Catalysis Today 190 (2012) 144–149

Contents lists available at SciVerse ScienceDirect

Catalysis Today

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

# p-Cymenesulphonic acid: An organic acid synthesised from citrus waste

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ARTICLE INFO

*Article history:*
Received 30 September 2011
Received in revised form 7 December 2011
Accepted 7 December 2011
Available online 4 January 2012

*Keywords:*
Acid catalysis
Citrus waste
*p*-Cymene
*p*-Cymenesulphonic acid
Green chemistry
Limonene

ABSTRACT

An organic acid, *p*-cymene-2-sulphonic acid, is synthesised from citrus waste and demonstrated to be comparable to *p*-toluenesulphonic acid in examples of acid catalysis. Firstly the essential oil found in citrus waste is extracted by either steam distillation or microwave irradiation. Oxidising the limonene in the citrus oil to *p*-cymene followed by sulphonation gives *p*-cymene-2-sulphonic acid.

## 1. Introduction

The use of *p*-toluenesulphonic acid (*p*-TSA) is ubiquitous throughout synthetic organic chemistry [1]. As a strong acid that is also soluble in organic solvents, it is widely used as a Brønsted acid catalyst for Fischer esterifications and similar reactions. Historically *p*-TSA was synthesised by the sulphonation of toluene as an intermediate in the production of *p*-cresol [2]. Because this valuable process is based on a petrochemical substrate it is beneficial to seek a sustainable alternative. As prices and demand for limited oil resources continue to rise worldwide, alternative renewable feedstocks will become a necessity. The general public, followed by the retail sector, are pushing for greener products and formulations and in doing so increasing the need for bio-chemicals. Recent developments in EU directives and future standards on bio-based products will encourage greater use of biomass instead of finite resources towards a point where it becomes both economically and environmentally beneficial to do so.

The most easily accessible renewable replacement for toluene is *p*-cymene, derived from naturally occurring monoterpenes. It is a major component of the spruce turpentine obtained from the sulphite wood pulping process [2,3]. *p*-Cymene can fulfil an analogous role to toluene in many respects. Primarily the sulphonation of *p*-cymene gives *p*-cymene-2-sulphonic acid (*p*-CSA) [3–7]. *p*-Cresol can also be made from *p*-cymene *via* its hydroperoxidation. Although the reaction benefits from acetone as a value-adding co-product the transformation is no longer performed industrially.

The sulphonation of *p*-cymene from turpentine has been performed as a means of obtaining carvacrol, analogous to the alkali fusion of *p*-TSA by which *p*-cresol is made [3]. Sulphonation occurs primarily at the 2-position relative to the methyl group, and this isomer can be selectively recrystallised from the reaction mixture (Scheme 1). Sodium *p*-cymenesulphonate is regarded as a good hydrotrope [8].

An alternative route for obtaining *p*-cymene is the oxidation of the (*R*)-(+)-limonene (henceforth referred to as limonene) present in the peel of citrus fruits [9,10]. Although commercially significant terpenes have been artificially synthesised since the 1950s, limonene is marketed as a natural product sought for its aroma and solvent properties. In terms of international trade, citrus fruits are considered as a commodity product on a par with coffee or tea. As the largest fruit crop in the world with over 110 million tonnes grown every year [11], the processing industry, where up to 60% of the whole fruit is discarded, generates citrus waste (peel, seeds, membrane, and pulp) on a massive scale [12]. Orange processing is responsible for 90% of the citrus waste created by juicing operations [13]. The largest contributing nation is Brazil, producing 8 million tonnes of orange waste every year. The waste does not currently have any high-value applications. Instead the majority is disposed of or pelletised for animal feed [11,12].

Citrus oil yields of up to 5% based on the dry citrus waste mass have been obtained using supercritical carbon dioxide extraction technology, although steam distillation and its variants are more routine methods where extraction efficiencies of over 90% are obtainable [14,15]. Considering that 5 kg of essential oil can be

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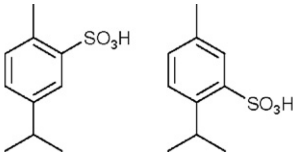
doi:10.1016/j.cattod.2011.12.007



**Scheme 1.** The 2- (left) and 3- (right) isomers of *p*-cymenesulphonic acid. For simplicity *p*-CSA is used in this work to refer to the former isomer only.

extracted from a tonne of oranges, then almost 92,000 tonnes of essential oil could be obtained from Brazil's production of oranges alone [12]. Because limonene constitutes at least 90% of the essential oil from oranges, Brazil could potentially produce in the order of 82,500 tonnes of limonene annually.

