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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

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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.

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].

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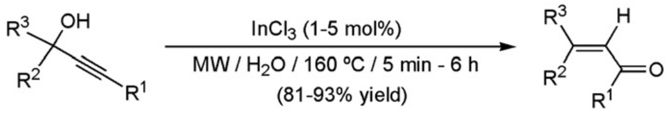


Scheme 1. MW-assisted $InCl_3$-catalyzed Meyer–Schuster rearrangement of propargylic alcohols in water.

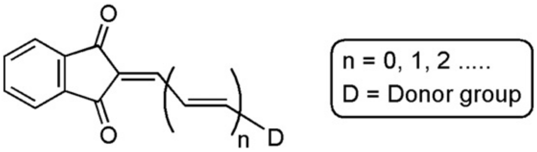


Fig. 1. General structure of indanedione-based push–pull polyenes.

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

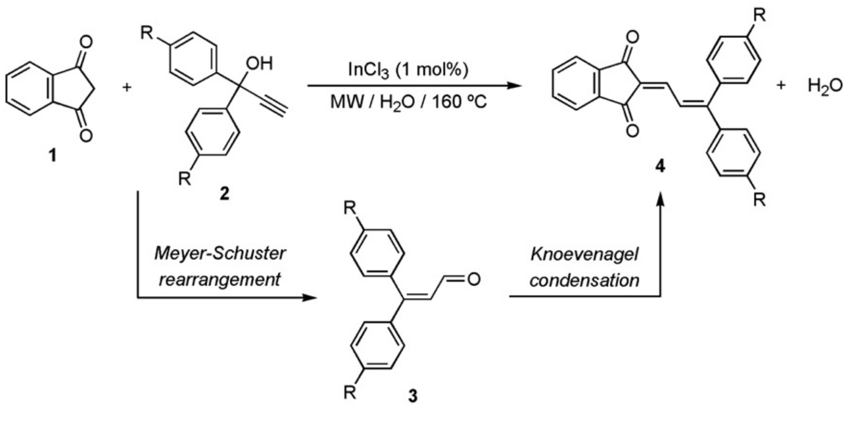
A pressure-resistant septum-sealed glass microwave reactor vial was charged with indan-1,3-dione **1** (0.146 g, 1 mmol), the corresponding propargylic alcohol (**2a–g**; 1 mmol), $InCl_3$ (2.2 mg, 0.01 mmol), a magnetic stirring bar and water (1 mL). The vial was then placed inside the cavity of a CEM 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.

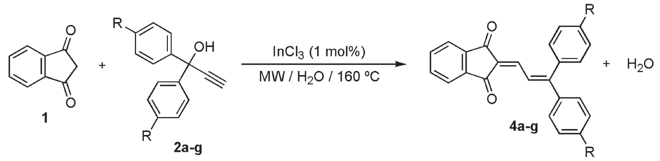
We must note that the condensation between **3a** and **1** also takes place in the absence of $InCl_3$, however a longer irradiation period (2 h) was in this case needed to generate **4a** in high yield (84%). On the other hand, no reaction occurred when an aqueous mixture of 1,1-diphenyl-2-propyn-1-ol **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).

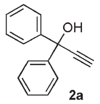
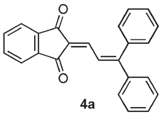
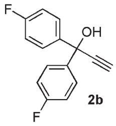
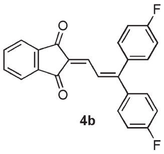
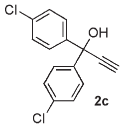
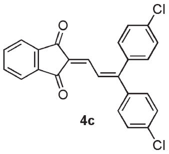
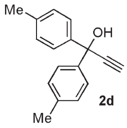
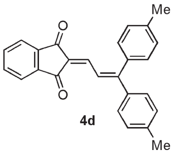
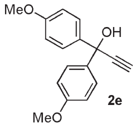
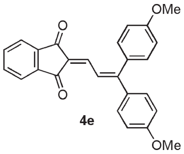
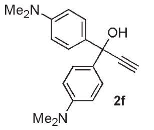
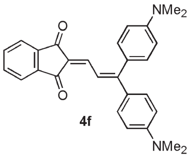
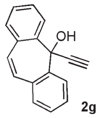
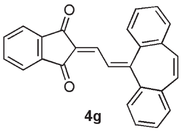
As shown in Table 1, other 1,1-diaryl substituted propargylic alcohols **2b–g** also reacted with indan-1,3-dione **1**, in water and in the presence of $InCl_3$ (1 mol%), to afford the corresponding conjugated 2-(3,3-diarylallylidene)-indan-1,3-diones **4b–g** in good to excellent yields (85–95%) after 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.

