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ORIGINAL ARTICLE

1st Nano Update

BF_3·nano SiO_2 as a catalytic system for one-pot green synthesis of pyrophthalone derivatives under microwave conditions

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Abstract The expeditious and solvent-free approach that involves the exposure of neat reactants to microwave (MW) irradiation in conjunction with the use of supported catalysts was described. A simple one-pot and green reaction of methylpyridine derivatives and phthalic anhydride derivatives on the surface of a nano silica gel impregnated with BF_3 as solid supported catalysts under microwave irradiation without any solvent according to green chemistry was developed. The salient features of these high yield protocols are the enhanced reaction rates, greater selectivity and the experimental ease of manipulation.

1. Introduction

Heterogeneous organic reactions have proven useful to chemists in the laboratory as well as in the industrial context. These reactions are affected by the reagents immobilized on the porous solid supports and have advantages over the conventional solution phase reactions because of the good dispersion of active reagent sites, associated selectivity and easier work-up. The recyclability of some of these solid supports renders these processes into truly eco-friendly green protocols. In recent years, the use of solid supports under microwave irradiation has become more popular in synthetic organic chemistry (Ranu et al., 2000; Gershonov et al., 2007) and heterogeneous reactions facilitated by supported reagents on various solid inorganic surfaces have received more attention (Song and Lee, 2002). Solvent-free microwave irradiation is well known as an environmentally benign method, which offers several advantages including shorter reaction times, cleaner reaction profiles and simple experimental/product isolation procedures (Zhang et al., 2008). It is well known that microwave (MW) irradiation

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can accelerate a great number of chemical processes, and, in particular, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions (Loupy, 2002). On the other hand, the most successful examples of microwave applications are necessarily found to be related to the use of solvent-free systems, in which microwaves interact directly with reagents and, therefore, can more efficiently drive chemical reactions (Deshayes et al., 1999; Bogdal et al., 2003). The acceleration of reactions by microwaves results from material–microwave interactions leading to thermal and non-thermal effects (Perreux and Loupy, 2001; Jacob et al., 1995; Caddick, 1995).

Indane-1,3-dione derivatives that contain a heterocyclic nitrogen-containing substituent are called phthalones. Pyrophthalone derivatives have been proposed as photo semiconductors for the preparation of electrophotographic materials (Tomanek-Kunitzer, 1968). A study of the electrophysical properties of pyrophthalones in thin-film systems (Balode, 1971) showed that pyrophthalone, tetrachlorophyrophthalone and γ-pyrophthalone have considerable photosensitivity and the quantum efficiency (β) is 10^{-3}–10^{-1} electron/photon at 300–500 nm. Some of the pyrophthalone derivatives display considerable anticoagulant activity and low toxicity. Antiphlogistic and analgesic action have been found for these compounds (Ploquin et al., 1973; Le Bant et al., 1973). The complexation properties of some derivatives of pyrophthalone, and quinophthalone towards some transition metal ions have been studied (Bontchev et al., 1983; Mitewa et al., 1983, 1985). These ligands are used as dyes, organic semiconductors, and anti-inflammatory and anaesthetic agents (Manukian and Mangini, 1970;Tomanek-Kunitzer, 1968; Ploquin et al., 1972; Bant et al., 1974; Neiland and Katzen, 1975). Pyrophthalone was first synthesized by Jacobsen and Reimer (Jacobsen and Reimer, 1883) and later by von Huber (Huber, 1903) by the condensation of α-picoline with phthalic anhydride. Kuhn (1903) used dimethyl sulfate and the sodium salt of pyrophthalone for the synthesis of N-methylpyrophthalone. Herein we have modified the method for the synthesis of pyrophthalone derivatives by one-pot reaction of methylpyridine derivatives (**1a**–**c**) and phthalic anhydride derivatives (**2a**–**e**), under microwave irradiation without any-solvent in the presence of BF_3·nano SiO_2 as catalyst (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.

