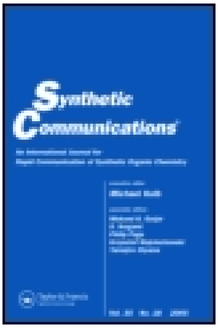


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Ethanol Initiates Reactions Using Microwaves. A Technique for Aromatic Ester Synthesis

G. Brattulescu [a], Y. Le Bigot [a] & M. Delmas [a]

[a] Institut National Polytechnique de Toulouse, Ecole Nationale Supérieure de Chimie de Toulouse, Laboratoire de Catalyse, Chimie Fine et Polymères, 118 route de Narbonne, 31077, Toulouse cedex 4, France

To cite this article: G. Brattulescu , Y. Le Bigot & M. Delmas (2000) Ethanol Initiates Reactions Using Microwaves. A Technique for Aromatic Ester Synthesis, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:1, 171-176, DOI: 10.1080/00397910008087305

To link to this article: http://dx.doi.org/10.1080/00397910008087305

SYNTHETIC COMMUNICATIONS, 30(1), 171–176 (2000)

ETHANOL INITIATES REACTIONS USING MICROWAVES. A TECHNIQUE FOR AROMATIC ESTER SYNTHESIS

G. Brătulescu, Y. Le Bigot*, M. Delmas

Institut National Polytechnique de Toulouse, Ecole Nationale Supérieure de
Chimie de Toulouse, Laboratoire de Catalyse, Chimie Fine et Polymères, 118
route de Narbonne, 31077 Toulouse cedex 4 France

Abstract : Orthophthalic monoesters were synthesized through a reaction between phthalic anhydride and potassium phenoxides. Synthesis was performed by irradiating pastes containing organic reagents and a small quantity of ethanol.

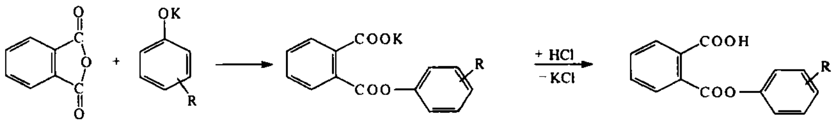
Microwaves have already been used to synthesize some esters, e.g. esters from condensation of an aromatic organic acid with aliphatic alcohol, using the following techniques: esterification of an aromatic organic acid by an alcohol(1-3), condensation between an aromatic carboxylate anion and a halogenated derivative(4-5) and transesterification(3).

Direct esterification of phenols with aliphatic or aromatic carboxylic acids is impossible(7). A reaction can be induced indirectly in phenols either in the form of phenolate or with pyridine on acid chlorides or anhydrides (Schotten-Baumann reaction)(7-8). However, this only works with aliphatic acid derivatives(7-9).

---

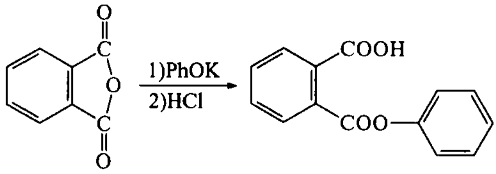
*To whom the correspondence should be addressed.

We recently designed an innovative approach for aromatic azoether (10) and aromatic ether synthesis(11) using microwaves. This approach requires neither solvent, nor specific absorbant medium of microwaves. The reagents' chemical structure, particularly their polarity, makes it possible to perform syntheses in solid media. This technique was used to esterify phthalic anhydride with potassium phenolates using microwaves. The role of the solid absorbant which creates hot spots in the reaction medium surprisingly was played by a small quantity of ethanol. Ethyl alcohol was used both to homogenize the reaction medium paste and to initiate a chemical reaction generating hot spots comparable to catalytic centers in the reaction medium. Any ethanol which did not react with phthalic anhydride evaporated during the reaction due to increased temperature which allowed the organic reagents to react. The following diagram illustrates the syntheses:



Initial salt was transformed into carboxylic acid by adding hydrochloric acid. Potassium phenolates were formed through an acid-base interaction between some phenols and potassium hydroxide. Solid potassium phenolates were obtained after water evaporation.

Experimental conditions were defined during 2-(phenoxycarbonyl) benzoic acid synthesis through a reaction between phthalic anhydride and potassium phenolate:



The experimental procedure can be summarized as follows: a highly concentrated phthalic anhydride solution was obtained after dissolving in a small quantity of ethanol under heat. Solid potassium phenolate was added to this solution. The resulting paste was irradiated in an open beaker in a standard microwave oven for the time indicated in Table 1. Medium temperature was noted after each radiation.

TABLE 1: 2-(Phenoxycarbonyl) benzoic acid synthesis

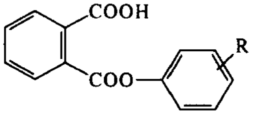
Time[s]	20	30	35	40	50	60
Temperature[°C]	50	87	123	130	145	150
Yield[%]	4	29	56	78	10	7

8 mmol phthalic anhydride, 8 mmol potassium phenolate, 5 mL 95% ethanol.

Maximum ester yield as shown in Table 1 was obtained after 40 seconds. Increased radiation time severely decreased yield. This can be explained by ester decomposition in the reaction medium due to increased temperature. This decomposition was demonstrated by the high amount of residue obtained during purification of 2-(phenoxycarbonyl) benzoic acid.

Higher yields were also obtained during orthophthalic acid monoester synthesis after a 40-seconds irradiation time. Yield values and final temperatures in the reaction medium strongly depend on type of phenolates used (see Table 2). The highest yield (90%) was obtained during 2-[4-(phenylazo)phenoxycarbonyl)] benzoic acid synthesis.

TABLE 2: Orthophthalic monoester synthesis using microwaves.



