Catalysis Communications 63 (2015) 10–14

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Easy entry to donor/acceptor butadiene dyes through a MW-assisted $InCl_3$-catalyzed coupling of propargylic alcohols with indan-1,3-dione in water

Javier Francos [a], Javier Borge [b], Josefina Díez [a], Sergio E. García-Garrido [a,*], Victorio Cadierno [a,*]

[a] Laboratorio de Compuestos Organometálicos y Catálisis (Unidad Asociada al CSIC), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Departamento de Química Orgánica e Inorgánica, IUQOEM, Facultad de Química, Universidad de Oviedo, Julián Clavería 8, E-33006 Oviedo, Spain
[b] Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Julián Clavería 8, E-33006 Oviedo, Spain

ARTICLE INFO

Article history:
Received 26 May 2014
Received in revised form 14 July 2014
Accepted 16 July 2014
Available online 25 July 2014

Keywords:
Homogeneous catalysis
Aqueous catalysis
Indium trichloride
Meyer–Schuster rearrangement
C–C couplings
Butadiene dyes

ABSTRACT

In this contribution, the high-yield preparation and optical properties of some donor-acceptor butadiene dyes, generated by coupling of different 1,1-diaryl-2-propyn-1-ols with indan-1,3-dione, are presented. The reactions, which involve the initial Meyer–Schuster rearrangement of the aromatic alkynols and subsequent condensation of the resulting enals with the β-dicarbonyl compound, proceeded cleanly in water, under MW irradiation, in the presence of catalytic amounts of the inexpensive Lewis acid $InCl_3$. A single-crystal X-ray diffraction study of one of these dyes is also included.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

During the last decades much attention has been paid to the development of synthetic organic chemistry in water, because water is cheaper, safer and environmentally benign compared with traditional organic solvents [1–3]. The use of microwave irradiation (MW) as a heating source has also become very popular since MW techniques enable high-speed syntheses at lower energetic costs [4–7]. In the search for synergistic effects and more sustainable synthetic protocols, the combined use of water and MW irradiation has also been considered, and a number of stoichiometric and catalytic transformations have been successfully developed in the most recent years under these experimental conditions [8–11]. In this context, we have described an efficient and general MW-assisted protocol for the Meyer–Schuster rearrangement of propargylic alcohols in water using inexpensive $InCl_3$ as catalyst (Scheme 1) [12]. It should be recalled that the Meyer–Schuster reaction represents one of the most straightforward and atom-economical routes presently available for the preparation of synthetically valuable and versatile α,β-unsaturated carbonyl compounds (enals and enones) [13,14].

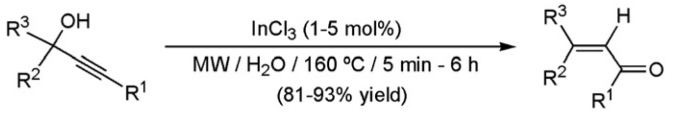
Based on this aqueous MW-assisted reaction, we report herein the high yield preparation of a family of push–pull 1,1-diaryl-butadiene-4,4-diones **4** through the coupling of indan-1,3-dione **1** with different 1,1-diaryl-2-propyn-1-ols **2** (Scheme 2). The process involves the Knoevenagel condensation of the *in situ* formed enals **3**, resulting from the Meyer–Schuster rearrangement of the 1,1-diaryl-2-propyn-1-ols, with the β-dicarbonyl compound. We should note that related tandem isomerization/condensation processes of propargylic alcohols with enolizable ketones have been previously described by us and others using ruthenium catalysts [15–17] and Brønsted acids [18] as promoters in organic media, but are unprecedented in water.

Polyenic push–pull compounds containing the indanedione fragment as the acceptor group (Fig. 1) have attracted considerable interest since they exhibit relevant optical and electronic properties, founding applications for example as second-order nonlinear optical chromophores [19–21]. These species are typically synthesized by Knoevenagel condensation of indan-1,3-dione **1** with the corresponding aldehyde. The method presented herein opens an alternative synthetic path starting from propargylic alcohols, *via in situ* generation of the aldehyde partner, and also represents a new example of an efficient and synthetically useful indium-catalyzed organic reaction in aqueous media [22,23].

---

* Corresponding authors. Tel.: +34 985103463, +34 985103453; fax: +34 985103446.
E-mail addresses: garciagsergio@uniovi.es (S.E. García-Garrido), vcm@uniovi.es (V. Cadierno).

http://dx.doi.org/10.1016/j.catcom.2014.07.028
1566-7367/© 2014 Elsevier B.V. All rights reserved.



Scheme 1. MW-assisted $InCl_3$-catalyzed Meyer–Schuster rearrangement of propargylic alcohols in water.

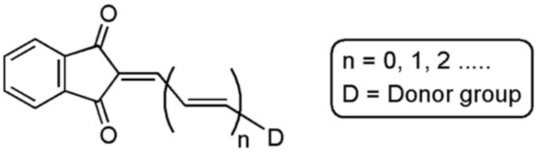


Fig. 1. General structure of indanedione-based push–pull polyenes.

2. Experimental

2.1. Materials and methods

All reagents were obtained from commercial suppliers and used without further purification with the exception of propargylic alcohols **2b** [24], **2c** [25], **2d** [26], **2e** [27], **2f** [27] and **2g** [28], which were prepared by following the methods reported in the literature. Flash chromatography was performed using Merck silica gel 60 (230–400 mesh). UV–Vis spectra were linearly recorded in wavelength on a Perkin-Elmer Lambda 20 spectrometer at 20 °C using a matched pair of quartz cells 1 cm in path length. Since the individual absorption bands in the spectra were overlapped, accurate λ_{max} values were determined by decomposition of the spectra in the sum of Gaussian functions, after applying a smoothing spline algorithm to the observed data followed by a derivative spectroscopy numerical method (only the negative peaks of the second derivatives of the smoothed spectra were used for the estimation of the position of the bands) [29]. All mathematical analyses were performed with MATLAB R2012b.

