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ORIGINAL ARTICLE

Microwave-assisted expeditious hydrolysis of isobenzofuranone derivatives using silica supported acid under organic solvent-free conditions

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Microwave irradiation

Abstract Silica sulfuric acid was found to be an efficient, reusable and environment-friendly catalyst for fast hydrolysis of various isobenzofuranone to corresponding 2-ketomethylquinoline derivatives in a high yield under solvent-free using microwave irradiation. As the activator of silica sulfuric acid the wet SiO_2 was chosen. The reactions in conventional conditions were compared with the microwave assisted reactions. This approach can prove beneficial since the recovery of solvents from conventional reaction systems always results in some losses.

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1. Introduction

The hydrolysis of carboxylic acid esters is one of the most studied chemical reactions (Varma et al., 1993). The reported ester hydrolysis could be catalyzed by acid, alkali (Theodorou et al., 2007), molecular iodine (Yadav et al., 2006), Zn(II) complexes Bazzicalupi et al., 2005, and Cu(II) complexes Kou et al., 2004.

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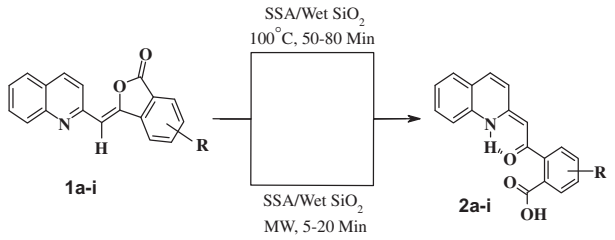
General acidic hydrolysis of the majority of common esters occurs in the presence of strong liquid protic acids such as HCl, TFA, H_2SO_4 (Strazzolini et al., 2005) and HNO_3 (Strazzolini et al., 2000), as catalysts dissolved in organic solvents. However, many of the above-mentioned liquid acid catalysts are corrosive and often cause heavy environmental pollution because of the difficult separation from the reaction medium. Furthermore, the reactions require long reaction times and often give unsatisfactory yields.

Over the past two decades, microwave-assisted procedures have been successfully employed in a number of synthetic transformations, resulting in rapid and efficient synthesis of different classes of organic compounds. In recent years, the use of solid supports under microwave irradiation has become more popular in synthetic organic chemistry (Varma, 1999; Gershonov et al., 2007) and heterogeneous reactions facilitated by supported reagents on various solid inorganic surfaces have



Scheme 1 Microwave-assisted hydrolysis of isobenzofuranone derivatives in presence of SSA/Wet SiO_2.

received more attention (Varma and Saini, 1997; Song and Lee, 2002; Bahulayan et al., 2002). In general, solid acid catalysts are mainly based on clay (Varma and Meshram, 1997; Varma et al., 1997) or montmorillonite (Bosch et al., 1995) and silica (Zolfigol et al., 2004, 2005).

In terms of convenience, silica-based catalysts are inexpensive, easy to prepare, and insoluble in most of the organic solvents, which means that they have the advantage of recovery and recycle from various reactions. Recently, silica sulfuric acid has been used as a solid acid catalyst in many reactions such as nitration of aromatic compounds (Riego et al., 1996), aldol condensation (Salehi et al., 2004), acetylization (Mirjalili et al., 2004; Varma et al., 1993), oxidation of alcohols and sulfides (Varma and Dahiya, 1997; Varma et al., 1997), reduction reaction (Varma and Sanini, 1997), desilylation reactions (Varma et al., 1993), direct etherification of trimethylsilylethers (Zolfigol et al., 2003) and so forth.

In continuation of our work on the synthesis of new isobenzofuranone derivatives (Safari et al., 2007), we decided to apply silica sulfuric acid with wet SiO_2 as the activator to hydrolysis of 3-[(E)-1-(2-quinolyl)methylidene]-1(3H)-isobenzofuranone derivatives under conventional heating conditions and using microwave irradiation (Scheme 1).

