Contribution of microwaves in organic synthesis: statement of a methodology for the microwave-induced preparation of benzofuran-2(3*H*)-one and its comparison with classical heating

Paulo Goncalo,[a] Christophe Roussel,[b] Jean Marie Mélot*[a] and Joel Vébrel[a]

[a] *IUT Département Chimie, 30, Avenue de l'Observatoire, B.P. 1559, 25009 Besançon Cedex, France*
[b] *Laboratoire de Chimie et Electrochimie Moléculaire, Route de Gray, 25030 Besançon, France*

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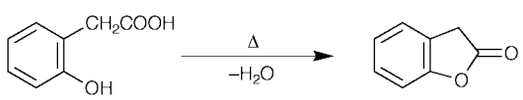
The intramolecular cyclisation of 2-hydroxyphenylacetic acid **1** into coumaran-2-one **2** was studied under both microwave irradiation and classical heating for comparison purposes. The use of a monomode oven allowed an accurate consideration of the temperature distribution in the microwave reaction vessel, which revealed a very strong and unexpected thermal heterogeneity. The reaction was facilitated by the presence of a trace of toluene-*p*-sulfonic acid, the catalytic role of which is demonstrated.

Introduction

Numerous papers dealing with the applications of microwave technology in organic synthesis have been published since the original works of Gedye[1] and Giguere.[2] Chemists now commonly use microwave heating in order to accelerate thermal reactions or to control the kinetics of such syntheses. Bose and co-workers have run their reactions with domestic microwave ovens and introduced the terminology of "MORE" chemistry;[3] the hypothesis of hot local temperatures would explain the increase in reaction kinetics.[3,4] The weak microwave absorption of most organic chemicals was circumvented by the use of solid supports (montmorillonite,[5] alumina,[6] potassium fluoride on alumina[7,8] or silica[9,10]), which strongly absorbed hyperfrequency beams but *also* acted as catalysts. As a consequence of their double properties, it was difficult to state the specific role of the hyperfrequency beam in such applications.[11–13] Moreover, the use of domestic microwave ovens was impeded by possible heterogeneity of the magnetic field, sometimes inducing insufficiently reproducible results.

On the other hand, the utilisation of monomode systems led the microwave beam to be focused on the sample and the application of these ovens should be favoured in spite of being more expensive. However, an accurate comparison between microwave and classical heating could not be established without any temperature control.[14–17] For this reason, the most recent works were performed using infrared pyrometry[18] or optical fluorescence (thermometers fitted with fiber optic cables);[19] the first technique gave the *surface* temperature of the reaction mixture, whereas the second one allowed the estimation of *local* temperatures. However, it was still not possible to distinguish between purely thermal[20] or non-thermal[21] effects of microwaves. The generalisation of partial conclusions[22] remained very difficult without establishing *all* experimental parameters which would allow fully reproducible experiments, *e.g.* microwave frequency, power of the magnetron, type and materials of the reactors, *real* temperatures. We have therefore undertaken to establish a procedure taking all the parameters that could influence microwave-assisted syntheses into account. Our study was performed on a typical reaction, the thermal intramolecular cyclisation of 2-hydroxyphenylacetic acid **1** into coumaran-2-one **2**† (Scheme 1). At the end of our work, which included a comparison with classical heating, we could unambiguously ascertain whether hyperfrequencies had any thermal or non-thermal effect on this synthesis.



1 **2**

Scheme 1

Results and discussion

For other projects,[23,24] we needed abundant amounts of the lactone **2**, whose usual preparation consisted of heating **1** in rather drastic conditions with subsequent distillation. The yields were moderate, the overall described procedure very tedious and benzofuran-2(3*H*)-one **2** was obtained in its two allotropic forms.[25] Other methods giving very poor yields of **2** are also given in the literature.[26,27] The cyclisation of 2-hydroxyphenylacetic acid **1**, being a purely thermal reaction, was susceptible to activation by microwave irradiation.