2.2. Apparatus

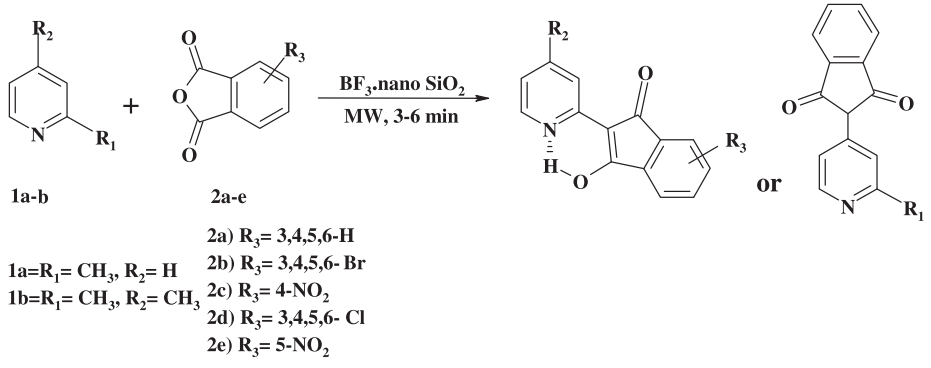
Melting points were determined in open capillaries using an Electrothermal Mk3 apparatus. The reactions were carried out in a microwave oven (ETHOS 1600, Milestone) with a power of 600 W specially designed for organic synthesis, with continuous stirring. IR spectra were recorded using a Perkin–Elmer FT-IR 550 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer for the sample as indicated with tetramethylsilane as an internal reference. UV spectra were recorded on a Hitachi 200-20 spectrophotometer using spectrophotometeric grade chloroform (Baker). MS spectra were recorded on a Finnigan MAT 44S, with an ionization voltage of 70 eV. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer 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. Preparation of Catalyst

5 ml of methanol containing 0.6 g (4.2 mmol) of BF_3–OEt_2 and 0.4 g of unpreheated nano silica gel was stirred for 1 h at room temperature. The slurry was dried slowly on a rotary evaporator at 40 °C. The obtained solid was dried at ambient temperature for 2 h and then stored in a dry container for at least 3 months.

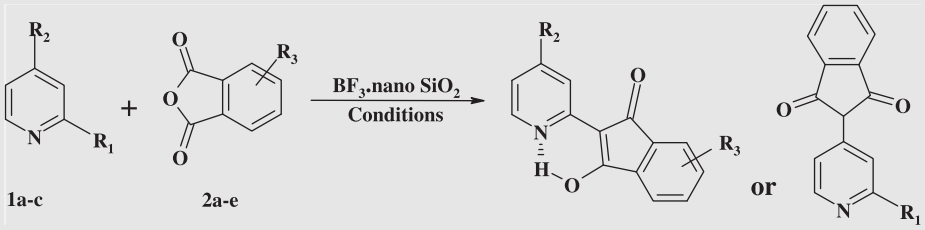
2.4. General synthesis of pyrophthalone derivatives

A mixture of methylpyridine derivative (1 mmol), phthalic anhydride (1mmol) and BF_3·nano SiO_2 (25 mg) were stirred well in a beaker at room temperature. Then the mixture was irradiated in a microwave oven (max. power 600 W, applied power up to 35%) for 3–6 min at the end of the reaction, the reaction mixture was cooled to room temperature and the catalyst was filtered off and the solvent was removed in vacuo to



Scheme 1 Green synthesis of pyrophthalone on BF_3·nano silica gel under microwave irradiation.

Table 1 Synthesis of Pyrophthalone derivatives under conventional conditions and microwave irradiation.



Entry	Product	Yield (%) Time (min)	
		Δ[a]	MW[a]
1	aa	72 (35)	90 (6)
2	ab	83 (24)	88 (3)
3	ac	75 (30)	88 (2)
4	ad	76 (30)	91 (3)
5	ae	82 (24)	92 (2)
6	ba	70 (35)	91 (6)
7	bb	80 (25)	95 (4)
8	bc	75 (30)	95 (3)
9	bd	77 (30)	97 (4)
10	be	80 (25)	91 (3)

[a] Isolated yield based on pyridine derivative.

yield the crude product, which was crystallized from ethanol and the pure pyrophthalones were obtained as crystalline in 88–97% yield (Table 1).

