropropanoyl chloride is quite double comparative with 2-chloroethanoyl chloride and 4-chlorobutanoyl chloride, proving that the last two are more reactive. These difference of reactivity is also confirmed under MW irradiation, where we may notice that the yields are lower in the case of 3-chloropropanoyl chloride. The most feasible explanation for this behaviour could be related to the reaction mechanism. The reactions occur by a tetrahedral mechanism and in the ionic intermediate formed after the nucleophilic attack of triethylamine, the dipole moment is smaller in the case of intermediate derived from 3-chloropropanoyl chloride (even number of carbon atoms) comparative with intermediate derived from 2-chloroethanoyl chloride and 4-chlorobutanoyl chloride (odd number of carbon atoms). Consequently, under MW irradiation the dipolar polarization mechanism

will have a smaller contribution in speeding up the reaction for chloroacyl chloride with even number of carbon atoms.

The structure of compounds was checked by elemental (C, H, N) and spectral analysis (IR, ^{1}H NMR, ^{13}C NMR, 2D-COSY, 2D-HETCOR (HMQC), long range 2D-HETCOR (HMBC). All the elemental and spectral data are in accordance with the proposed structure and are presented in the experimental part.

EXPERIMENTAL

All the reagents and solvents employed were of the best grade available and were used without further purification. Melting points were determined using an electrothermal apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra ($CDCl_3$), and two-dimensional experiments 2D-COSY, 2D-HETCOR (HMQC), long range 2D-HETCOR (HMBC) were recorded on a Bruker Avance 400 DRX spectrometer operating at 400 MHz (^{1}H) and 100 MHz (^{13}C). Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. The IR spectra were recorded in KBr on a FT-IR Shimadzu Prestige 8400s spectrophotometer.

General procedure for syntheses of aromatic bis-esters under conventional heating

To 10 mmoles of benzene diols and 10 mmoles (2.43 g) of magnesium curlings in 50 mL of anhydrous benzene, chloroacyl chloride (22 mmoles, in 30 mL anhydrous benzene) is added dropwise in one hour under stirring and refluxing the mixture. The stirring and reflux were continued for a period of 15 to 58 hours (according with the reagents nature, Table 1). The excess of magnesium was filtered off, the resulted oil was poured into water and the precipitate formed filtered. The product was crystallized from an appropriate solvent. When the oil doesn't precipitate in water, first it was separated by flash chromatography then crystallized.

General procedure for syntheses of aromatic monoesters under conventional heating

To 10 mmoles of benzene diols and 24 mmoles (24.24 g) triethylamine in 50 mL of methylene chloride, chloroacyl chloride (22 mmoles) is added dropwise in one hour under stirring and refluxing the mixture. The reaction mixture is stirred and refluxed for a period of 60 hours, the obtained monoester were filtered off and washed two times with 10 mL of used solvent. No other purification is required.

General procedure for syntheses of aromatic bis-esters under MW irradiation

MW assisted reactions were carried out using a monomod reactor (STAR-2, CEM corporation, USA). The best results were obtained using a constant irradiation power (25% from the full power of the magnetron, 800 W) and varying the temperature (the so-called "power control").

Ten mmoles of benzene diols and 24 mmoles (24.24 g) of triethylamine in 10 mL of anhydrous benzene were placed in the reaction vessel (Pyrex glass or quartz). Chloroacyl chloride (22 mmoles) is added dropwise in 3-5 minutes. The tube are then placed in the microwave cell and heated for the appropriate time. Once the heating cycle is complete and tube was cooled to ambient temperature, the tube was removed and the triethylamine chlorohydrate was filtered off. The resulted oil was poured into water and the precipitate formed filtered. The product was crystallized from an appropriate solvent. When the oil doesn't precipitate in water, first it was separated by flash chromatography then crystallized.

