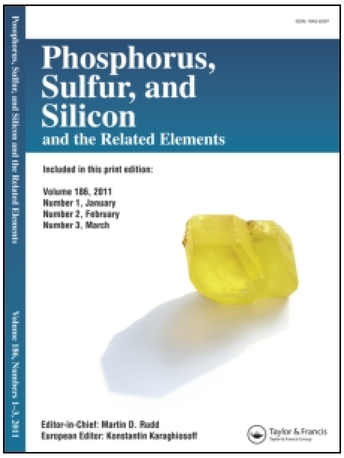

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TiO_2 Nanopowder Catalyzed Microwave-Induced One-Pot Synthesis of Novel Quinoline/Benzo[*h*]quinoline3-carbonitrile Under Solvent Free Conditions

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TiO_2 Nanopowder Catalyzed Microwave-Induced One-Pot Synthesis of Novel Quinoline/Benzo[*h*]quinoline-3-carbonitrile Under Solvent Free Conditions

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A rapid and efficient method for the synthesis of various carbonitrile quinoline/benzo[h]quinolines has been developed through the Knoevenagel condensation, Michael addition of aromatic aldehyde/amine with carbonyl compounds in the presence of a nanostructured TiO_2 photocatalyst by microwave irradiation under solvent-free conditions.

Keywords Microwave-solvent free; nanostructured TiO_2; quinoline; rapid-efficient

INTRODUCTION

In recent years, metal oxide semiconductor photocatalysis using particulate TiO_2 has proven to be a promising technology for use in photocatalytic reactions, in the cleanup of water contaminated with hazardous industrial byproducts,[1–6] or as a photoactive material in nanocrystalline solar cells.[7–13] Titanium dioxide is a photocatalyst of considerable interest because of its photocatalytic properties, and it is a choice for a large variety of applications because it is cheap, nontoxic, and has redox properties that are favorable both for oxidation of many organics and for reduction of a number of metal ions or organics in aqueous solution.

Quinolines and their derivatives are a very important class of compounds because of their wide occurrence in natural products[14] and

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biologically active compounds.[15] Furthermore, poly-substituted quinolines have been found to undergo hierarchical self-assembly into a variety of nano- and mesostructures with enhanced electronic and photonic functions.[16] In view of these points, a great deal of effort has been committed to develop new and efficient synthetic routes to quinoline derivatives in both synthetic organic and medicinal chemistry.

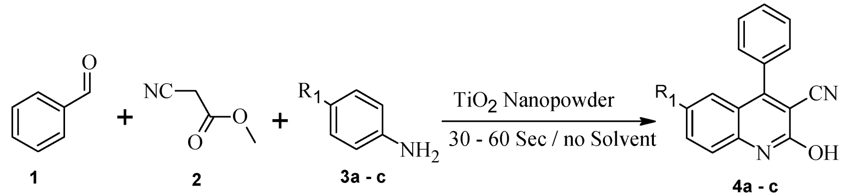
The use of scientific microwave apparatus in the development of efficient and selective greener methods has become a major focus of researchers worldwide, and selection of appropriate alternate eco-friendly reaction media has become an integral part of this paradigm shift.[17] Microwave (MW) irradiation as an alternative energy source in conjunction with water as reaction medium has proven to be a successful "greener" chemical approach.

Our approach is to develop a rapid and efficient scientifically based framework for greener preparation of these carbonitrile quinoline/benzoquinolines in a manner that renders the materials less mobile in the environment and reduces or eliminates the use and generation of hazardous substances. The following areas of opportunity are being exploited to engage green chemistry: (i) choice of solvent and (ii) the catalytic agent employed. We found microwave (MW) irradiation to be an efficient and selective mode of activation in rapid and efficient synthesis of 2-hydroxy-4-phenyl/benzo[*h*]quinoline -3-carbonitrile.

RESULTS AND DISCUSSION

The required colloidal TiO_2 was prepared according to a reported procedure by a dropwise addition of titanium(IV) tetrachloride to water cooled to 4°C. The temperature and component mixing of reactants were controlled by an apparatus developed for automatic colloid preparation.[18] Herein we utilized the photocatalytic activity of TiO_2 to synthesize biological molecules via microwave irradiation. The main drawback for using TiO_2 itself for catalytic action is that it absorbs light energy in the UV part of the spectrum. It has been found that surface atoms of TiO_2 are coordinated[19] with the organic molecules and provide an opportunity for alternating the effective band gap of nanoparticles.