Table 1
Synthesis of 2-(3,3-diarylallylidene)-indan-1,3-dione dyes **4a–g** by MW-assisted coupling of propargylic alcohols **2a–g** with indan-1,3-dione **1** in water.



Entry	Alkynol **2a–g**	Product **4a–g**	Time (min)	Yield (%)[a]
1	 **2a**	 **4a**	30	88
2	 **2b**	 **4b**	180	86
3	 **2c**	 **4c**	180	90
4	 **2d**	 **4d**	30	85
5	 **2e**	 **4e**	20	95
6	 **2f**	 **4f**	20	90
7	 **2g**	 **4g**	20	92

Reactions were performed under air atmosphere in a CEM Discover® S-Class microwave synthesizer at 160 °C, through moderation of the initial microwave power (300 W), starting from 1 mmol of the corresponding propargylic alcohol **2a–g** (1 M in water), 1 mmol of indan-1,3-dione **1**, and 0.01 mmol of $InCl_3$.

[a] Isolated yield after chromatographic work-up.

electron-donating functionalities (entries 5–6). As inferred by monitoring the catalytic reactions by GC, the rate limiting step of this tandem process is in all cases the Knoevenagel condensation between the intermediate enal $R^1R^2C=CHCHO$ **3a–g** and indan-1,3-dione **1**, which is obviously favored with electron-rich substrates.

The butadienic compounds **4a–g** were characterized by elemental analyses, mass spectrometry, and IR and NMR (^1H, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$) spectroscopy, all data being fully consistent with the structural proposal. In addition, the molecular structure of **4e** was determined by X-ray diffraction analysis, for which good quality crystals could be obtained by slow diffusion of *n*-hexane into a saturated solution of the compound in ethyl acetate. An ORTEP-type drawing of the molecule, along with selected bonding parameters, is shown in Fig. 2. In the structure it is seen that the indanedione moiety, the butadiene chain and one of the phenyl groups are largely coplanar, with the second phenyl group being perpendicularly twisted out of this plane (dihedral angle C(11)–C(12)–C(13)–C(14) of 67.39(16)°). As expected, the butadiene moiety reflects some π-electron delocalization, as indicated by the slightly longer C(9)–C(10) (1.356(2) Å) and C(11)–C(12) (1.363(2) Å), and shorter C(10)–C(11) (1.424(2) Å), lengths in comparison to those typically found for C_{sp2}–C_{sp2} double and single bonds (1.32 and 1.44 Å, respectively) [32].

The optical properties of compounds **4a–g** were investigated by means of UV–Vis spectroscopy in dichloromethane solution. The spectra showed intense absorption bands in the visible region, with maxima in the range of 405–565 nm (see Fig. 3 and Table 2). As can be seen in Fig. 3, the presence of the strong electron-donor dimethylamino substituents in **4f** resulted in a significant bathochromic shift of the absorption band, indicating a high degree of electronic conjugation for this compound.

The solvatochromic behavior of these dyes was also briefly evaluated using **4f**, absorbing at the longest wavelength, as model. The UV–Vis