Reaction in a multimode oven: preliminary results

Domestic microwave ovens did not allow the temperature to be linked to the power of the magnetron, and consequently any control of it was impossible. However, some studies have been carried out in such an apparatus in order to determine the behaviour of the acid **1** under microwave heating. A solvent was not used because of potentially dangerous effects in non-modified ovens. Impregnation of **1** on montmorillonite led to irreversible adsorption of most materials and, anyway, the use of a solid support should be excluded to avoid any interference between catalytic effects and distinctive microwave properties.[28] Direct irradiation of **1** was therefore undertaken; nevertheless, no dehydration was observed owing to the very weak microwave absorption by the acid. The reaction vessel was consequently immersed in an alumina bath. The isolated yield reached 40% with difficulty after 6 min and fell dramatically upon prolonged irradiation. Surprisingly, the addition to **1** of *ca.* 2 mol% of toluene-*p*-sulfonic acid (PTSA) gave coumaran-2-one **2** in an

† Coumaran is 2,3-dihydro-1-benzofuran.

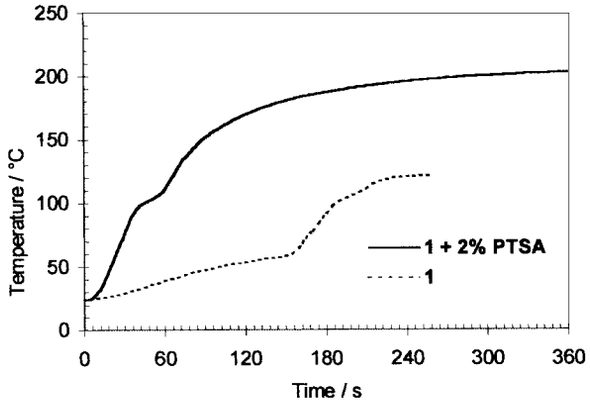


Fig. 1 Temperature profiles in a monomode oven at 300 W.

isolated reproducible yield of 85% after 6 min of irradiation at 450 W. In all cases, a final temperature of 165 °C was measured in the alumina bath. A similar experiment was carried out by classical heating in an oil bath at 165 °C, following rigorous identical conditions; the isolated yield of **2** did not exceed 35%. This comparison, however, posed one main question: the temperature of the reaction medium under direct microwave heating was not measurable and was certainly different from the temperature of the alumina bath; therefore, were temperatures of the oil bath in classical heating and the one reached by hyperfrequency irradiation rigorously the same? The insufficiency of multimode cavities in the field of temperature evaluation led us to use a monomode oven, in which this crucial parameter could be set and measured by infrared pyrometry.

Reaction in a monomode oven: comparison with classical heating

Measurement of temperatures by an infrared pyrometer. We performed all experiments in borosilicate glass rather than in quartz vessels; indeed, this latter did not absorb microwaves (inside temperature gradient of $+0.02\ °C\ s^{-1}$), and the rise in temperature of the acid **1** was induced by its own *very low* absorption only. Even with borosilicate glass vessels, the melting point of **1** (152 °C) was never reached and no dehydration occurred. The addition of minor amounts of PTSA led to the melting of **1** within 3.5 min of irradiation. We thought at first that the mixture of 2-hydroxyphenylacetic **1** and PTSA absorbed the hyperfrequency beam to a greater extent than **1** alone; however, this hypothesis alone was insufficient, following the study of the thermal behaviour of both **1** and **1** + PTSA by the use of differential scanning calorimetry (DSC). A better absorption was admittedly noticed even in the solid state (Fig. 1); indeed, the respective temperature gradients were of $+0.25\ °C\ s^{-1}$ for **1** alone and $+2\ °C\ s^{-1}$ for **1** + PTSA. More interestingly, the melting point of **1** not only decreased in the presence of PTSA (112 °C instead of 152 °C), but the formation of the lactone also occurred at a dramatically lower temperature (Fig. 2). The yield of isolated coumaran-2-one **2**, which was reproducible, reached 85 ± 1% at 200 ± 3 °C after 6 min of irradiation at 300 W.