Limonene is not the only useful product that can be retrieved from citrus waste [12]. Ethanol or succinic acid can be produced by fermentation after removal of the essential oil [15,16]. Then pectin can be retrieved before the remaining residues are anaerobically digested to afford methane [16]. This bio-refinery model has been demonstrated as being economically viable [17], offering a profitable and environmentally valuable alternative to current waste disposal practices. In doing so it is possible to harness the chemical potential of waste using green chemical technologies to obtain sought-after properties for everyday products.

Demand for *p*-cymene has made its synthesis from limonene a viable chemical process. One burgeoning application is the synthesis of terephthalate polyesters using limonene as the start material for terephthalic acid *via* *p*-cymene [18–20]. Metal functionalised clays have been shown to be active dehydrogenation catalysts in the conversion of limonene to *p*-cymene. Microwave assisted methods give quantitative yields of *p*-cymene from limonene but require almost 1.5 equivalents of an iron impregnated clay (based on iron loading) [21]. Reducing the catalyst loading to 4 mol% resulted in 88% selectivity. More exotic catalysts have also been used, notably palladium. This approach is hindered by the disproportionation of limonene to give substantial quantities of *p*-menthane. A $Pd/SiO_2$ catalyst is effective for this transformation only if 1-decene is used as a hydrogen acceptor [22].

## 2. Experimental

All reactions were conducted under an ambient atmosphere and without any purification of reagents prior to use. The Hammett acidity functions were determined using a Jasco V-550 UV/visible spectrophotometer. Thermal decomposition temperatures were obtained using a PL Thermal Sciences system (STA 625). Characterisation of reaction products was consistent with authentic samples where available.

### 2.1. Synthesis of p-cymene

A mixture of 10 wt% Pd/C (0.788 g, 1 mol%) and K-10 montmorillonite clay (1.48 g) was heated to 140 °C, and limonene (12 mL, 74.1 mmol) slowly added dropwise. The mixture was stirred at 140 °C for 1 h. The reaction then was cooled to room temperature and water (100 mL) added prior to steam distillation. The organic phase of the distillate was dried to give *p*-cymene as a colourless liquid (8.87 g, 89% yield, 71% selectivity as determined by GC–MS and $^1H$ NMR spectroscopy). NMR (400 MHz in $CDCl_3$): $\delta_H$ 7.22 (4H, m), 2.98 (1H, m), 2.43 (3H, s), 1.35 (6H, d)/ppm. NMR (100 MHz in $CDCl_3$): $\delta_C$ 146.1, 135.3, 129.2, 126.5, 33.9, 24.3, 21.1/ppm. MS (+EI): $m/z = 135$ ($M^+$).

### 2.2. Sulphonation of p-cymene

To *p*-cymene (5 mL) was slowly added 20% fuming sulphuric acid (5 mL). The reaction was stirred at room temperature for 4 h. After this time had elapsed stirring was stopped and water (6 mL) carefully added to avoid the mixture becoming hot. The diluted mixture was left to stand in a refrigerator overnight to produce a solid, which could be recrystallised from concentrated hydrochloric acid to give *p*-cymene-2-sulphonic acid dihydrate, 7.29 g, 91%. NMR (400 MHz in DMSO-$d_6$): $\delta_H$ 7.61 (1H, s), 7.08 (2H, m), 6.10 (1H, s), 2.83 (1H, m), 2.46 (3H, s), 1.14 (6H, d)/ppm. NMR (100 MHz in DMSO-$d_6$): $\delta_C$ 145.3, 145.1, 133.1, 131.2, 127.4, 124.7, 33.2, 24.3, 19.9/ppm. MS (−EI): $m/z = 213$ ($M^-$). Melting point ($T_m$): 50–51 °C.

### 2.3. Steam extraction of citrus waste

The flavedo (outer peel) was separated from the albedo (inner peel) of sixteen oranges (Navel late variety, diameter of 70–80 mm). Using a fine grater gave 110 g of wet citrus waste. To the separated flavedo was added 150 mL of water and distilled for 1 h. The organic phase of the distillate was dried to give 5.71 g of the essential oil (5.2 wt%).