2. Experimental

2.1. Materials

Chemicals were purchased from the Merck Chemical Company in high purity. All of the materials were of commercial reagent grade. Silica sulfuric acid was prepared according to the reported procedure (Zolfigol et al., 2005).

2.2. Apparatus

Melting points were determined in open capillaries using an Electrothermal Mk3 apparatus. The reactions were carried out in a microwave oven (ETHOS 1600, Milestone) with a power of 600 W specially designed for organic synthesis, with continuous stirring. IR spectra were recorded using a Perkin-Elmer FT-IR 550 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer for sample as indicated with tetramethylsilane as internal reference. UV spectra were recorded on a Hitachi 200-20 spectrophotometer using spectrophotometric grade chloroform (Baker). MS spectra were recorded on a Finnigan MAT 44S, with an ionization voltage of 70 eV. The element analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyser carried out on Perkin-Elmer 240c analyzer, their results were found to be in good agreement (±0.2%) with the calculated values. Yields refer to isolated products.

2.3. General synthesis of isobenzofuranone derivatives

Isobenzofuranone (1a–i) were synthesized by the reaction of 2-methyquinoline (1.0 ml, 6.66 mmol), phthalic anhydride (1.0 g, 6.66 mmol) and acetic anhydride (1.5 ml). Mixture was stirred well. The whole mixture was irradiated by microwave oven (ETHOS 1600, Milestone) with a power of 600 W specially designed for organic synthesis as described in Safari et al. (2007).

2.4. Typical procedure for the hydrolysis of 3-[(E)-1-(2-quinolyl) methylidene]-1(3H)-isobenzofuranone (1a–i)

A mixture of substrate 1a–i (10 mmol; see Table 3 for substrates and stirring times) and silica sulfuric acid (0.1 g) was heated at 100 °C for 50–80 min or irradiated in a microwave oven (max. power 600 W, applied power up to 35%) for 5–20 min. The reaction was monitored by TLC using a 3:7 mixture of ethyl acetate–petroleum ether as an eluent. After completion of the reaction the mixture was cooled to room temperature and the solid materials residue was then washed with acetone and the solvent was evaporated to give the crude product. For further purification it was crystallized from 9:1 acetone–water mixture to afford pure product (2a–i, Table 3).

2.5. Spectral data for new products

2.5.1. 2-[2-(2(1H)quinolinylidene)acethyl]benzoic acid (2a, $C_{18}H_{13}NO_3$)

Yield: 88%, mp: 151–153 °C. IR (KBr, cm^{-1}): 3405, 1726, 1640, 1588, 1103 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 15.2 (s, 1H, NH enaminone form), 11.7 (s, 1H, OH carboxylic acid), 8.1 (d, 1H, ^3J = 9.2 Hz), 7.9 (d, 1H, ^3J = 9.2 Hz), 7.7–7.8 (m, 4H), 7.5–7.6 (m, 4H), 7.4 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.7 (C═O), 187.0 (C═O), 111.0 (C), 154.3 (CH), 138.5 (C), 138.3 (C), 132.9 (CH), 132.6 (CH), 132.2 (CH), 130.8 (CH), 129.8 (C), 129.3 (CH), 123.8 (CH), 121.0 (C), 120.4 (CH), 119.4 (CH), 117.5 (CH), 98.2 (CH) ppm. MS (70 eV) m/z = 291 ($M^{+\cdot}$, 100), 273, 217 (26), 143 (16), 170 (22), 143 (48), 76 (23). UV (EtOH): $\lambda_{max}(\varepsilon)$ = 413, 314, 233 nm. *Anal.* Calc. for $C_{18}H_{13}NO_3$: C, 74.22; H, 4.50; N, 4.81. Found: C, 74.11; H, 4.51; N, 4.83%.