This result was compared with the one obtained by classical heating under similar conditions. The reactor type, the reaction temperature and time and the percentage of added PTSA were of course identical; but it was also crucial that internal temperature profiles during heating were as similar as possible in both processes because of the brevity of the reaction. Since we noticed that no dehydration occurred below 130 °C, we have only taken temperatures higher than this into account. The two temperature profiles—classical and microwave heating—were almost superimposable when an oil bath regulated at 210 °C was used. Under these conditions, after a heating period of 6 min, the isolated yield of **2** did not exceed 65%. Moreover,

Table 1 Synthesis of coumaran-2-one; comparative study

	Isolated yield (%)	
Reaction time/min [a]	Classical heating [b]	Microwave [c]
1.5	7	9
3	17	43
4.5	39	72
6	63 ± 1	85 ± 1

[a] Classical heating: immersion time; microwave monomode oven: irradiation time. [b] Oil bath at 210 °C. [c] 300 W.

Table 2 Temperature distribution in the reactor after 240 s of irradiation (monomode oven)

Entry [a]	*x*/mm [b]	*y*/mm [c]	*T*/°C [d]
a	0	0	259
b	0	1.5	256
c	0	3	262
d	3	0	245
e	3	3	265
f	6	0	275
g	6	3	290

[a] Height of liquid = 5 mm. [b] Horizontal co-ordinate from the axis of the reactor. [c] Vertical co-ordinate from the bottom of the reactor. [d] Measured by optical fluorescence.

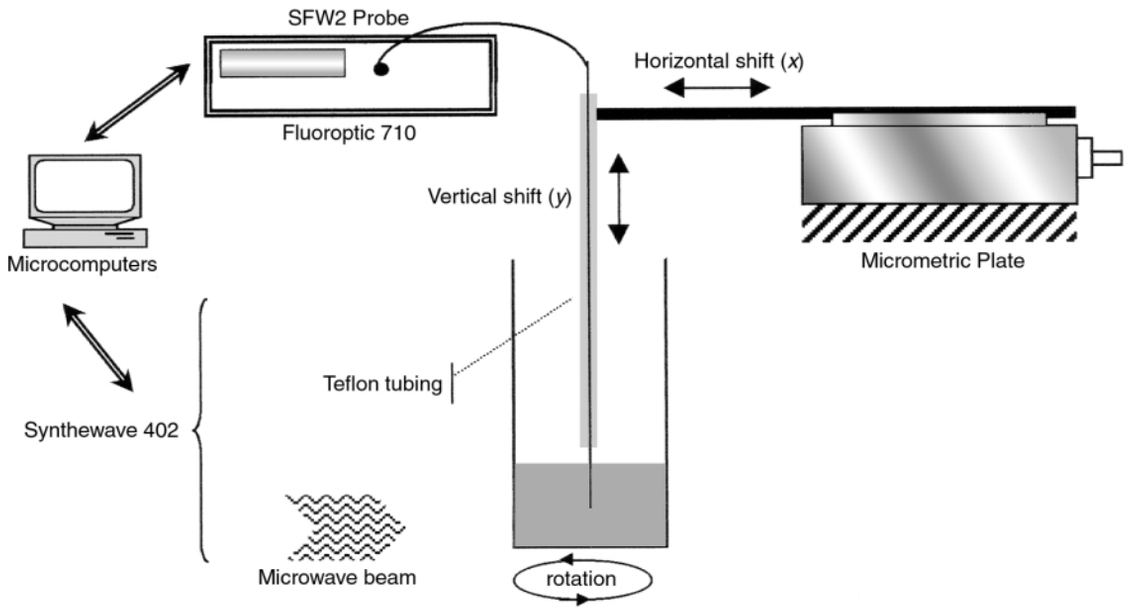
Table 1 indicates that the cyclisation was far more rapid by microwave irradiation.