### 2.4. Microwave assisted extraction of citrus waste

The microwave treatment of the whole orange peel (160 g) was conducted in a Milestone ROTO SYNTH Rotative Solid Phase Microwave Reactor with a 2.45 GHz multimode cavity. The extraction was performed for 12.5 min with a power gradient applied, increasing from 400 W to 1200 W (average power input 1025 W $min^{-1}$) until reaching a final temperature of 200 °C. Liquid products were then collected by distillation. The aqueous phase was extracted with ethyl acetate and the combined organic fractions dried to give 1.71 g of the essential oil (1.1 wt%). Analysis by GC confirmed the similarity of the citrus oil to that extracted by steam distillation, being predominantly limonene (≥90%).

### 2.5. Complete synthesis of p-CSA from the essential oil of oranges

The steam extracted citrus oil of sixteen oranges was added dropwise to a mixture of 10 wt% Pd/C (0.434 g, 1 mol%) and K-10 montmorillonite clay (0.815 g), pre-heated to 140 °C, and stirred for an hour once addition of the citrus oil was complete. The reaction was allowed to cool and 100 mL of water added. The solution was distilled, and the organic phase of the distillate dried to give crude *p*-cymene (4.43 g, 88% yield based on limonene content of citrus oil, 70% selectivity). To this colourless liquid was carefully added 3.5 mL of 20% fuming sulphuric acid. The reaction was stirred at room temperature for 4 h. After this time had elapsed stirring was stopped and water (4.2 mL) carefully added to avoid the mixture becoming hot. At this stage the *p*-menthane co-product caused by limonene disproportionation can be decanted. The diluted mixture was left to stand in a refrigerator overnight to solidify. The solid was retrieved by filtration to give *p*-cymene-2-sulphonic acid dihydrate (27% yield based on the *p*-cymene content of the reaction distillate, 16% total yield based on the limonene content of the citrus oil, and 27 wt% based on the mass of citrus oil).

### 2.6. Esterification kinetic experiments

To a solution of benzyl alcohol (0.541 g, 5.0 mmol) and the acid catalyst (*p*-TSA or *p*-CSA, 0.05 mmol) in the chosen solvent (5 mL) stirred at 50 °C was added acetic acid (0.330 g, 5.5 mmol). Aliquots of the reaction mixture were removed at convenient intervals and diluted with deuterated chloroform to allow the reaction progress to be monitored by $^1H$ NMR spectroscopy by the same method described by Welton and co-workers [23]. Comparison of the benzylic signals of benzyl alcohol (*e.g.* 4.73 ppm where *p*-cymene was the reaction solvent) and benzyl acetate (*e.g.* 5.14 ppm where *p*-cymene was the reaction solvent) could be used to determine the extent of acetylation using the integrated form of the second order rate equation as follows:

$$k_2t = \frac{1}{[B]_0 - [A]_o} \cdot \ln\left\{\frac{[A]_0([B]_0 - [P]_t)}{[B]_0([A]_0 - [P]_t)}\right\}$$

Key: $k_2$, rate constant (dm$^3$ mol$^{-1}$ s$^{-1}$); $t$, time (s); $[A]_0$, initial concentration of reactant A (mol dm$^{-3}$); $[B]_0$, initial concentration of reactant B (mol dm$^{-3}$); $[P]_t$, concentration of product P at time $t$ (mol dm$^{-3}$).

Reactions were typically allowed to proceed beyond 50% conversion to guarantee accuracy in the calculation of rate constants. Predicted conversions were also calculated using the integrated second order rate equation. Spectra were recorded with a Bruker 400 MHz spectrometer, and chemical shifts calibrated against the residual solvent signal. No calibration of the NMR proton signal integrals was found to be necessary.

### 2.7. Synthesis of ethyl levulinate

To a solution of levulinic acid (0.581 g, 5.0 mmol) in the chosen solvent (5 mL) was added either a Brønsted acid (*p*-TSA or *p*-CSA, 0.05 mmol) or a Lewis acid (In(OTf)$_3$, InCl$_3$, or FeCl$_3$, 0.25 mmol) followed by ethanol (0.230 g, 5.0 mmol). The reaction mixture was stirred at 50 °C under the ambient atmosphere for 20 h. After this time, the reaction was cooled and potassium carbonate added. Filtration of the reactions performed in either toluene or 2-MeTHF gave a filtrate that could be concentrated *in vacuo* to give the desired product, ethyl levulinate, in yields of up to 73% of the theoretical yield. Reactions conducted in *p*-cymene were similarly filtered and purified by column chromatography (hexane:ethyl acetate) to give ethyl levulinate (up to 76% yield).