2.5. Spectral data for products

2.5.1. 3-Hydroxy-2-(2-pyridyl)-1H-indene-1-one (aa, $C_{14}H_9NO_2$)

Yield: 90%, mp: 280–282 °C. IR (KBr, cm^{-1}): 1675, 1640, 1620, 1455 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 13.7 (s, 1H, O–H, imine enol form), 7.2 (dd, 1H, ^3J: 5.1, ^3J: 7.9, Ar–H), 8.3 (dd, 1H, ^3J: 5.1, ^4J: 2.2, Ar–H), 8.0 (dd, 1H, ^3J: 7.1, ^4J: 1.7, Ar–H), 7.4-7.7 (m, 5H, Ar–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190 (C═O), 176.2 (C–O), 162.0 (C), 149.0 (C), 146.1 (CH), 144.1 (CH), 137.0 (CH), 134.5 (C), 131.8 (CH), 128.1 (CH), 127.1 (CH), 126.6 (CH), 124.6 (CH), 116.8 (C) ppm. MS (70 eV) m/z = 225 (M+.), 197, 78. UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 390, 323, 236 nm. MS (70 eV) m/z = 225 (M+.), 197, 78. Anal. Calcd for $C_{14}H_9NO_2$: C, 75.213; H, 4.06; N 6.27. Found: C, 74.90; H 3.92; N 6.13.

2.5.2. 4, 5, 6, 7-Tetrabromo-3-hydroxy-2-(2-pyridyl)-1H-indene-1-one (ab, $C_{14}H_5NO_2Br_4$)

Yield: 88%, mp: 300–301 °C. IR (KBr, cm^{-1}): 1675, 1646, 1615, 1460 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 13.5 (s, 1H, O–H, imine enol form), 7.1 (ddd, 1H, ^3J: 7.8, ^3J: 5.4, ^4J: 1.9, Ar–H), 7.3 (dd, 1H, ^3J: 7.6, ^4J: 1.9, Ar–H), 7.7 (ddd, 1H, ^3J: 7.8, ^3J: 7.6, ^4J: 2.0, Ar–H), 8.5 (dd, 1H, ^3J: 5.4, ^4J: 2.0, Ar–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.2 (C═O), 178.1 (C–O), 159.6 (C), 148.0 (CH), 146.1 (C), 144.0 (C), 139.0 (CH), 136.5 (C), 131.2 (C), 125.0 (C), 122.5 (CH), 120.1 (CH), 119.2 (C), 114.6 (C). MS (70 eV) m/z = 535 (M+.), 537 (M + 2), 539 (M + 4), 541 (M + 6), 543 (M + 8), 507, 78. UV (EtOH): $\lambda_{max}(\varepsilon)$ = 392, 320, 235 nm. Anal. Calcd for $C_{14}H_5NO_2Br_4$: C (31.21), H (0.94), N (2.06). Found: C (31.08), H (0.88), N (1.96).

2.5.3. 3-Hydroxy-2-(2-pyridyl)-7-nitro-1H-indene-1-one (ac, $C_{14}H_8N_2O_4$)

Yield: 88%, mp: 293–294 °C. IR (KBr, cm^{-1}): 1678, 1640, 1620, 1450, 1550, 1334 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 13.8 (s, 1H, O–H, imine enol form), 7.1 (ddd, 1H, ^3J: 5.5, ^3J: 7.8, ^4J: 2.1, Ar–H), 7.3 (dd, 1H, ^3J: 7.5, ^4J: 2.1, Ar–H), 7.6 (ddd, 1H, ^3J: 7.5, ^3J: 7.8, ^4J: 2.0, Ar–H), 7.9 (dd, 1H, ^3J: 7.7, ^3J: 8.2, Ar–H), 8.2 (dd, 1H, ^3J: 7.7, ^4J: 2.1, Ar–H), 8.4 (dd, 1H, ^3J: 8.2, ^4J: 2.1, Ar–H), 8.6 (dd, 1H, ^3J: 5.5, ^4J: 2.0, Ar–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.0 (C═O), 185.0 (C–O), 153.1 (C), 150.2 (C), 146.8 (CH), 143.2 (C), 140.5 (CH), 136.3 (CH), 132.7 (CH), 127.9 (CH), 125.3 (C), 118.9 (CH), 116.4 (CH), 108.5 (C) ppm. MS (70 eV) m/z = 268 ($M^{+\cdot}$), 238, 222, 194, 78. UV (EtOH): $\lambda_{max}(\varepsilon)$ = 394, 297, 218. Anal. Calcd for $C_{14}H_8N_2O_4$: C (62.69), H (3.01), N (10.44). Found: C (62.51), H (2.92), N (10.31).