These results should be qualified: since the temperature measured in the microwave oven was the *surface* and not the *internal* one, the comparison was only valid if we assumed that only a slight heterogeneity of temperatures in the irradiated reagents occurred and that the infrared pyrometer gave a correct average temperature of the reaction mixture with little typical variance. In order to confirm or invalidate our suppositions, it appeared consequently necessary to measure the temperatures within the reagents themselves.

Measurement of temperatures by means of optical fluorescence. In order to realise a valid comparative study with conventional heating, we have measured the distribution of temperatures in the reactor by means of a micrometric plate (Scheme 2). Amazingly, a temperature as high as 255 °C was reached in the centre of the reactor after 4 min at 300 W (Table 2, a–c) and a value of 290 °C was measured near the inner vertical walls of the vessel (Table 2, g). The previous comparisons between microwave and classical heating were therefore invalidated. Indeed, the results were very different from the simple expected convex curve (maximal temperature in the centre of the vessel). This extreme heterogeneity was a characteristic of microwave heating; in classical heating, temperatures tended to homogenise very quickly.

Then, for comparison purposes, which temperature should we apply to the oil bath? We decided to carry out the reaction at the lowest previously observed temperature *i.e.* 245 °C ± 3 °C (Table 2, d). Under these conditions, **2** was isolated either by classical or microwave heating with the same yield of 85% (±2%).

When all was said and done, there was no *real* microwave effect during the synthesis of coumaran-2-one **2**. The fundamental phenomenon generated by the irradiation was the achievement of local temperatures considerably higher than the ones set by the regulator and the strong consecutive heterogeneity of this essential physical parameter. We had observed a *purely thermal* effect. We noticed not only quite different values (40 °C for a gap of 2–3 mm in the irradiated liquid), but also an unexpected distribution of them. We should hence emphasise



Scheme 2 Measurement of local temperatures by optical fluorescence in a monomode oven: synoptic view.

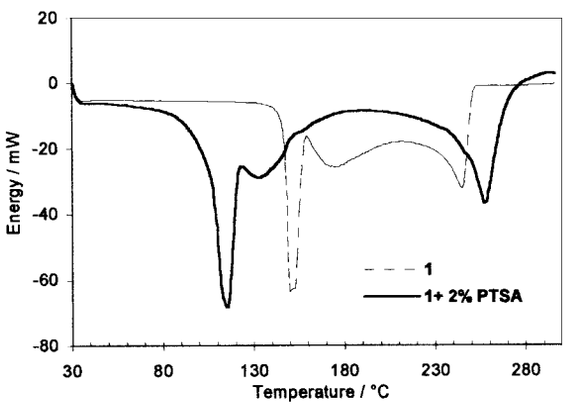


Fig. 2 DSC curves of 2-hydroxyphenylacetic acid (Φ = 10 K min^{-1}).

that all parameters should be taken into account before any valid comparison can be made, and in particular, the control and measurement of temperatures and the use of identical reactors (form, thickness, materials) should be considered.

The role of toluene-*p*-sulfonic acid: thermodynamic and spectroscopic studies

The mixture of **1** and PTSA showed thermal behaviour quite different from **1** alone (Fig. 2). We thought at first that the decrease in melting point might be due to the possible formation of a mixed compound exhibiting a eutectic point. However, differential scanning calorimetry (DSC) analyses of different mixtures of **1** + PTSA (from 1 to 5 mol% of PTSA) were identical and exhibited the same melting point of 112 ± 1 °C.