From the above results, it can be seen that the generality of this facile condensation was established in the presence of titanium dioxide nanosurface under solvent-free conditions to furnish the corresponding quinolines. By comparison, substrates **4a–c** and **d** demonstrate a superior reaction activity to the conventional method of approach, which consumed 39–50 min for completion of the reaction, in which the employed microwave output is only 150 W. Because the foregoing



SCHEME 1 Synthetic route for quinoline-3-carbonitriles (where R1 = H, CH_3, and OCH_3).

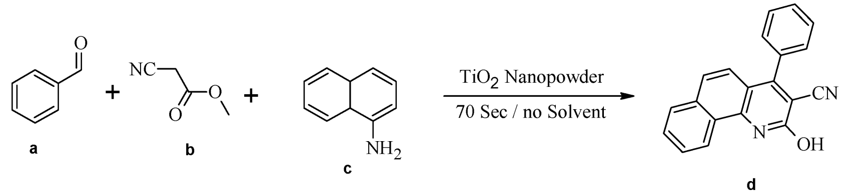
optimization work has demonstrated that this kind of reaction can also be efficiently promoted by conventional heating under neat conditions, we tried to obtain all the above products under solvent-free conditions (Schemes 1 and 2).

CONCLUSION

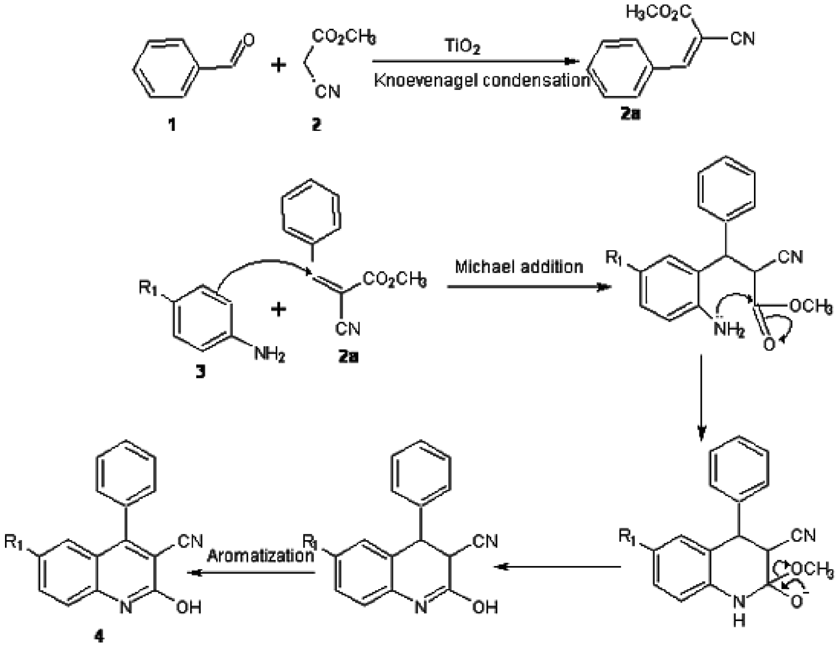
In conclusion, we have described the efficient synthesis of novel quinoline/benzo[*h*]quinoline -3-carbonitriles by using TiO_2 nano catalyst. The structures of **4a–c, d** were confirmed by elemental analysis, IR, NMR, and mass spectroscopic data. Finally, the obtained molecular ion peaks matching to their exact molecular weights for all the compounds (**4**, **4a**, **4b**, and **d**) provides additional strong evidence for the expected structure. This also provided proof that further aromatization took place successfully. A plausible mechanism for formation of target molecules (**4**, **4a**, **4b,** and **d**) is outlined in Scheme 3. We tried to gain the intermediates by carrying out the same reactions under dry nitrogen, but the same products were obtained.

EXPERIMENTAL

A dry, 50 mL flask was charged with arylaldehyde (5 mmol), cyano acetate (5 mmol), aniline (5 mmol), and titanium dioxide (TiO_2) nanopow-



SCHEME 2 Synthetic route for benzo[*h*]quinoline-3-carbonitrile.



SCHEME 3 A suggested mechanism for both 2-hydroxy-4-phenyl/ benzo[*h*]quinoline -3-carbonitrile.

der (500 mg). The mixture was well mixed, and then irradiated in a SANYOEM-350S microwave oven at 300W or 150W for a designated time (60 sec) as required for completing the reaction (determined by TLC); see Table I. Then, after being cooled to room temperature, under these conditions, the reaction mass was poured on crushed ice, the solid material was filtered off, and the crude product was purified by recrystallization from DMF. The similar reaction procedure has been followed for other derivatives.