2.5.4. 4, 5, 6, 7-Tetracholoro-3-hydroxy-2-(2-pyridyl)-1H-indene-1-one (ad, $C_{14}H_5NO_2Cl_4$)

Yield: 91%, mp: 297–299 °C. IR (KBr, cm^{-1}): 1675, 1642, 1610, 1450 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 13.8 (s, 1H, O–H, imine enol form), 7.2 (ddd, 1H, ^3J: 7.7, ^3J: 5.5, ^4J: 2.2, Ar–H), 7.5 (dd, 1H, ^3J: 7.6, ^4J: 2.2, Ar–H), 7.8 (ddd, 1H, ^3J: 7.8, ^3J: 7.6, ^4J: 2.0, Ar–H), 8.7 (dd, 1H, ^3J: 5.5, ^4J: 2.0, Ar–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2 (C═O), 183.5 (C–O), 161.2 (C), 148.8 (CH), 146.2 (C), 144.3 (C), 138.6 (CH), 137.2 (C), 132.5 (C), 125.4 (C), 124.5 (CH), 120.2 (CH), 118.5 (C), 114.5 (C) ppm. MS (70 eV) m/z = 359 ($M^{+\cdot}$), 361 (M + 2), 363 (M + 4), 365 (M + 6), 367 (M + 8), 331, 78. UV (EtOH): $\lambda_{max}(\varepsilon)$ = 390, 317,

230 nm. Anal. Calcd for $C_{14}H_5NO_2Cl_4$: C (64.58), H (1.4), N (3.88). Found: C (64.41), H (1.1), N (3.70).

2.5.5. 3-Hydroxy-2-(2-pyridyl)-6-nitro-1H-indene-1-one (ae, $C_{14}H_8N_2O_4$)

Yield: 92%, mp: 292–294 °C. IR (KBr, cm^{-1}): 1675, 1640, 1613, 1450, 1550, 1330 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ = 13.8 (s, 1H, O–H, imine enol form), 7.2 (ddd, 1H, ^3J: 5.4, ^3J: 7.8, ^4J: 2.2, Ar–H), 7.5 (dd, 1H, ^3J: 7.7, ^4J: 2.2, Ar–H), 7.7 (ddd, 1H, ^3J: 7.7, ^3J: 7.8, ^4J: 2.0, Ar–H), 7.9 (d, 1H, ^3J: 8.0, Ar–H), 8.3 (dd, 1H, ^3J: 8.0, ^4J: 2.2, Ar–H), 8.6 (dd, 1H, ^3J: 5.5, ^4J: 2.0, Ar–H), 8.7 (d, 1H, ^4J: 2.2, Ar–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.0 (C═O), 189.0 (C–O), 152.4 (C), 151.4 (C), 150.7 (CH), 146.0 (C), 142.1 (CH), 139.6 (C), 129.1 (CH), 121.9 (CH), 117.0 (CH), 115.5 (CH), 115.2 (CH), 104.5 (C) ppm. MS (70 eV) m/z = 238 ($M^{+\cdot}$, 100), 222 (26), 194 (16), 78(22), UV (EtOH): $\lambda_{max}(\varepsilon)$ = 395, 305, 232 nm. Anal. Calcd for $C_{14}H_8N_2O_4$: C (62.69), H (3.01), N (10.44). Found: C (62.51), H (2.92), N (10.31).

2.5.6. 3-Hydroxy-2-(4-methyl-2-pyridyl)-1H-indene-1-one (ba, $C_{15}H_{11}NO_2$)

Yield: 91%, mp: 290–293 °C. 1675, 1643, 1610, 1450 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 13.7 (s, 1H, O–H, imine enol form), 7.1 (dd, 1H, ^3J: 5.1, ^4J: 2.1, Ar–H), 8.2 (d, 1H, ^3J: 5.1, Ar–H), 8.0 (dd, 1H, ^3J: 7.1, ^4J: 1.7, Ar–H), 7.5-7.7 (m, 4H, Ar–H). ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.0 (C═O), 174.5 (C–O), 160.0 (C), 149.0 C), 145.8 (CH), 145.1 (C), 136.0 (CH), 134.0 (C), 131.2 (CH), 129.4 (CH), 128.2 (CH), 126.0 (CH), 124.2 (CH), 116.3 (C), 20.1 (CH_3). ppm. MS (70 eV) m/z = 237 ($M^{+\cdot}$, 100), 222 (16), 209 (26). UV (EtOH): $\lambda_{max}(\varepsilon)$ = 388, 318, 234 nm. Anal. Calcd for $C_{15}H_{11}NO_2$: C (75.94), H (4.67), N (5.90). Found: C (75.85), H (4.60), N (5.82).

