TiO2 nanotubes catalyzed the synthesis of azo-linked xanthenes under ultrasonic conditions

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ABSTRACT
A series of new azo-linked xanthene derivatives was synthesized via the eco-friendly multi-component condensation of azo-linked salicylaldehyde derivatives and dimedone under ultrasound irradiation as green energy source in the presence of TiO2 nanotubes (TNTs) as suitable heterogeneous catalyst. TNTs have moderate surface areas (S_{BET} = 238 m2.g−1) and high physiochemical stability (> 250°C). The yield of 74–87% was achieved within 10 min at room temperature. The current method has advantages such as the simple experimental procedure, green conditions, utilization of reusable TiO2 nanotubes catalyst, and good to excellent yield of products.

Introduction
The researchers are attempting to develop novel processes which facilitate the development of organic compounds focused in the area of medicinal and green chemistry. Azo dyes are synthetic colors that contain only one azo group, but some contain two (disazo), three (trisazo), or more. Azo dyes account for approximately 60–70% of all dyes used in food and textile manufacture. The azo group can be stabilized by making aromatic groups around the N=N bond as a part of an extended delocalized system. Aromatic azo compounds are usually stable and tend to produce strong vivid colors. A coupling component and a diazo component are required for making an azo dye. Since these can be altered considerably, an enormous range of possible dyes are available. Xanthenes and their analogues display a broad range of applications in medicinal and pharmaceutical industries as antimicrobial, antioxidiant, antimalarial, anti-inflammatory, and anticancer agents. They were also used in dyes and pigments and as luminescent sensors.

Ultrasound as an eco-environmental technology in green chemistry has advantages over the traditional thermal methods as enhanced reaction rates, formation of purer products, improved yields, suppression of side products, increased selectivity, easier experimental procedures, and use of milder conditions. Titanium dioxide (TiO2) nanotubes (TNTs) have attracted extensive research because of its novel properties such as chemical stability, large surface area, non-toxicity, and low production cost. A large number of diverse applications that include solar dye-sensitized solar cells have been found, photocatalysts, orthopedic and bioimplant applications, solid-phase extraction adsorbents, solar energy applications, and photo-electrochemical cells for the solar generation of hydrogen.

The heterogeneous catalysis offers three main advantages over homogeneous catalysis: (1) the catalyst can be recycled; (2) the separation and purification of the biodiesel and glycerol products is easier due to the absence of salts and diminished soaps formation; and (3) significant reduction in the water required to wash the product phases.

In pursuit of our recent studies to develop environmentally friendly synthetic methodologies and the reported synthesis of azo-linked dihydropyridines, the present work envisioned the green chemical approach involving ethanol mediated domino reaction in efficient synthesis of the 9-[5-(E)-(aryl diazenyl)-2-hydroxyphenyl]-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2H-xanthene-1,8(5H,9H)-diones with ecological benefits under ultrasonic condition at room temperature. To the best of our knowledge, for the first time, an eco-friendly process was developed for the synthesis of novel 9-[5-(aryl diazenyl)-2-hydroxyphenyl]-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2H-xanthene-1,8(5H,9H)-dione from 5-(E)-(aryl diazenyl)-2-hydroxynaldehyde and dimedone in the presence of TNTs under ultrasound irradiation. The environmental impact is reduced by the fact that all reactions are carried out in ethanol, which is easy and cheap to obtain.

Experimental

Materials
Unless specified, all chemicals were analytical grade and purchased from Merck, Aldrich, and Fluka Chemical Companies and used without further purification. The purity