2.5.2. 3-Nitro-2-[2-(2(1H)quinolinylidene)acethyl]benzoic acid (2b, $C_{18}H_{12}N_2O_5$)

Yield: 93%, mp: 165–167 °C. IR (KBr, cm^{-1}): 3409, 1728, 1643, 1535, 1330, 1108 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 15.4 (s, 1H, NH enaminone form), 11.8 (s, 1H, OH carboxylic acid), 8.7 (dd, 1H, ^3J = 8.6, ^4J = 2.0 Hz), 7.9 (d, 1H, ^3J = 9.2 Hz), 7.6–7.8 (m, 3H), 7.3–7.4 (m, 4H), 7.1 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.0 (C═O), 187.3 (C═O), 154.3 (C), 138.5 (C), 138.0 (CH), 132.6 (C), 132.2 (CH), 129.1 (C), 130.3 (CH), 129.4 (CH), 129.0 (CH), 123.4 (CH), 121.4 (C), 120.9 (CH), 119.0 (CH), 117.0 (C), 111.5 (CH), 98.7 (CH) ppm. MS (70 eV) m/z = 336 ($M^{+\cdot}$, 100), 337, 338 (26), 318 (16), 262 (22). UV (EtOH): $\lambda_{max}(\varepsilon)$ = 414, 316, 232 nm. *Anal.* Calc. for

$C_{18}H_{12}N_2O_5$: C, 64.29; H, 3.60; N, 8.33. Found: C, 64.27; H, 2.59; N, 8.30%.

2.5.3. 4-Nitro-2-[2-(2(1H)quinolinylidene) acethyl] benzoic acid (2c, $C_{18}H_{12}N_2O_5$)

Yield: 91%, mp: 174–177 °C. IR (KBr, cm^{-1}): 3410, 1728, 1648, 1596, 1108 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 15.6 (s, 1H, NH enaminone form), 11.9 (s, 1H, OH carboxylic acid), 9.1 (d, 1H, ^4J = 2.7 Hz), 8.8 (dd, 1H, ^3J = 8.6, ^4J = 2.7 Hz), 8.5 (d, 1H, ^3J = 8.6 Hz), 7.9 (d, 1H, ^3J = 9.4 Hz), 7.5–7.7 (m, 2H), 7.3–7.5 (m, 3H), 7.1 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.0 (C═O), 187.0 (C═O), 154.5 (C), 139.0 (C), 138.3 (C), 132.3 (CH), 132.8 (C), 129.6 (CH), 130.8 (CH), 129.9 (C), 129.4 (CH), 123.0 (C), 121.9 (CH), 121.2 (CH), 119.7 (CH), 117.8 (CH), 112.2 (CH), 98.1 (CH) ppm. MS (70 eV) m/z = 336 ($M^{+\cdot}$, 100), 337, 338 (26), 318 (16), 262 (22). UV (EtOH): $\lambda_{max}(\varepsilon)$ = 415, 318, 235 nm. *Anal.* Calc. for $C_{18}H_{12}N_2O_5$: C, 64.29; H, 3.60; N, 8.33. Found: C, 64.27; H, 2.59; N, 8.30%.

2.5.4. 3,6-Difluoro-2-[2-(2(1H)quinolinylidene)acethyl]-benzoic acid (2d, $C_{18}H_{11}F_2NO_3$)