2.5.7. 4, 5, 6, 7-Tetrabromo-3-hydroxy-2-(4-methyl-2-pyridyl)-1H-indene-1-one (bb, $C_{15}H_7NO_2Br_4$)

Yield: 95%, mp: 310–312 °C. IR (KBr, cm^{-1}): 1675, 1642, 1610, 1450 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 13.7 (s, 1H, O–H, imine enol form), 7.0 (d, 1H, ^3J: 5.4, Ar–H), 7.4 (s, 1H, Ar–H), 8.5 (d, 1H, ^3J: 5.4, Ar–H), 2.4 (s, 3H, CH_3). ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6 (C═O), 177.1 (C–O), 160.8 (C), 147.2 (C), 145.8 (CH), 143.3 (C), 138.5 (C), 136.8 (C), 131.7 (C), 124.2 (C), 122.5 (CH), 119.4 (CH), 116.0 (C), 114.2 (C), 20.4 (CH_3) ppm. MS (70 eV) m/z = 549 ($M^{+\cdot}$, 100), 551 (M + 2), 553 (M + 4), 555 (M + 6), 557 (M + 8), 470, 416, 335, 230. UV (EtOH): $\lambda_{max}(\varepsilon)$ = 391, 320, 235 nm. Anal. Calcd for $C_{15}H_7NO_2Br_4$: C (32.59), H (1.28), N (2.53). Found: C (32.45), H (1.23), N (2.48).

2.5.8. 3-Hydroxy-2-(4-methyl-2-pyridyl)-7-nitro-1H-indene-1-one (bc, $C_{15}H_{10}N_2O_4$)

Yield: 95%, mp: 303–304 °C. IR (KBr, cm^{-1}): 1675, 1639, 1613, 1450, 1550, 1334 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 13.7 (s, 1H, O–H, imine enol form), 7.0 (d, 1H, ^3J: 5.5, Ar–H), 7.3 (s, 1H, Ar–H), 7.8 (dd, 1H, ^3J: 7.7, ^3J: 8.2, Ar–H), 8.1 (dd, 1H, ^3J: 7.7, ^4J: 2.1, Ar–H), 8.4 (dd, 1H, ^3J: 8.2, ^4J: 2.1, Ar–H), 8.8 (d, 1H, ^3J: 5.5, Ar–H), 2.5 (s, 3H, CH_3). ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.0 (C═O), 188.0 (C–O), 152.2 (C), 150.7 (C), 144.8 (C), 142.5 (CH), 139.5 (C), 135.3 (CH), 130.7 (C), 126.9 (CH), 124.3 (CH), 116.9 (CH), 115.4 (CH), 105.5 (C), 20.8 (CH_3) ppm. MS (70 eV) m/z = 282 ($M^{+\cdot}$, 100), 283 (M + 1), 284 (M + 2), 236, 76. UV (EtOH): $\lambda_{max}(\varepsilon)$ = 390, 293, 218 nm. Anal. Calcd for $C_{15}H_{10}N_2O_4$: C (63.83), H (3.57), N (9.92). Found: C (63.77), H (3.50), N (9.88).

2.5.9. 4, 5, 6, 7-Tetracholoro-3-hydroxy-2-(4-methyl-2-pyridyl)-1H-indene-1-one (bd, $C_{15}H_7NO_2Cl_4$)

Yield: 97%, mp: 308–310 °C. IR (KBr, cm^{-1}): 1675, 1643, 1610, 1450 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 13.8 (s, 1H, O–H, imine enol form), 7.2 (d, 1H, ^3J: 5.5, Ar–H), 7.5 (s, 1H, Ar–H), 8.7 (d, 1H, ^3J: 5.5, Ar–H), 2.4 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6 (C═O), 174.2 (C–O), 161.8 (C), 149.0 (C), 146.5 (CH), 144.3 (C), 139.1 (C), 138.8 (C), 132.7 (C), 125.6 (C), 123.5 (CH), 120.5 (CH), 117.0 (C), 115.2 (C), 20.8 (CH_3) ppm. MS (70 eV) m/z = 373 ($M^{+\cdot}$, 100), 375 (M + 2), 377 (M + 4), 379 (M + 6), 381 (M + 8), 358, 345. UV (EtOH): $\lambda_{max}(\varepsilon)$ = 391, 320, 235 nm. Anal. Calcd for $C_{15}H_7NO_2Cl_4$: C (48.04), H (1.88), N (3.73). Found: C (47.91), H (1.83), N (3.70).