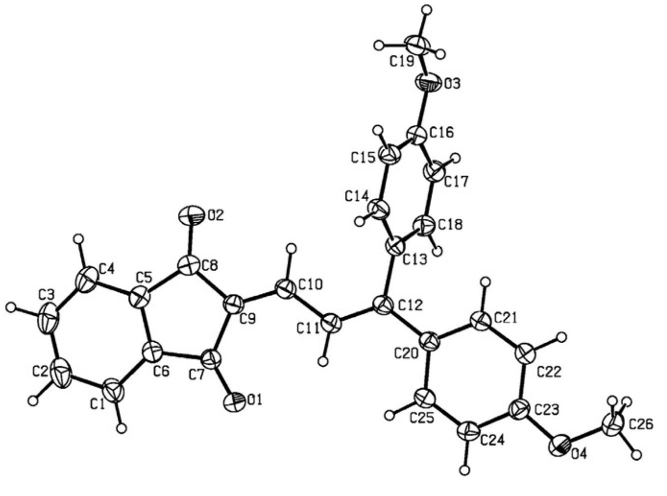


Fig. 2. ORTEP-type view of the structure of compound **4e** showing the crystallographic labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): C(7)–O(1) = 1.218(2); C(7)–C(9) = 1.480(2); C(8)–O(2) = 1.218(2); C(8)–C(9) = 1.483(2); C(9)–C(10) = 1.356(2); C(10)–C(11) = 1.424(2); C(11)–C(12) = 1.363(2); C(12)–C(13) = 1.496(2); C(12)–C(20) = 1.471(2); C(7)–C(9)–C(8) = 107.6(1); C(7)–C(9)–C(10) = 129.5(1); C(8)–C(9)–C(10) = 122.8(1); C(9)–C(7)–O(1) = 128.0(1); C(9)–C(8)–O(2) = 126.9(1); C(9)–C(10)–C(11) = 127.0(1); C(10)–C(11)–C(12) = 123.8(1); C(11)–C(12)–C(13) = 120.4(1); C(11)–C(12)–C(20) = 122.7(1); C(13)–C(12)–C(20) = 117.0(1).

Table 2
Absorption properties of dyes **4a–g** in dichloromethane solution.[a]

Compound	λ_{max} (nm)	ε ($M^{-1}\cdot cm^{-1}$)
4a	405	35,440
4b	405	38,230
4c	404	26,250
4d	421	34,750
4e	453	37,184
4f	565	32,801
4g	416	18,100

[a] Spectra recorded using 6×10^{-5} M solutions.

Table 3
λ_{max} values of dye **4f** in various solvents together with the π^*_{azo} values of solvents.[a]

Solvent	λ_{max} (nm)	π^*_{azo}
n-Hexane	530	−0.09
Diethyl ether	549	0.16
Ethyl acetate	558	0.37
1,4-Dioxane	558	0.34
Toluene	560	0.38
Benzene	564	0.40
2-Butanone	571	0.61
Acetone	571	0.53
Acetonitrile	575	0.63
Chlorobenzene	575	0.58
Chloroform	578	0.62
Dichloromethane	578	0.62
Pirydine	586	0.80
N,N-dimethylformamide	586	0.86
Benzonitrile	587	0.82
Ethanol	590	0.86
Nitrobenzene	591	0.91
Methanol	592	0.89
Dimethyl sulfoxide	595	1.00

[a] Spectra recorded using 6×10^{-5} M solutions. π^*_{azo} values taken from reference [33].

spectra of this compound recorded in different organic solvents showed a significant bathochromic shift of the absorption maximum with increasing the solvent polarity, *i.e.* $\Delta\lambda_{max} = 65$ nm on going from *n*-hexane to dimethyl sulfoxide (see Table 3). In addition, a good linear correlation ($r = 0.9926$) was observed with the π^*_{azo} scale [33], one of the most popular empirical scales used for the quantification of solvent polarity (see Fig. 4) [34,35]. This fact clearly indicates the great potential of this type of indan-1,3-dione-based butadiene dyes as new solvatochromic polarity probes.

Finally, we would like to stress that the present C–C coupling process is also operative with secondary propargylic alcohols, as exemplified by the high yield preparation of the known compound **5** [19] starting from indan-1,3-dione and 1-phenyl-2-propyn-1-ol (**2h**) (Scheme 3). In complete accord with our previous results in the $InCl_3$-catalyzed Meyer–Schuster rearrangement of secondary propargylic alcohols [12], only the *E*-isomer of compound **5** was formed ($^3J_{HH} = 15.8$ Hz).

Also of note is that other 1,3-dicarbonyl compounds, such as 2,4-pentanedione (**6**), can be employed. Thus, the reaction of **6** with 1,1-diphenyl-2-propyn-1-ol (**2a**), under identical experimental conditions, allowed us to generate the butadiene derivative **7** [18] in 87% isolated yield (Scheme 3). All these facts confirm the great potential of this aqueous transformation for the construction of keto-functionalized butadiene frameworks.