Yield: 92%, mp: 201–204 °C. IR (KBr, cm^{-1}): 3409, 1727, 1648, 1596, 1108 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): ^1H NMR (500 MHz, $CDCl_3$): δ = 15.7 (s, 1H, NH enaminone form), 11.5 (s, 1H, OH carboxylic acid), 8.8 (ddd, 1H, ^3J = 9.8, 8.0, ^4J = 6.4 Hz), 8.5 (ddd, 1H, ^3J = 9.6, 8.0, ^4J = 6.4 Hz), 7.7–7.8 (m, 2H), 7.4–7.5 (m, 3H), 7.2 (d, 1H, ^3J = 9.2 Hz), 7.0 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.7 (C═O), 187.2 (C═O), 167.5 (CF), 154.5 (CF), 164.3 (C), 139.0 (C), 138.3 (CH), 132.8 (CH), 129.6 (CH), 130.8 (CH), 129.9 (CH), 129.4 (C), 123.0 (C), 121.9 (CH), 121.2 (C), 119.7 (CH), 112.2 (CH), 98.1 (CH) ppm. MS (70 eV) m/z = 327 ($M^{+\cdot}$, 100), 309, 253 (26), 206 (16), 179 (22). UV (EtOH): $\lambda_{max}(\varepsilon)$ = 413, 312, 232 nm. *Anal.* Calc. for $C_{18}H_{11}F_2NO_3$: C, 66.06; H, 3.39; N, 4.28. Found: C, 65.96; H, 3.36; N, 4.24%.

2.5.5. 3,6-Dichloro-2-[2-(2(1H)quinolinylidene)acethyl]-benzoic acid (2e, $C_{18}H_{11}Cl_2NO_3$)

Yield: 91%, mp: 213–216 °C. IR (KBr, cm^{-1}): 3410, 1728, 1642, 1593, 1110 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): ^1H NMR (500 MHz, $CDCl_3$): δ = 15.6 (s, 1H, NH enaminone form), 11.6 (s, 1H, OH carboxylic acid), 8.6 (d, 1H, ^3J = 8.3 Hz), 8.4 (d, 1H, ^3J = 8.3 Hz), 7.9 (d, 1H, ^3J = 9.3 Hz), 7.7 (dd, 1H, ^{3} J = 8.2, 4J = 2.3 Hz), 7.2 (d, 1H, ^3J = 9.3 Hz), 7.4–7.5 (m, 3H), 7.0 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.0 (C═O), 187.0 (C═O), 166.7 (C), 153.2 (CH), 163.2 (C), 138.0 (C), 137.2 (C), 131.7 (CH), 128.1 (CH), 130.5 (CH), 129.5 (C), 128.3 (CH), 120.3 (C), 121.6 (C), 121.5 (CH), 118.7 (CH), 112.8 (CH), 97.6 (CH) ppm. MS (70 eV) m/z = 360 ($M^{+\cdot}$, 100), 342, 286 (26), 239 (16), 212 (22). UV (EtOH): $\lambda_{max}(\varepsilon)$ = 416, 313, 234 nm. *Anal.* Calc. for $C_{18}H_{11}Cl_2NO_3$: C, 60.02; H, 3.08; N, 3.89. Found: C, 59.80; H, 3.04; N, 3.86%.

2.5.6. 4,5-Difluoro-2-[2-(2(1H)quinolinylidene)acethyl]-benzoic acid (2f, $C_{18}H_{11}F_2NO_3$)

Yield: 95%, mp: 224–227 °C. IR (KBr, cm^{-1}): 3409, 1725, 1648, 1596, 1108 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): ^1H NMR (500 MHz, $CDCl_3$): δ = 15.5 (s, 1H, NH enaminone form), 11.6 (s, 1H, OH carboxylic acid), 8.4 (dd, 1H, ^3J = 9.5, ^4J = 6.2 Hz), 8.2 (d, 1H, ^3J = 9.2 Hz), 7.7–7.8 (m, 2H), 7.4–7.5 (m, 3H), 7.2 (d, 1H, ^3J = 9.2 Hz), 7.0 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.0 (C═O), 187.8 (C═O), 167.5 (CF), 164.3 (CF), 154.5 (C), 139.0 (C), 138.3 (C), 132.8 (CH), 129.6 (CH), 130.8 (CH), 129.9 (C), 129.4 (C), 123.0 (CH), 121.9 (CH), 121.2 (CH), 119.7 (CH), 112.2 (CH), 98.1 (CH) ppm. MS (70 eV) m/z = 327 ($M^{+\cdot}$, 100), 309, 253 (26), 206 (16), 179 (22). UV (EtOH): $\lambda_{max}(\varepsilon)$ = 413, 312, 232 nm. *Anal.* Calc. for $C_{18}H_{11}F_2NO_3$: C, 66.06; H, 3.39; N, 4.28. Found: C, 66.01; H, 3.36; N, 4.24%.