Chloroacetic acid, 1,2-phenylene ester (4). Obtained from pyrocatechol, as white crystals, m.p. 54-56ºC. Calc. for $C_{10}H_8Cl_2O_4$ (263): C 45.66, H 3.07; found: C 45.58, H 3.00. **IR** (KBr, cm^{-1}): 3016 (C-H arom.), 2975 (C-H aliph.), 1782, 1751 (C=O est.), 1601, 1515, 1491, 1416 (C=C), 1248, 1128 (C-O-C), 814, 761 (C-Cl). **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 4.33 (s, 4H: $H_{2'}$, $H_{2''}$), 7.24–7.27 [m, 2H (overlaped peaks): H_4, H_5], 7.30–7.33 [m, 2H (overlaped peaks): H_3, H_6]. **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 43.77 ($C_{2'}$, $C_{2''}$), 123.45 (C_3, C_6), 126.83 (C_4, C_5), 141.88 (C_1, C_2), 169.01 ($C_{1'}$, $C_{1''}$: C=O).

3-Chloropropionic acid, 1,2-phenylene ester (5). Obtained from pyrocatechol, as white-yellow crystals, m.p. 45-47ºC. Calc. for $C_{12}H_{12}Cl_2O_4$ (291): C 49.51, H 4.15; found: C 49.57, H 4.12. **IR** (KBr, cm^{-1}): 3080 (C-H arom.), 2976 (C-H aliph, 1763 (C=O est.), 1496, 1438, 1419, 1404 (C=C), 1244, 1232, 1139, 1124 (C-O-C), 760 (C-Cl). **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 3.03 (t, *J*= 6.0, 4H: $H_{2'}$, $H_{2''}$), 3.83 (t, *J*= 6.0, 4H: $H_{3'}$, $H_{3''}$), 7.19–7.22 [m, 2H (overlaped peaks): H_4, H_5], 7.26–7.28 [m, 2H (overlaped peaks): H_3, H_6]. **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 37.41 ($C_{2'}$, $C_{2''}$), 38.82 ($C_{3'}$, $C_{3''}$), 123.47 (C_3, C_6), 126.95 (C_4, C_5), 141.77 (C_1, C_2), 167.82 ($C_{1'}$, $C_{1''}$: C=O).

4-Chlorobutyric acid, 1,2-phenylene ester (6). Obtained from pyrocatechol, as white-grey crystals, m.p. 41-42ºC. Calc. for $C_{14}H_{16}Cl_2O_4$ (319): C 52.68, H 5.05; found: C 52.74, H 5.01. **IR** (KBr, cm^{-1}): 3071 (C-H arom.), 2964 (C-H aliph.), 1757 (C=O est.), 1592, 1547, 1491, 1409 (C=C), 1240, 1207, 1128, 1113 (C-O-C), 763 (C-Cl). **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.16–2.23 (m, 4H: $H_{3'}$, $H_{3''}$), 2.77 (t, *J*= 7.2, 4H: $H_{2'}$, $H_{2''}$), 3.68 (t, *J*= 6.4, 4H: $H_{4'}$, $H_{4''}$), 7.18–7.20 [m, 2H (overlaped peaks): H_4, H_5], 7.25–7.27 [m, 2H (overlaped peaks): H_3, H_6]. **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 27.42 ($C_{3'}$, $C_{3''}$), 30.81 ($C_{2'}$, $C_{2''}$), 43.79 ($C_{4'}$, $C_{4''}$), 123.44 (C_3, C_6), 126.69 (C_4, C_5), 141.94 (C_1, C_2), 170.11 ($C_{1'}$, $C_{1''}$: C=O).

Chloroacetic acid, 1,3-phenylene ester (7). Obtained from resorcine, as redish crystals, m.p. 66-68ºC. Calc. for $C_{10}H_8Cl_2O_4$ (263): C 45.66, H 3.07; found: C 45.57, H 3.02. **IR** (KBr, cm^{-1}): 3090 (C-H arom.), 2954 (C-H aliph.), 1766, (C=O est.), 1593, 1544, 1481, 1406 (C=C), 1234, 1182, 1141 (C-O-C), 785 (C-Cl). **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 4.28 (s, 4H: $H_{2'}$, $H_{2''}$), 7.02 (s, 1H: H_2), 7.07 (d, *J*= 8.4, 2H: H_4, H_6), 7.41 (t, *J*= 8.4, 1H: H_5). **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 40.78 ($C_{2'}$, $C_{2''}$), 114.77 (C_2), 119.18 (C_4, C_6), 130.13 (C_5), 150.71 (C_1, C_3), 165.47 ($C_{1'}$, $C_{1''}$: C=O).