We first examined whether there were any noticeable differences in activation energies when the cyclisation of **1** was carried out in the presence or absence of PTSA. This determination was possible from DSC curves recorded with different heating rates, since they all displayed an endothermic peak corresponding to the cyclisation process.[29–31] The kinetics being of first order, the general equation linking "x" to "E" was given by eqn. (1), where x was the molar fraction of **1** reacted, E the

$$\frac{dx}{dt} = A \times (1 - x) \times e^{-\frac{E}{RT}} \quad (1)$$

activation energy and A the frequency factor. When the reaction rate was at a maximum, its derivative with respect to time was zero. The maximum value of dx/dt was reached for a temperature T_m defined by eqn. (2). The value of T_m corresponded

$$A \times e^{-\frac{E}{RT_m}} = \frac{E}{RT_m^2} \times \frac{dT}{dt} \quad (2)$$

to the maximum of the thermal peak in DSC.[32] Considering the heating rate $\Phi = dT/dt$ in the DSC oven, eqn. (2) became eqn. (3)

$$\frac{d\left(\ln\frac{\Phi}{T_m^2}\right)}{d\left(\frac{1}{T_m}\right)} = -\left(\frac{E}{R}\right) \quad (3)$$

or eqn. (4). Ploting "lnΦ" against "1/T_m" gave the activation

$$\frac{d(\ln\Phi)}{d\left(\frac{1}{T_m}\right)} = -\left(\frac{E}{R} + 2T_m\right) \quad (4)$$

energy E. Results are summarised in Table 3. We have found for the dehydration of **1** alone and **1** + 2% PTSA eqns. (5) and (6),

$$\ln\Phi = -1.23 \times 10^{-4} \times \left(\frac{1}{T_m}\right) + 29.8 \qquad E_1 = 99 \text{ kJ mol}^{-1} \quad (5)$$

$$\ln\Phi = -0.75 \times 10^{-4} \times \left(\frac{1}{T_m}\right) + 21.3 \qquad E_2 = 63 \text{ kJ mol}^{-1} \quad (6)$$

Table 3 Cyclisation of 2-hydroxyphenylacetic acid **1**; determination of the activation energy by DSC

Φ, Heating rate/ °C min^{-1}	T_m for **1** alone/°C	T_m for **1** + 2% PTSA/°C
2	150.9	102.1
4	158.8	106.7
6	165	107.6
8	169.6	111.2
10	176.1	132.6
20	—	138.2
30	—	147.8

respectively. Thus, PTSA significantly lowered the activation energy for the dehydration of **1** and behaved like a catalyst for this reaction.

Spectroscopic studies of **1** and **1** + PTSA were then undertaken in order to examine the exact function of the catalyst. However, investigations were neither satisfactory nor clear enough, probably because of the lack of sensitivity of the spectrometric tools. The infrared spectra of the mixture of 2-hydroxyphenylacetic acid **1** with 2% of PTSA (KBr dispersion or attenuated total reflection IR spectra) showed two O–H vibrations and, particularly, a broadened intense band around 3200 cm^{-1}; the corresponding band appeared very much sharper and weaker in the spectrum of the acid alone. In all cases, the carbonyl band was located at 1700 ± 3 cm^{-1}, thus excluding any participation of this function in hydrogen bonding. We have noticed that the difference between the previously calculated activation energies E_1 and E_2 was close to a value typical of a hydrogen bond involving a carboxylic acid function (25–35 kJ mol^{-1}).[33] We suggest that such an interaction was favoured where PTSA was present. Proton and ^{13}C NMR spectra, recorded in DMSO, were entirely similar for **1** and its admixture with PTSA. The strong polar character of this solvent should destroy any hydrogen bond. The formation of some mixed anhydride between **1** and PTSA *upon heating* could be conceived—but not proven—thus favouring the subsequent lactonisation.

Conclusion

The intramolecular cyclisation of 2-hydroxyphenylacetic acid **1** occurred quickly when promoted by microwave irradiation in the presence of catalytic amounts of toluene-*p*-sulfonic acid; the latter permitted a greater absorption of the hyperfrequency beam and lowered the activation energy of the cyclisation. The strict correlation between microwave and classical heating did not yield any improvement of the reaction kinetics as previously suggested. First studies in multimode or monomode ovens have led to erroneous hypotheses because of either the absence of, or inaccuracies in, the measurement of temperatures in the reaction vessel. The hyperfrequency beam generated a strong heterogeneity in temperatures; this was its *distinctive* property and this thermal effect led to hot local temperatures different from those fixed by the regulator.