2.5.7. 2,3,4,5-Tetrafluoro-6-[2-(2(1H)quinolinylidene)acethyl]-benzoic acid (2g, $C_{18}H_9F_4NO_3$)

Yield: 97%, mp: 213–215 °C. IR (KBr, cm^{-1}): 3411, 1729, 1648, 1595, 1110 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 15.6 (s, 1H, NH enaminone form), 11.8 (s, 1H, OH carboxylic acid), 8.2 (d, 1H, ^3J = 9.3 Hz), 8.0 (dd, 1H, ^{3} J = 8.2, 4J = 2.4 Hz), 7.7 (ddd, ^3J = 8.4, 7.8, ^4J = 2.4 Hz, 1H), 7.3–7.5 (m, 3H), 7.0 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.5 (C═O), 190.0 (C═O), 156.5 (CF), 144.0 (CF), 141.6 (C), 138.8 (CF), 137.0 (CF), 135.6 (C), 132.2 (CH), 129.9 (CH), 128.4 (CH), 124.8 (CH), 124.0 (C), 122.4 (C), 118.9 (CH), 118.2 (C), 116.0 (CH), 98.0 (CH) ppm. MS (70 eV) m/z = 363 ($M^{+\cdot}$, 100), 345, 289 (26), 242 (16), 215 (22). UV (EtOH): $\lambda_{max}(\varepsilon)$ = 413, 314, 235 nm. *Anal.* Calc. for $C_{18}H_9F_4NO_2$: C, 59.51; H, 2.50; N, 3.86. Found: C, 59.49; H, 2.48; N, 3.83%.

2.5.8. 2,3,4,5-Tetrachloro-6-[2-(2(1H)quinolinylidene)-acethyl]benzoic acid (2h, $C_{18}H_9Cl_4NO_3$)

Yield: 95%, mp: 223–225 °C. IR (KBr, cm^{-1}): 3408, 1732, 1641, 1563, 1113 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 15.5 (s, 1H, NH enaminone form), 11.8 (s, 1H, OH carboxylic acid), 8.3 (d, 1H, ^3J = 9.6 Hz), 7.9 (dd, 1H, ^{3} J = 8.2, 4J = 2.2 Hz), 7.7 (ddd, 1H, ^3J = 8.5, 7.8, ^4J = 2.2 Hz), 7.3–7.4 (m, 3H), 7.1 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.0 (C═O), 186.8 (C═O), 154.5 (C), 142.0 (C), 140.3 (C), 137.3 (C), 135.8 (C), 132.6 (C), 130.2 (CH), 129.0 (CH), 127.4 (C), 124.0 (CH), 122.0 (C), 121.8 (C), 118.2 (CH), 117.8 (CH), 114.2 (CH), 97.5 (CH) ppm. MS (70 eV) m/z = 431 ($M^{+\cdot}$, 100), 433, 435 (26), 437 (16), 439 (22), 212, 170, 143. UV (EtOH): $\lambda_{max}(\varepsilon)$ = 415, 318, 235 nm. *Anal.* Calc. for $C_{18}H_9Cl_4NO_3$: C, 50.39; H, 2.11; N, 3.26. Found: C, 50.37; H, 2.9; N, 3.25%.