3-Chloropropionic acid, 1,3-phenylene ester (8). Obtained from resorcine, as yellow oil. Calc. for $C_{12}H_{12}Cl_2O_4$ (291): C 49.51, H 4.15; found: C 49.51, H 4.11. **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.97 (t, *J*= 6.8, 4H: $H_{2'}$, $H_{2''}$), 3.77 (t, *J*= 6.8, 4H: $H_{3'}$, $H_{3''}$), 6.99 (s, 1H: H_2), 7.03 (d, *J*= 8.4, 2H: H_4, H_6), 7.38 (t, *J*= 8.4, 1H: H_5). **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 36.68 ($C_{2'}$, $C_{2''}$), 38.23 ($C_{3'}$, $C_{3''}$), 113.74 (C_2), 119.05 (C_4, C_6), 129.38 (C_5) 150.74 (C_1, C_3), 169.33 ($C_{1'}$, $C_{1''}$: C=O).

4-Chlorobutyric acid, 1,3-phenylene ester (9). Obtained from resorcine, as yellow oil. Calc. for $C_{14}H_{16}Cl_2O_4$ (319): C 52.68, H 5.05; found: C 52.72, H 5.02. **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.15–2.22 (m, 4H: $H_{3'}$, $H_{3''}$), 2.75 (t, *J*= 6.4, 4H:

$H_{2'}$, $H_{2''}$), 3.67 (t, *J*= 7.6, 4H: $H_{4'}$, $H_{4''}$), 6.92 (s, 1H: H_2), 6.98 (dd, *J*= 8.0, 2H: H_4, H_6), 7.36 (t, *J*= 8.0, 1H: H_5). **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 27.22 ($C_{3'}$, $C_{3''}$), 31.18 ($C_{2'}$, $C_{2''}$), 43.81 ($C_{4'}$, $C_{4''}$), 115.27 (C_2), 118.89 (C_4, C_6), 129.68 (C_5), 150.91 (C_1, C_3), 170.73 ($C_{1'}$, $C_{1''}$: C=O).

Chloroacetic acid, 1,4-phenylene ester (10). Obtained from hydroquinone, as white crystals, m.p. 122-123ºC. Calc. for $C_{10}H_8Cl_2O_4$ (263): C 45.66, H 3.07; found: C 45.71, H 3.01. **IR** (KBr, cm^{-1}): 3003 (C-H arom.), 2953 (C-H aliph.), 1770, 1761 (C=O est.), 1506, 1409, 1311 (C=C), 1188, 1232, 1146 (C-O-C), 736 (C-Cl). **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 4.30 (s, 4H: $H_{2'}$, $H_{2''}$), 7.17 (s, 4H: H_2, H_3, H_5, H_6). **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 40.98 ($C_{2'}$, $C_{2''}$), 122.45 (C_2, C_3, C_5, C_6), 148.20 (C_1, C_4), 165.39 ($C_{1'}$, $C_{1''}$: C=O).

3-Chloropropionic acid, 1,4-phenylene ester (11). This compound was obtained from hydroquinone, as white crystals, m.p. 88-90ºC. Calc. for $C_{12}H_{12}Cl_2O_4$ (291): C 49.51, H 4.15; found: C 49.59, H 4.10. **IR** (KBr, cm^{-1}): 3080 (C-H arom.), 2976 (C-H aliph.), 1753 (C=O est.), 1503, 1437, 1410, 1378 (C=C), 1176, 1141 (C-O-C), 767 (C-Cl). **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 3.04 (t, *J*= 6.8, 4H: $H_{2'}$, $H_{2''}$), 3.86 (t, *J*= 6.8, 4H: $H_{3'}$, $H_{3''}$), 7.13 (s, 4H: H_2, H_3, H_5, H_6). **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 37.77 ($C_{2'}$, $C_{2''}$), 38.99 ($C_{3'}$, $C_{3''}$), 122.60 (C_2, C_3, C_5, C_6), 148.12 (C_1, C_4), 168.93 ($C_{1'}$, $C_{1''}$: C=O).