TABLE I Reaction Time Data of Both Conventional and MW Methods

Compound	Time (min)—Conventional heating	Time (Sec)—MW
4a	45	60
4b	48	65
4c	39	60
4d	50	70

2-Hydroxy-4-phenylquinoline-3-carbonitrile (4a)

Pale red solid, Yield 85%, mp 132°C ; IR (ν) (KBr) cm^{-1}; 3019 (C-H, Ar-H); 2224 (C=N); 3278 (OH); ^{1}H NMR (DMSO d$_6$), δ 7.65 (d, 1H, Ar-H, $J = 8.03$ Hz), 7.58 (d, 1H, Ar-H, $J = 7.63$ Hz), 7.36 (d, 1H, Ar-H, $J = 7.45$ Hz), 7.94 (d, 1H, Ar-H, $J = 8.77$ Hz), 7.24 (d, 1H, Ar-H, $J = 7.13$ Hz), 7.27 (d, 1H, Ar-H, $J = 7.35$ Hz), 7.47 (d, 1H, Ar-H, $J = 7.37$ Hz), 7.45 (d, 1H, Ar-H, $J = 7.37$ Hz), 7.34 (d, 1H, Ar-H, $J = 7.47$ Hz), 11.2 (s, 1H, O-H, $J = 11.03$ Hz); m/z (%) [M]+ :[246]+; Elemental anlysis, Found: C, 78.04; H, 4.08; N, 11.37. Calculated for $C_{16}H_{10}N_2O$: C, 78.03; H, 4.09; N, 11.38.

2-Hydroxy-6-methyl-4-phenylquinoline-3-carbonitrile (4b)

Brown solid, Yield 68%, mp 121°C ; IR (ν) (KBr) cm^{-1}; 3025 (C-H, Ar-H); 2231 (C=N); 3298 (OH); 2950 (C-H of CH_3); ^{1}H NMR (DMSO d$_6$), δ 7.43 (d, 1H, Ar-H, $J = 7.68$ Hz), 7.45 (d, 1H, Ar-H, $J = 7.61$ Hz), 7.85 (d, 1H, Ar-H, $J = 8.05$ Hz), 7.48 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.32 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.22 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.32 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.48 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.34 (d, 1H, Ar-H, $J = 7.47$ Hz), 2.36 (d, 3H, CH_3), 11.5 (s, 1H, O-H, $J = 11.03$ Hz); m/z (%) [M]+ :[260]+; Elemental anlysis, Found: C, 78.43; H, 4.66; N, 10.77. Calculated for $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76.

2-Hydroxy-6-methoxy-4-phenylquinoline-3-carbonitrile (4c)

Brown solid, Yield 76%, mp 112°C ; IR (ν) (KBr) cm^{-1}; 3021 (C-H, Ar-H); 2236 (C=N); 3284 (OH); 1250 (C-O-C of OCH_3); ^{1}H NMR (DMSO d$_6$), δ 6.94 (d, 1H, Ar-H, $J = 7.68$ Hz), 7.31 (d, 1H, Ar-H, $J = 7.61$ Hz), 7.84 (d, 1H, Ar-H, $J = 8.05$ Hz), 7.50 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.35 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.28 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.28 (d, 1H, Ar- H, $J = 7.26$ Hz), 7.54 (d, 1H, Ar-H, $J = 7.26$ Hz), 3.73 (d, 3H, OCH_3), 11.2 (s, 1H, O-H, $J = 11.03$ Hz); m/z (%) [M]+ :[276]+; Elemental anlysis, Found: C, 73.91; H, 4.39; N, 10.13. Calculated for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14.

2-Hydroxy-4-phenylbenzo[h]quinoline-3-carbonitrile (4d)

Dark violet solid, Yield 81%, mp 151°C; IR (ν) (KBr) cm^{-1}; 3015 (C-H, Ar-H); 2225 (C=N); 3271 (OH); ^{1}H NMR (DMSO d$_6$), δ 7.64 (d, 1H, Ar-H, $J = 7.68$ Hz), 7.35 (d, 1H, Ar-H, $J = 7.43$ Hz), 7.67 (d, 1H, Ar-H, $J = 7.67$ Hz), 7.32 (d, 1H, Ar-H, $J = 7.32$ Hz), 7.34 (d, 1H, Ar-H, $J = 7.32$ Hz), 7.72 (d, 1H, Ar-H, $J = 7.68$ Hz), 7.48 (d, 1H, Ar-H, $J = 7.26$

Hz), 7.32 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.22 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.32 (d, 1H, Ar-H, $J = 7.26$ Hz), 7.48 (d, 1H, Ar-H, $J = 7.26$ Hz), 11.8 (s, 1H, O-H, $J = 11.03$ Hz); m/z (%) [M]+ :[296]+; Elemental anlysis, Found: C, 81.08; H, 4.07; N, 9.46. Calculated for $C_{20}H_{12}N_2O$: C, 81.07; H, 4.08; N, 9.45.

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