We have now established a methodology for this microwave-assisted synthesis, which could be generally applied and is summarised below.

The reactions should be performed whenever possible without any solvent—for safety reasons—or mineral support, reagents being in the molten state; providing that the reaction is accompanied by any thermal event, preliminary DSC studies give useful information concerning the thermal behaviour of all molecules and the suitable working temperature. The behaviour of reagents under microwave heating furnishes other practical information: for instance, the strength of the absorption of the hyperfrequency beam by the sample and the profile of its temperature rise are determined. The heterogeneity and the average temperature of the reaction medium are also carefully estimated. A valuable comparison with classical heating can be carried out if necessary.

Since the contribution of irradiation was negligible for the synthesis of coumaran-2-one **2**, how should we carry out the cyclisation of **1** in practice? The use of the monomode oven compared with classical heating was nevertheless attractive and safe: the rapid reaction time of 6 min included the rise in temperature, the latter taking at least thirty minutes with a final dangerously hot oil bath. From an economical point of view, the expenditure of energy was estimated to be 108 kJ under microwave—whole process—and 540 kJ by classical heating—magnetic stirrer at 1500 W; this latter value excluded the pre-heating required to reach the temperature of the reaction, which was estimated to be at least 3000 kJ.

Experimental

General

Melting points were taken using a Dr Tottoli apparatus and were uncorrected. The FT-IR spectra were recorded on a Bruker Spectrospin IFS 45 spectrophotometer, the products being examined in a KBr suspension. The attenuated total reflection (ATR) IR spectra were obtained from a Bruker Spectrospin IFS 66 TF with a mixed salt as a highly reflecting crystal (thallium bromide–thallium iodide, KRS5–45°). The ^1H and ^{13}C NMR spectra were run on a Bruker Spectrospin AC200 spectrometer at 200.13 MHz (^1H) and 50.32 MHz (^{13}C). Samples were dissolved in $CDCl_3$ or CD_3–SO–CD_3 with 0.1% TMS as internal reference. The ^{13}C NMR spectra were obtained from proton-noise decoupled spectra. Chemical shifts are in ppm on the δ scale.

Ovens

A domestic microwave oven from Philips-Whirlpool (Ref. 5964, 2450 MHz) was used for all syntheses carried out in multimode cavities. The power was set from 100 to 800 W. The monomode system was purchased from Prolabo (Synthewave 402™, $\nu = 2450$ MHz, $0 \leq P \leq 300$ W) and coupled together with a microcomputer. The temperature of the reagents was measured by infrared pyrometry and the power of the magnetron was automatically controlled to maintain the set temperature with a proportional integral corrector. Uniform irradiation of reagents was obtained by the regular and automatic rotation of the reaction vessel. The reactors (quartz or borosilicate glass) had the following dimensions: inside diameter: 15 mm; glass thickness: 1.2 mm; maximum content: 10 cm^3.

Differential scanning calorimetry

A DSC apparatus according to Hemminger[34] was available from Mettler and included: 1) a Mettler DSC 20™ cell fitted with a ceramic probe of medium sensitivity and a thermoelectric battery of 14 gold–nickel thermocouples; 2) a TA 4000 microprocessor (version 6.3), which gave access to the specific heats of samples; 3) a Graphware TA 72 computer for acquisition, memorising and processing of experimental data; 4) a precision balance Mettler AT 621™. The characteristics of the DSC system were as follows: temperature scale: 0–600 °C; measurement between −60 and +60 mW; temperature accuracy: ±0.2 °C; dynamic working with a temperature gradient $0 < \Phi < 100$ °C min^{-1}.