4-Chlorobutyric acid, 1,4-phenylene ester (12). Obtained from hydroquinone, as white crystals, m.p. 48-50ºC. Calc. for $C_{14}H_{16}Cl_2O_4$ (319): C 52.68, H 5.05; found: C 52.64, H 5.00. **IR** (KBr, cm^{-1}): 3076 (C-H arom.), 2952 (C-H aliph.), 1755, 1745 (C=O est.), 1508, 1440, 1423, 1380 (C=C), 1219, 1194, 1162, 1140 (C-O-C), 786 (C-Cl). **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.17–2.23 (m, 4H: $H_{3'}$, $H_{3''}$), 2.76 (t, *J*= 7.2, 4H: $H_{2'}$, $H_{2''}$), 3.67 (t, *J*= 6.4, 4H: $H_{4'}$, $H_{4''}$), 7.10 (s, 4H: H_2, H_3, H_5, H_6). **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 27.44 ($C_{3'}$, $C_{3''}$), 31.23 ($C_{2'}$, $C_{2''}$), 43.88 ($C_{4'}$, $C_{4''}$), 122.35 (C_2, C_3, C_5, C_6), 147.95 (C_1, C_4), 171.06 ($C_{1'}$, $C_{1''}$: C=O).

Chloroacetic acid, 2-hydroxy-phenyl ester (13). This compound was obtained from pyrocatechol, as white crystals, m.p. 132-134ºC. Calc. for $C_8H_7ClO_3$ (186): C 51.50, H 3.78; found: C 51.39, H 3.70. **IR** (KBr, cm^{-1}): 3430 (O-H), 3076 (C-H arom.), 2971 (C-H aliph.), 1734 (C=O est.), 1598, 1506, 1467, 1400 (C=C), 1251, 1126 (C-O-C), 741 (C-Cl). **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 4.64 (s, 2H: CH_2), 6.08 (s, 1H: OH), 6.69–6.72 (m, 1H: H_5), 6.79–6.84 [m, 3H (overlaped peaks): H_3, H_4, H_6]. **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 65.63 ($C_{2'}$, CH_2), 114.39 (C_6), 116.06 (C_4), 119.11 (C_3), 121.93 (C_5), 146.08 (C_2), 146.87 (C_1), 170.62 ($C_{1'}$, C=O).

Chloroacetic acid, 3-hydroxy-phenyl ester (14). This compound was obtained from resorcine, as white crystals, m.p. 121-123ºC. Calc. for $C_8H_7ClO_3$ (186): C 51.50, H 3.78; found: C 51.37, H 3.68. **IR** (KBr, cm^{-1}): 3447 (O-H), 3056 (C-H arom.), 2969 (C-H aliph.), 1747 (C=O est.), 1599, 1506, 1443, 1402 (C=C), 1251, 1162 (C-O-C), 811 (C-Cl). **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 4.29 (s, 2H: CH_2), 5.11 (s, 1H: OH), 6.61–6.67 [m, 3H (overlaped peaks): H_2, H_4, H_6], 6.97–6.99 [m, 1H: H_5]. **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 46.64 ($C_{2'}$, CH_2), 110.06 (C_2), 112.24 (C_6), 115.32 (C_4), 128.72 (C_5), 151.86 (C_3), 156.12 (C_1), 167.16 ($C_{1'}$, C=O).