2.5.10. 3-Hydroxy-2-(4-methyl-2-pyridyl)-6-nitro-1H-indene-1-one (be, $C_{15}H_{10}N_2O_4$)

Yield: 91%, mp: 300–302 °C. IR (KBr, cm^{-1}): 1675, 1640, 1613, 1450, 1550, 1330 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 13.8 (s, 1H, O–H, imine enol form), 7.0 (d, 1H, ^3J: 5.1, Ar–H), 7.3 (s, 1H, Ar–H), 8.2 (dd, 1H, ^3J: 8.3, ^4J: 2.5, Ar–H), 7.9 (d, 1H, ^3J: 8.3, Ar–H), 8.7 (d, 1H, ^3J: 5.1, Ar–H), 9.6 (d, 1H, ^4J: 2.5, Ar–H), 2.5 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.0 (C═O), 189.0 (C–O), 152.4 (C), 151.4 (C), 150.7 (C), 146.0 (C), 142.1 (CH), 139.6 (C), 129.1 (CH), 121.9 (CH), 117.0 (CH), 115.9 (CH), 115.2 (CH), 104.5 (C), 20.8 (CH_3) ppm. MS (70 eV) m/z = 282 ($M^{+\cdot}$, 100), 283 (M + 1), 284 (M + 2), 236, 75. UV (EtOH): $\lambda_{max}(\varepsilon)$ = 391, 303, 231 nm. Anal. Calcd for $C_{15}H_{10}N_2O_4$: C (63.83), H (3.57), N (9.92). Found: C (63.74), H (3.45), N (9.90).

3. Results and discussion

To determine the optimum quantity of BF_3·nano SiO_2, the reaction of 2-methylpyridine (**1a**) and phthalic anhydride (**2a**)

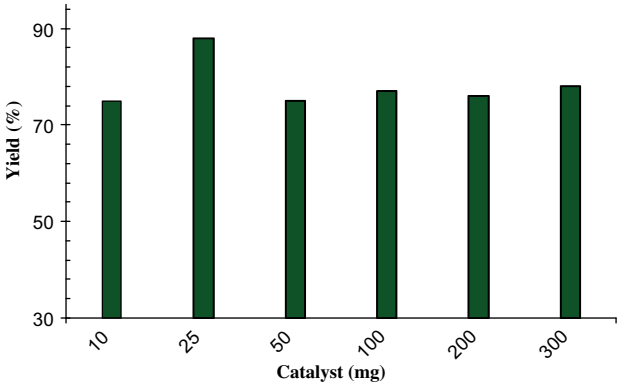


Figure 1 Optimization quantity of BF_3·nano SiO_2.

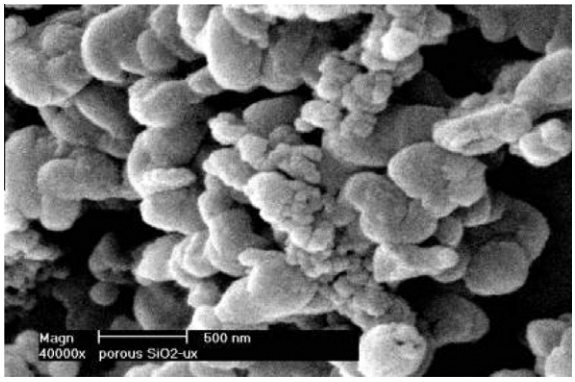


Figure 2 SEM image of the BF_3·nano SiO_2.

as starting materials was carried out under microwave irradiation as a model reaction. The use of 25 mg of catalyst resulted in the highest yield in 6 min (Fig. 1), consequently this catalyst was selected for subsequent experiments.