Nr	R	Compound	Elementary analysis $\frac{\text{calculated}}{\text{found}}$		Yield [%](T)	$T_f(T_l)$[°C]	Bands IR [cm^{-1}]
			%C	%H			
1	H	$C_{14}H_{10}O_4$	69.42 69.40	4.13 4.01	78(130)	103(103°)	ν_{OH}:3410m ν_{CO}:1710vs ν_{OAr}:1305s 1158s
2	2-CH_3	$C_{15}H_{12}O_4$	70.31 69.95	4.68 4.57	35(91)	95-96	ν_{OH}:3426m ν_{CO}:1713vs ν_{OAr}:1295s 1175s
3	3-CH_3	$C_{15}H_{12}O_4$	70.31 70.21	4.68 4.53	47(115)	107-108	ν_{OH}:3400m ν_{CO}:1711vs ν_{OAr}:1305vs 1154s
4	4-CH_3	$C_{15}H_{12}O_4$	70.31 70.15	4.68 4.28	57(140)	111-112	ν_{OH}:3300m ν_{CO}:1714vs ν_{OAr}:1259s 1172m
5	4-NO_2	$C_{14}H_9NO_6$	58.53 58.42	3.13 3.12	28(210)	129-130	ν_{OH}:3367m ν_{CO}:1704vs ν_{OAr}:1289s 1168m ν_{NO2}:1516s 1337s
6	2-C_6H_5	$C_{20}H_{14}O_4$	75.47 75.46	4.40 4.38	34(113)	92-93	ν_{OH}:3417m ν_{CO}:1710vs ν_{OAr}:1285s 1136m
7	2-(3-MeO)C_6H_5CO	$C_{22}H_{16}O_6$	70.21 70.11	4.25 4.30	33(104)	85-86	ν_{OH}:3001m ν_{CO}:1726vs $\nu_{OH}+\nu_{OMe}$: 1261vs 1164m
8	4-$C_6H_5N_2$	$C_{20}H_{14}N_2O_4$	69.36 69.35	4.04 4.01	90(112)	180-181	ν_{OH}:3097m ν_{CO}:1701m ν_{OAr}:1218s 1141s $\nu_{N=N}$: 1416m

8 mmol phthalic anhydride; 8 mmol potassium phenolate; 5 mL 95% EtOH; Irradiation time 40[s]; IR: m-medium, s-strong, vs-very strong; T_f- fusion temperature, T_l- reference fusion temperature, T[°C]- temperature after irradiation

Despite the modest yield obtained in these aromatic ester syntheses, this method for obtaining aromatic monoesters of orthophthalic acid using microwaves has several advantages: no absorbant medium, easy experimental set-up, quick product separation and purification, less than 1 minute irradiation times.

EXPERIMENTAL SECTION

All reagents were purchased from FLUKA.

IR/FT spectra were recorded on KBr pellets using a Perkin-Elmer 1600 spectrometer.

Elementary analyses were performed with a Carlo Erba model 1106 apparatus.

Fusion points were measured using a Tottoli apparatus.

A Bauknecht microwave oven was used: emission power=650W, λ=12.2 cm.

Temperatures after irradiation were measured used a HANNA model HI 8757 thermocouple thermometer.

Experimental Procedure

5 mL of water, 8 mmol of potassium hydroxide and 8 mmol of phenol were placed in a beaker. The suspension was agitated until it formed a solution. Solid potassium phenolate was obtained after vacuum evaporation of the water. 8 mmol of phthalic anhydride were dissolved in 5 mL of 95% ethanol in another beaker. The solid potassium phenolate was then added to the phthalic anhydride solution. Potassium phenolate dissolved rapidly and formed a paste. This paste was then irradiated in an open beaker in a microwave oven for the indicated time. The mixture obtained after reaction was dissolved by adding 5 mL of water and 0.5

mL of concentrated hydrochloric acid was added to this solution. 15 mL of chloroform were introduced to extract the reaction product. Chloroform was then evaporated and the resulting product was purified by recrystallization from toluene and dried.

REFERENCES

1) - Gedye, R.N.; Smith, F.E. and Westaway, K.C., *Can.J.Chem.*,**1988**,*66(1)*,17

2) -Majetich,G. and Hicks, R.J.,*Microwave Power Electromag.Energy*,**1995**,*30*,27

3) - Loupy, A.; Petit, A.; Ramdani, M.; Yvanaeff, C.; Majdoub, M.; Labiad, B. and Villemin, D., *Can.J.Chem.*, **1993**,*71(1)*,90

4) - Gutierrez, E.; Loupy, A.; Bram, G. and Ruiz-Hitzky, E., *Tetrahedron Lett.*, **1989**,*30(8)*,945

5) - Loupy, A.; Petit, A.; Hamelin, J.; Texier-Boullet, F.; Jacquault, P. and Mathé, D., *Synthesis*, **1998**,1213

6) - Bischoff, C. and Hendenstron, A., *Ber.*,**1902**,*35*,4092

7) - Beyer, H. and Walter, W., "*Handbook of organic chemistry*",Prentice Hall Europe, London-Munich,**1996**,p.497

8) - Vollhardt, K.P.C. and Schore, N.E., "*Organic chemistry*",2th,W.H.Freeman and company,New York, **1994**,p.880

9) - Hocking, M.B., *J.Chem.Educ.*,**1980**,*57*,527

10) - Bratulescu, G.; Le Bigot, Y and Delmas,M., *Synth.Commun.*, **1997**,*27(6)*,1037

11) - Bratulescu, G.; Le Bigot, Y.; Delmas, M. and Pogany, I., *Revue.Roum.Chim.*, **1998**,*43(4)*,321

(Received in the USA 29 May 1999)