Chloro-acetic acid, 4-hydroxy-phenyl ester (15). This compound was obtained from hydroquinone, as white crystals, m.p. 107-109ºC. Calc. for $C_8H_7ClO_3$ (186): C 51.50, H 3.78; found: C 51.44, H 3.72. **IR** (KBr, cm^{-1}): 3464 (O-H), 3051 (C-H arom.), 2966 (C-H aliph.), 1752 (C=O est.), 1598, 1509, 1445, 1400 (C=C), 1252, 1167 (C-O-C), 814 (C-Cl). **^{1}H-NMR** ($CDCl_3$, δ, ppm, J, Hz): 4.28 (s, 2H: CH_2), 5.14 (s, 1H: OH), 6.80 (dd, *J*= 6.8, 2H: H_3, H_5), 6.97 (dd, *J*= 6.8, 2H: H_2, H_6). **^{13}C-NMR** (TMS, $CDCl_3$, δ, ppm): 40.87 ($C_{2'}$, CH_2), 116.12 (C_3, C_5), 122.09 (C_2, C_6), 143.79 (C_1), 153.79 (C_4), 166.52 ($C_{1'}$, C=O).

CONCLUSIONS

A fast, general, environmentally friendly, and facile method for preparation of phenyl bis-esters under microwave irradiation in liquid phase is presented. Selective reaction pathways in order to get phenyl bis-esters only (using Et_3N under MW irradiation or Mg under conventional heating) or phenyl monoesters only (using Et_3N, conventional heating) have been found. The microwave enhances remarkably the esterification rate, the reaction time decreasing dramatically, the reaction conditions are milder, the consumed energy decreases considerably and the amount of used solvents is reduced substantially. Consequently, the microwave assisted esterification reaction could be considered eco-friendly. In the most cases, under MW irradiation the yields are higher, in some cases substantially (at least 75 percents). A certain difference of reactivity of benzenediols and chloroacyl chloride in the esterification reaction was observed. A feasible explanation for the MW efficiency is presented, ionic conduction mechanism having the higher contribution but the dipolar polarisation mechanism could not be neglected. A comparative study, microwave-conventional conditions (liquid solvents) was done.

Acknowledgements: This work was financially supported by the Roumanian Ministry of Education and Research, grant C.N.C.S.I.S. cod 88 under PN-II-ID-PCE-2008 Program.

REFERENCES

1. A. Loupy, " Microwaves in Organic Synthesis", Wiley-VCH, Weinheim, 2006.
2. C. O. Kappe and A. Stadler, "Microwaves in Organic and Medicinal Chemistry", Wiley-VCH, Weinheim, 2005.
3. J. T. Tierney and P. Lindström, "Microwave assisted Organic Synthesis", Blackwell, Oxford 2005.
4. a) B. Bacsa, K. Horváti, S. Bősze, F. Andreae and C. O. Kappe, *J. Org. Chem*., **2008**, *73*, 7532-7542; b) J. M. Kremsner, A. Stadler and C. O. Kappe, *Top. Curr. Chem*., **2006**, *266*, 233-278.
5. C. Villa, S. Baldassari, R. Gambaro, E. Mariani and A. Loupy, *Int. J. Cosmetic Sci.*, **2005**, *27*, 11-16.
6. P. Lidström, J. Tierney, B. Wathey and J. Westman, *Tetrahedron*, **2001**, *57*, 9225-9283.
7. a) R. Butnariu and I. I. Mangalagiu, *Bioorgan. Med. Chem.*, **2009**, *17*, 2823-2829; b) Gh. Zbancioc and I. I. Mangalagiu, *Synlett*, **2006**, 804-806; c) Gh. Zbancioc, M. Caprosu, C. Moldoveanu and I.I. Mangalagiu, *Rev. Roum. Chim*.,

2005, *50*, 353-358; d) St. Dima, I. I. Mangalagiu, M. Caprosu, M. Georgescu and M. Petrovanu, *Rev. Roum. Chim*., **2000**, *45*, 555-560.
8. J. L. Verelst, J. F. Willemas and R. L. Florens, *Eur. Pat. Appl.*, 1231194, 1971.
9. A. M. Balan, Gh. Zbancioc, E. Bentea, I. Carja, M. Ungureanu, C. Tuchiluș and I. I. Mangalagiu, *Rev. Chim. (Bucharest)*, **2009**, *60*, 1021-1024.