In order to investigate the effect of irradiation, various pyrophthalones were prepared from pyridine derivatives and phthalic anhydride derivatives under (i) conventional and solvent-free condition (ii) microwave irradiation, in the presence of a catalyst. The results are summarized in Table 1.

As shown in Table 1, in microwave irradiation condition, the yield of the reaction was high and the reaction time was low toward thermal condition. Also the suppotred nano SiO_2 increase contact surface of material to react quickly. The SEM image of BF_3·nano SiO_2 is shown in Fig. 2. As can be seen, the sample shows a nanocrystalline structure with a spherical like shape.

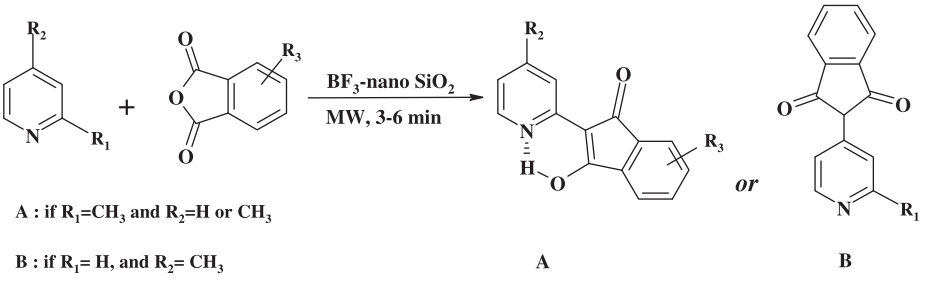
Study out on products indicated that the methyl group in 2-position of pyridine ring is more active and reactive than methyl group in 4-position (Scheme 2).

Several limiting structures-intraionic (betainlike) (C, C′), enaminone form (B), and enol (D) can be written for pyrophthalones .23. An interamolecular hydrogen bond is formed in each of the four cases (Scheme 3).

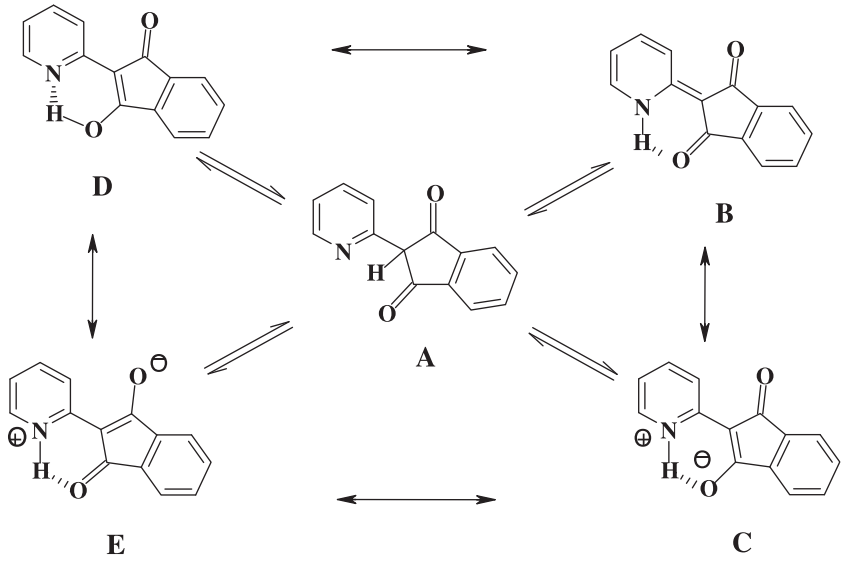
The structure of the pyrophthalone products have confirmed by their spectroscopic data. These data demonstrated a stabilized pseudo aromatic enol cheated ring (D). In IR spectra, the presence of signals at 1640 and 1670 cm^{-1} are related to the carbonyl groups in a conjugated system. In the ^1H NMR spectra enolic proton could be seen at δ 13.8 ppm.

4. Conclusion

The combination of supported reagents and microwave irradiation can be used to carry out a wide range of reactions in



Scheme 2 Regioselectivity in synthesis of pyrophthalone.



Scheme 3 Tautomeric forms in pyrophthalone structure.

short times and with high conversions and selectivity, without the need for solvents. This approach can prove beneficial since the recovery of solvents from conventional reaction systems always results in some losses. Recovery of both products and inorganic support/catalyst is generally possible, leading to an efficient and low waste route to a range of products. Replacement of liquid acids with solid acid is among all the 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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