2.5.9. 2,3,4,5-Tetrabromo-6-[2-(2(1H)quinolinylidene)-acethyl]benzoic acid (2i, $C_{18}H_9Br_4NO_3$)

Yield: 91%, mp: 234–236 °C. IR (KBr, cm^{-1}): 3409, 1727, 1642, 1592, 1104 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 15.3 (s, 1H, NH enaminone form), 11.9 (s, 1H, OH carboxylic acid), 8.1 (d, 1H, ^3J = 9.3 Hz), 7.9 (dd, 1H, ^{3} J = 8.4, 4J = 2.1 Hz), 7.6 (ddd, ^3J = 8.6, 7.8, ^4J = 2.1 Hz, 1H), 7.2–7.4 (m, 3H), 6.9 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.0 (C═O), 186.9 (C═O), 153.2 (C), 141.1 (C), 140.0 (C), 136.8 (C), 135.1 (CH), 131.9 (CH), 129.7 (CH), 129.0 (C), 126.4 (C), 124.5 (C), 122.2 (C), 121.8 (C), 117.2 (CH), 116.2 (CH), 114.5 (CH), 95.5 (CH) ppm. MS (70 eV) m/z = 603 ($M^{+\cdot}$, 100), 605, 607 (26), 608 (16), 610 (22), 558, 143. UV (EtOH): $\lambda_{max}(\varepsilon)$ = 415, 318, 235 nm. *Anal.* Calc. for $C_{18}H_9Br_4NO_3$: C, 35.62; H, 1.49; N, 2.31. Found: C, 35.50; H, 1.42; N, 2.2%.

3. Results and discussion

The poor thermal stability of isobenzofuranone limits the application of heat and strong acidic media, therefore, we decided to use SSA/wet SiO_2 and microwave irradiation. Efficiency of the reaction is mainly affected by the amount of catalyst, temperature and presence of wet SiO_2. As it is compiled in Table 1, the best results have been obtained at 100 °C with a amount of 0.1 g SSA in terms of yield. The increasing in the quantity of SSA up to 0.4 g not only increases the yield but results clearly indicate that even 0.1 g of SSA is sufficient to the hydrolysis of the isobenzofuranone. It is important to note that in the absence of wet SiO_2 the reaction yield is decreased to zero even at 100 °C after 24 h. Also increasing the quantity of wet SiO_2 was found to be not effective in the reaction yields and time.

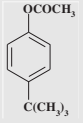
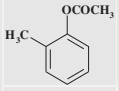
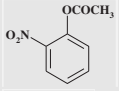
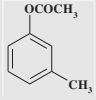
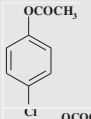
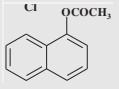
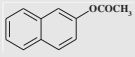
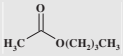
The successful results of silica sulfuric acid catalyzed hydrolysis of various isobenzofuranone under solvent-free classical heating conditions and using microwave irradiation in presence of wet SiO_2 are given in Table 3. In a typical experiment, a mixture of isobenzofuranone derivatives (1a–i, 1 mmol) and silica sulfuric acid (0.1 g) and wet SiO_2 was stirred for 50–80 min under conventional heating conditions at 100 °C and using microwave irradiation for 5–20 min. The results clearly show that microwave irradiation improves the hydrolysis of isobenzofuranone derivatives and gives yields higher than those from conventional experiments. Experiment was conducted to study the hydrolysis of 1a under the optimized conditions obtained in the absence of silica sulfuric acid. The yield

Table 1 Optimization of the hydrolysis of isobenzofuranone under classical heating conditions.

Experimental number	Catalyst (g)	Time (h)	Temperature (°C)	Yield[a] (%)
1	0	1	100	16
2	0.1	1	60	20
3	0.1	1	80	45
4	0.1	1	100	58
5	0.1	1	120	56
6	0.1	1	150	49
7	0.2	1	100	40
8	0.4	1	130	34

[a] Isolated yield.