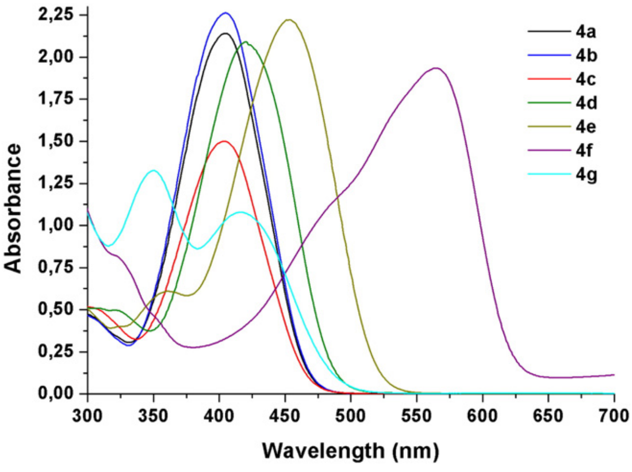


Fig. 3. UV–Vis spectra of compounds **4a–g** in CH_2Cl_2.

4. Conclusions

In summary, a new and efficient protocol for the preparation of indanedione-based butadiene derivatives has been developed employing inexpensive $InCl_3$ as catalyst, environmentally friendly water as solvent and microwave irradiation as the heating source. The classical preparation of this type of compounds involves the Knoevenagel condensation of indan-1,3-dione with aldehydes, but here we have shown that propargylic alcohols instead of aldehydes can be alternatively employed as the starting materials due to the ability of $InCl_3$ to promote the Meyer–Schuster reaction. Further studies directed to the application of this new C–C coupling process to the preparation of other butadienic

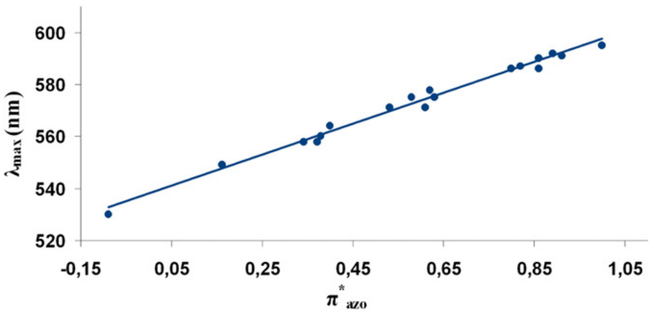
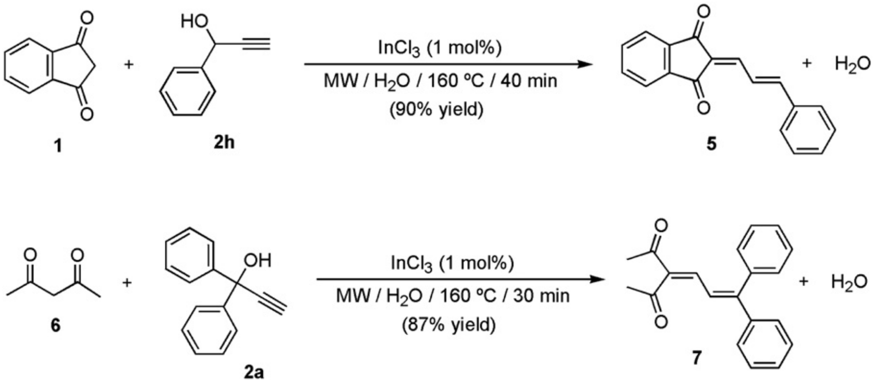


Fig. 4. λ_{max} *vs* π^*_{azo} values for dye **4f** (fitting results: $\lambda_{max} = 538.10 + 59.35\pi^*_{azo}$).



Scheme 3. MW-assisted InCl$_3$-catalyzed synthesis of the 1,3-butadiene compounds **5** and **7** in water.

push–pull dyes are now in progress in our laboratory and will be the subject of future contributions.

Acknowledgments

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Appendix A. Supplementary data

Characterization data for compounds **4a–g**, X-ray crystal structure determination of compound **4e**, and copies of the NMR spectra of **4a–g**, **5** and **7**. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.07.028.

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