2.2. General procedure for the catalytic synthesis of the indane-1,3-dione-based dyes

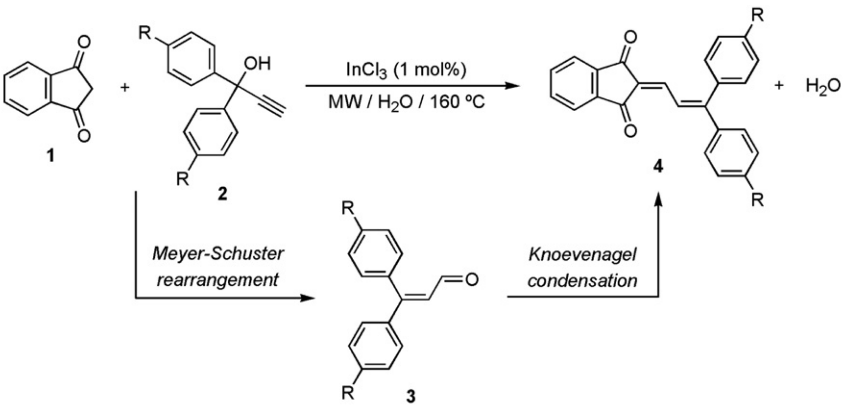
A pressure-resistant septum-sealed glass microwave reactor vial was charged with indan-1,3-dione **1** (0.146 g, 1 mmol), the corresponding propargylic alcohol (**2a–g**; 1 mmol), $InCl_3$ (2.2 mg, 0.01 mmol), a magnetic stirring bar and water (1 mL). The vial was then placed inside the cavity of a CEM Discover® S-Class microwave synthesizer and power was held at 300 W until the desired temperature was reached (160 °C). Microwave power was automatically regulated for the remainder of the experiment to maintain the temperature (monitored by a built-in infrared sensor). The internal pressure during the reaction ranged between 15 and 90 psi. After completion of the reaction (see Table 1), the vial was cooled to room temperature, the reaction mixture transferred to a flask, the solvent evaporated under vacuum, and the crude residue purified by flash chromatography over silica gel using EtOAc/hexane (1:10) as eluent. Characterization data for compounds **4a–g** have been included as Supplementary Information in Appendix A.

3. Results and discussion

Following the optimal experimental conditions previously found to promote the catalytic Meyer–Schuster rearrangement of 1,1-diphenyl-2-propyn-1-ol **2a** into 3,3-diphenylpropenal **3a** by indium trichloride, *i.e.* employing 1 mol% of $InCl_3$, 1 M solution of **2a** in water and MW heating at 160 °C (300 W) [12], we studied the reaction in the presence of 1 equivalent of indan-1,3-dione **1**. To our delight, clean formation of the butadienic derivative 2-(3,3-diphenylallylidene)-indan-1,3-dione **4a** was observed after 30 min of irradiation, with no side products being observed in the reaction crude by GC (only traces of the reactants and the intermediate enal **3a** were detected) [30]. Solvent removal and chromatographic work-up on silica gel provided analytically pure **4a** in 88% yield (entry 1 in Table 1). Remarkably, neither an inert atmosphere nor an organic co-solvent was required. In an independent experiment, we confirmed that treatment of isolated 3,3-diphenylpropenal **3a** with indan-1,3-dione **1** under identical reaction conditions proceeds cleanly to generate the butadiene derivative **4a** in 85% after 20 min, thus confirming the proposed Meyer–Schuster/Knoevenagel sequence.

We must note that the condensation between **3a** and **1** also takes place in the absence of $InCl_3$, however a longer irradiation period (2 h) was in this case needed to generate **4a** in high yield (84%). On the other hand, no reaction occurred when an aqueous mixture of 1,1-diphenyl-2-propyn-1-ol **2a** and indan-1,3-dione **1** was irradiated in the absence of $InCl_3$. This fact is in complete accord with our previous observations that showed the need of a Lewis acid to promote the Meyer–Schuster rearrangement of **2a** into **3a**. Also of note is the fact that the use of organic solvents (such as toluene, 1,4-dioxane or DMF) instead of water led, under identical experimental conditions, to **4a** in very low yields (<30% by CG after 30 min of irradiation).

As shown in Table 1, other 1,1-diaryl substituted propargylic alcohols **2b–g** also reacted with indan-1,3-dione **1**, in water and in the presence of $InCl_3$ (1 mol%), to afford the corresponding conjugated 2-(3,3-diarylallylidene)-indan-1,3-diones **4b–g** in good to excellent yields (85–95%) after 20–180 min of MW irradiation (see entries 2–7) [31]. A significant influence of the electronic properties of the aryl rings on the reaction rates was observed. Thus, alkynols with electron-withdrawing groups showed a lower reactivity (entries 2–3) in comparison with the unsubstituted one (entry 1) and those containing



Scheme 2. MW-assisted $InCl_3$-catalyzed synthesis of butadienes **4** in water.

Download English Version:

https://daneshyari.com/en/article/50354

Download Persian Version:

https://daneshyari.com/article/50354

Daneshyari.com