Table 2 Hydrolysis of various carboxylic acid esters catalyzed by silica sulfuric acid under microwave irradiation.[a]

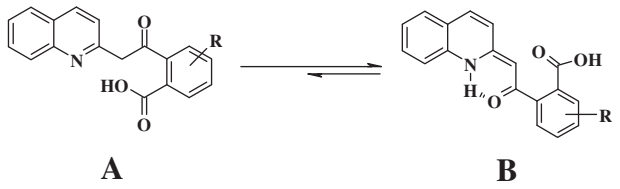
Entry	Ester	Yield (%) time (min)	
		Δ	MW
1		80 (70)	94 (10)
2		75 (85)	93 (15)
3		80 (75)	98 (15)
4		75 (40)	94 (7)
5		75 (55)	94 (8)
6		85 (95)	99 (15)
7		75 (45)	94 (10)
8		80 (60)	93 (10)
9		75 (100)	92 (9)
10		80 (95)	93 (10)

[a] All products were characterized by comparison of their melting or boiling points, IR, and ^1H NMR spectra with those of authentic samples.

Table 3 Hydrolysis of isobenzofuranone derivatives to the corresponding enaminone.

Entry	*R*	Yield (%) Time (min)		M.p. (°C)	
		Δ[a]	MW[b]	Found	Reported
2a	H	43 (80)	88 (20)	154–155	155–156[c]
2b	4-NO_2	51 (60) (51, 50, 48, 47)	93 (10) (92, 90, 89, 87)	165–167	–
2c	5-NO_2	48 (70)	91 (15)	174–177	–
2d	4,7-F	53 (60)	92 (10)	201–204	–
2e	4,7-Cl	53 (75)	91 (15)	213–216	–
2f	5,6-F	52 (50)	95 (7)	224–227	–
2g	4,5,6,7-F	58 (40)	97 (5)	213–215	–
2h	4,5,6,7-Cl	51 (60)	95 (10)	223–225	–
2i	4,5,6,7-Br	49 (75)	91 (15)	234–236	–

[a] Under classical heating conditions at 100 °C.
[b] Using microwave irradiation.
[c] See reference (Eibner and Hofmann, 1904).



Scheme 2 Tautomeric form of 2-ketomethylquinoline derivatives.

of product 2a was only 16%, while reaction occurred with wet SiO_2 even after 24 h. To explore the generality of this work, we repeat this method for the hydrolysis of some carboxylic acid esters. It is noteworthy that not only aromatic carboxylic acid esters but also aliphatic carboxylic acid esters were smoothly hydrolyzed under the given conditions (Table 2).

We believe that the presence of wet SiO_2 provides an effective surface area for *in situ* generation of H_2SO_4. As indicated in Table 3, we have repeated the reaction numerous times with good success each time. In fact, we observed that the catalyst can be recycled and reused at least four times (Table 3, entry 2b).

The structures of products 1(a–i) were deducted by ^1H and ^{13}C NMR spectroscopy, mass spectrometry FT-IR and elemental analysis. The mass spectrum of 1a displayed the molecular ion (M^+) peak at m/z 291, which was consistent with the adduct structure.

The ^1H NMR spectrum of 2a exhibited two broad singlet, arising from the NH group (δ 15–16 ppm) and OH carboxylic acid (δ 11–12 ppm). Also one sharp singlet related to =CH (δ 5.83 ppm). In IR spectra, the presence of absorption band at 1726 cm^{-1} due to C=O related to the carboxylic acid and signal at 3410 cm^{-1} due to O–H related to the hydroxyl group of the carboxylic acid. We conclude that the compounds are rather in the enaminone form (Gnichtel and Moller, 1981; Case and Schilt, 1979). In $CDCl_3$ as solvent the structure of (B) is major (Scheme 2).

4. Conclusion

In conclusion, from our experimental results it is evident that the solvent-free reaction using microwave irradiation proceeds with significant decrease in reactions times and comparably high chemical yields and purity, without involvement of toxic solvents, formation of any undesirable side products and epimerization toward classical heating conditions. Replacement of liquid acids with solid acid is all among desirable factors for the chemical industry which we have considered in our green chemistry approach. Moreover, a new feature here is the fact that the reaction is heterogeneous. We believe that the present methodology would be an important addition to existing methodologies.

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