Measurements

Differential thermal analyses (DTA) were performed with 10.0 mg of substance between 30 °C and 300 °C, with a heating rate of 10 °C min^{-1}. The activation energies of the cyclisation were obtained from DSC curves from 10.0 mg of **1**, or **1** + 2 mol% PTSA, and with different temperature gradients Φ ($2 \leq \Phi \leq 30$ °C min^{-1}). Temperatures within reagents during microwave irradiation were attainable by an optical fluorescence thermometer (Luxtron Fluoroptic 710™, temperature scale: −200/+450 °C); the characteristics during experiments were as follows: calibration temperature T_C at 200 °C; temperature accuracy of 0.5 °C at $T = T_C \pm 50$ °C and of 1 °C at $T = T_C \pm 100$ °C; response time of 250 ms; SFW2 probe of 1.5 mm diameter; thickness of the sensitive area: 0.125 mm. A synoptic view of the whole apparatus is given in Scheme 2. As a result of the reactor rotation, displacing the probe according to a half-plane going through the reactor centre was sufficient in order to achieve a three-dimensional representation of the temperatures.

General procedure for the preparation of coumaran-2-one 2 and comparative studies

All operations were repeated at least thrice to control the reproducibility of the cyclisation under each particular set of conditions. All yields were calculated by weighing the synthesised **2**.

Classical heating. 2-Hydroxyphenylacetic acid **1** (5g, 33 mmol) was ground alone or together with toluene-*p*-sulfonic acid monohydrate (0.125g, 0.66 mmol) and the solid mixture placed in the *microwave* reactor. The vessel was immersed in a preheated silicone oil bath for the appropriate time. After cooling to room temperature, saturated sodium hydrogen carbonate (2–5 cm^3) was added in order to neutralise any unreacted **1** and PTSA. The precipitated lactone was then filtered, washed with cold water (2 × 10 cm^3) and air-dried to afford **2** as a yellow solid. The lactone was quite pure as indicated by its melting point and ^1H NMR spectrum (see below).

Syntheses in a multimode oven. Chromatographic alumina (Merck 90, neutral, Art.1.01077.1000) was dehydrated under microwave heating (450 W) to constant weight and kept in a cool dry place (desiccator over activated silica gel). 2-Hydroxyphenylacetic acid **1** (5 g, 33 mmol)—alone or with PTSA monohydrate (0.125 g, 0.66 mmol)—was ground to a homogeneous powder and placed in the *microwave* vessel covered with a watch glass in order to minimise evaporation. The reactor was immersed in the alumina bath (100 g) and irradiated for the appropriate time. The bath temperature was measured *immediately* after irradiation with a thermocouple (range: −40/+1000 °C, accuracy: ±1 °C). After cooling, the contents of the vessel were worked up as above.

Syntheses in a monomode oven. The cyclisation was carried out as above from **1** and PTSA, the power of the magnetron being assigned as 300 W. The intimate mixture of 2-hydroxyphenylacetic acid **1** (0.76 g, 5 mmol) and PTSA monohydrate (19 mg, 0.1 mmol) gave **2** (0.57 g, 85% yield) after 6 min of microwave irradiation. Mp 49 °C (lit.,[35] 28.5 °C and 49 °C); ν_{max}/cm^{-1}: 1804 (C=O); δ_H (200 MHz, $CDCl_3$) 3.74 (s, 2H), 7.15–7.35 (m, 4H arom).

Spectroscopic analyses of 2-hydroxyphenylacetic acid 1

Infrared spectrophotometry. The acid **1** and its admixture with PTSA (2 mol%) exhibited the same characteristic O–H bands at 3375 and 3200 cm^{-1}; their relative intensities were approximately 2/1 and 1/1 respectively. The FT-IR and ATR spectra differed in the position of the carbonyl band, located respectively at 1700 and 1715 cm^{-1}.

Nuclear magnetic resonance spectroscopy of 1 and 1 + 2 mol% PTSA. $\delta_C(CD_3–SO–CD_3)$ 34.6 (*C*H_2), 114.3, 118.1, 121.1, 127.1, 130.2 (5 aromatic carbons), 154.7 (*C*-OH), 172.0 (*C*OOH).

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