

## A NOVEL SYNTHETIC PATHWAY FOR OBTAINING AROMATIC CARBOXYLIC ESTERS STARTING FROM DIARYL OXALATES

Constantin I. CHIRIAC,\* Fulga TANASĂ and Marioara NECHIFOR

Institute of Macromolecular Chemistry “Petru Poni”, Aleea Grigore Ghica Voda 41 A, Iasi 700487, Roumania

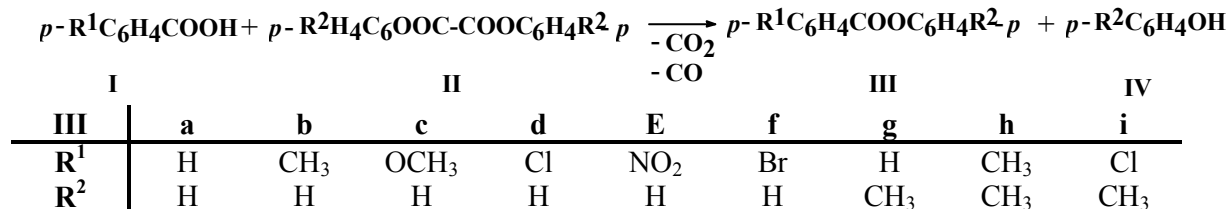
Received August 3, 2006

Aromatic carboxylic esters have been prepared in 83-96% yields by a new synthesis from aromatic carboxylic acids and diaryl oxalates, in pyridine as solvent and in the presence of 4-dimethylaminopyridine (DMAP) and imidazol as bases, at 30-60°C, for 8-12 hours. Using these reagents, namely diaryl oxalates, obtaining aromatic carboxylic esters at low temperatures and in high yields became possible.

Aromatic carboxylic esters can be prepared from aromatic carboxylic acids and diaryl carbonates,<sup>1</sup> diaryl sulfides<sup>2</sup> or triaryl phosphites.<sup>3</sup> We already reported on some of our latest investigations concerning direct condensation reactions.<sup>4</sup>

We have now found that direct synthesis of aromatic carboxylic esters is also possible using diaryl oxalates, which the novelty of this communication resides in.

By stepwise investigation, we established that aromatic carboxylic acids **I** can react with diaryl oxalates **II**, in the mole ratio 1:1, resulting in aromatic carboxylic esters **III** and phenols **IV**, CO<sub>2</sub> and CO, as by-products, as presented in Scheme 1.



Scheme 1

This synthesis has high yields in basic medium. In order to fulfill this requirement and based on experimental data, we used a combination of 4-DMAP and imidazole in the molar ratio 1:2, which resulted in a suitable basic medium for this reaction.

Our experimental results showed that without a suitable solvent this reaction is difficult to perform. Therefore, we have tested many solvents such as: dimethylsulfoxide (DMSO), dimethylformamide (DMF), N-methyl-pyrrolidin-2-one (NMP), hexamethylphosphortriamide (HMPTA), pyridine and we selected pyridine because of its convenient behaviour under the conditions of this synthesis.

The reaction evolves at moderate temperatures, depending on the structure of the reagents, as follows: at 30-60°C for aromatic carboxylic acids with withdrawing substituents, and at 30-40°C for donating substituents ones, during 8-12 h (see Table 1). As example, the compound **IIIe** was obtained in 83% yield when the reaction was conducted at 50-60°C, but the yield decreased to 40-43% when the reaction was performed at 30-35°C, under the same conditions.

\* Corresponding author: cchiriac@icmpp.ro

Table 1  
Aromatic carboxylic esters obtained with diaryl oxalates

Aromatic esters <sup>a</sup>	Yield <sup>b</sup> (%)	React. time (h)	Temperature (°C)	M. p. <sup>c</sup> (°C)	Lit. m. p. (°C)
III a	89	9	30-40	70-71	70-71 <sup>5</sup>
III b	96	8	30-35	74-76	75-76 <sup>6</sup>
III c	93	9	30-35	72-74	73-74 <sup>6</sup>
III d	85	10	50-60	103-105	104-105 <sup>6</sup>
III e	83	12	50-60	126-128	127-128 <sup>7</sup>
III f	87	11	50-60	116-117	116-117 <sup>2</sup>
III g	92	9	30-40	69-71	70-71 <sup>8</sup>
III h	95	8	30-40	90-91	90-91 <sup>6</sup>
III i	88	10	50-60	88-90	89-90 <sup>8</sup>

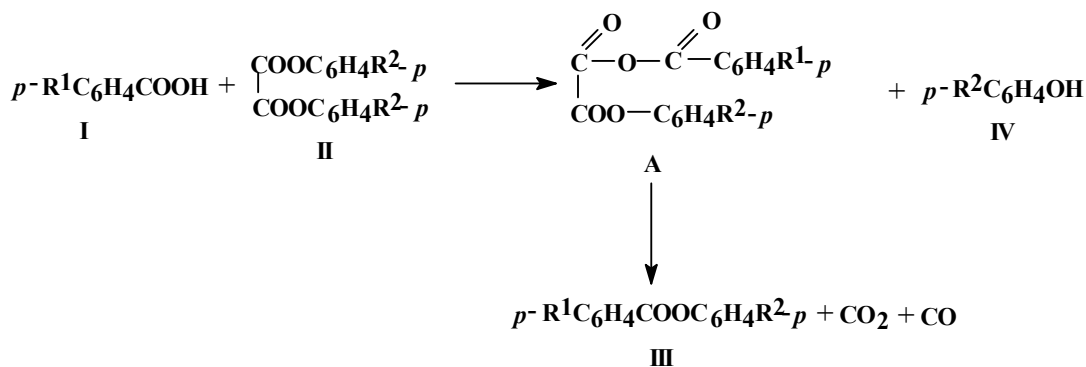
<sup>a</sup> The aromatic carboxylic esters obtained were identified by comparison of their m. p. and IR spectra with authentic samples.

<sup>b</sup> Yields calculated based on the aromatic carboxylic acids **I** employed.

<sup>c</sup> After recrystallization.

As can be seen in Table 1, we obtained aromatic carboxylic esters **III** in yields which ranged from 83 to 96%, depending on the reaction conditions and structure of the aromatic carboxylic acids. Due to the structure of the aromatic carboxylic acid **Ie** (which has a substituent with a strong withdrawing behaviour), the corresponding ester **IIIe** was obtained in the lowest yield. Aromatic esters with electron donating groups were obtained in high yields.

We suppose that, similar to other cases,<sup>1,2</sup> this reaction involves a unstable reaction intermediary A (Scheme 2), which is a mixed anhydride, resulting in aromatic esters **III** and phenols **IV**, CO<sub>2</sub> and CO as by-products.



Scheme 2

The detailed mechanism of this new interesting reaction will be discussed in a separate communication.

In conclusion, we have found a novel synthetic pathway for obtaining aromatic esters in high yields, using diaryl oxalates as a new reagent, in basic medium and at moderate temperatures. This procedure enables a convenient approach to prepare aromatic esters which are appealing intermediates for synthesis of other condensates (amides, hydrazides, etc.).

## EXPERIMENTAL

General procedure for the synthesis of aromatic esters – In a 100 mL three-necked Claisen flask, fitted with a mechanical stirrer and a condenser, 0.01 mole aromatic carboxylic acid **I**, 0.01 mole diaryl oxalate **II** (prepared from anhydrous oxalic acid and phenol<sup>9</sup>), 0.02 mole imidazole, 0.01 mole 4-DMAP and 4 mL pyridine were added. The solution obtained was stirred at 30-60°C, for 2-12 h (see Table 1), when CO<sub>2</sub> and CO as by-products resulted. At the end of the reaction, the final solution was treated with 70-80 mL water and ice and then with 20% NaOH solution, up to pH=9-10, when the aromatic ester **III** precipitates and phenol **IV** is solubilized in water as sodium salt. Rapidly, the cooled solution is filtered and the final product **III** was washed three times with 15-20 mL cold water and then dried. Yields ranged from 83-96% (see Table 1).

## REFERENCES

1. (a) T. Wieland, *Ann. Chem.*, **1962**, 655, 189; (b) C. I., Chiriac; M., Onciu, M., Tibirna, F., Tanasa, I., Truscan, R., Ropot, *Rev. Roum. Chim.*, **1998**, 43(11), 1065; (c) F., Tanasa, M., Onciu, C. I., Chiriac, *Rev. Roum. Chim.*, **2003**, 48 (11), 869.
2. B., Iselin, *Helv. Chim. Acta*, **1957**, XL, 376.
3. L., Lorentz, *Angew. Chem.*, **1965**, 77, 1031.
4. (a) C. I., Chiriac, F., Tanasa, M., Onciu, *Tetrahedron Lett.*, **2003**, 44, 3579; (b) C. I., Chiriac, F., Tanasa, M., Onciu, *Des. Monom. Polym.*, **2004**, 7(4), 331; (c) C. I., Chiriac, F., Tanasa, M., Onciu, *Molecules*, **2005**, 10, 481.
5. I., Furukawa, *Bull. Chem. Soc. Jpn.*, **1981**, 54, 2227.
6. H., Reinbolt, *Quimica*, **1951**, 3, 52; *CA*, **1952**, 46, 7552 o.
7. J. H., Brewster, *J. Amer. Chem. Soc.*, **1955**, 77, 6215.
8. J. F., Kirsch, *J. Org. Chem.*, **1968**, 33, 128.
9. J., Adickes, *J. Pract. Chem.*, **1931**, 130, 163.