### 2.8. Synthesis of 4-bromochalcone

A mixture of acetophenone (0.25 mL, 2.03 mmol), 4-bromobenzaldehyde (0.562 g, 3.04 mmol, and the acid catalyst (*p*-TSA or *p*-CSA, 0.10 mmol) was stirred at 120 °C under the ambient atmosphere for 24 h. The reaction was then allowed to cool, giving rise to fine needles of a white solid and an amorphous orange solid. The latter could be removed by recrystallisation with ethanol to give 4-bromochalcone (73% yield).

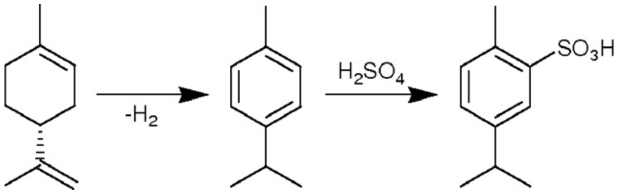
### 2.9. Synthesis of 2-(4-nitrophenyl)-1,3-dioxolane

A suspension of 4-nitrobenzaldehyde (1.511 g, 10.00 mmol) and the acid catalyst (*p*-TSA or *p*-CSA, 0.200 mmol) in cyclohexane was heated to reflux in Dean–Stark apparatus, at which point the mixture became homogeneous. 1,2-Ethanediol (0.621 g, 10.00 mmol) was then added and the reaction stirred at reflux under the ambient atmosphere for 5 h. The reaction was the left to cool, allowing the product, 2-(4-nitrophenyl)-1,3-dioxolane, to precipitate and be isolated by filtration (92% yield).

## 3. Results and discussion

### 3.1. Synthesis of p-CSA

The conversion of limonene to *p*-CSA consists of three distinct stages (Scheme 2). Firstly the isolation of the essential oil from citrus waste, followed by the aromatisation of limonene to *p*-cymene, and finally sulphonation to give the acid. For optimisation purposes, our initial studies were performed on pure limonene (Sigma–Aldrich®) for the transformation to *p*-cymene is key in this synthesis. Despite a catalogue of successful examples in the literature, the reaction is not uncomplicated as the sequential isomerisation-dehydrogenation of limonene is prone to interference by unwanted side reactions. The initial isomerisation of limonene to α-terpinene *in situ* can be acid catalysed but the use of strong acids was observed to lead to the decomposition of the substrate. The isomerisation of limonene to terpinolene is slow, while the irreversible isomerisation of this intermediate to α-terpinene is relatively rapid [24]. Under acidic conditions at elevated temperatures, α-terpinene is expected to be in equilibrium with the other terpinene isomers, although only α-terpinene can be directly dehydrogenated to give *p*-cymene. Therefore it is desirable to suppress the reactions of the unwanted isomers and intercept the isomerisation of limonene at the stage where dehydrogenation to *p*-cymene can occur. Heating a slurry of limonene and K-10 montmorillonite clay to 100 °C for 1 h was again unsatisfactory, as was the use of clay supported metal salts. However reducing the loading of K-10 montmorillonite clay to 1 mol% (based on the number of acid sites [25]) and applied in conjunction with 10 wt% Pd/C improved selectivity from 28% to 54%. Increasing the palladium load beyond 1 mol% had minimal benefit, but increasing the reaction temperature from 100 °C to 140 °C gave 71% selectivity. The predominant co-product of the reaction was *p*-menthane, produced in the disproportionation of limonene [22]. Attempts to use hydrogen acceptors (1-decene, levulinic acid) actually inhibited the reaction. Diluting the reaction using *p*-cymene as a solvent did not improve the selectivity of the reaction either.

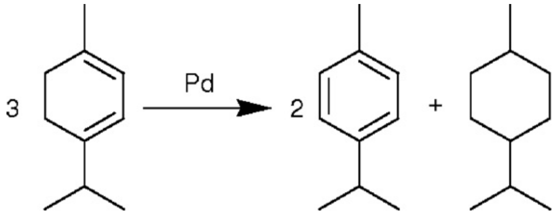


**Scheme 2.** Two step synthesis of *p*-CSA from limonene.

Concerned by the rarity and market price of palladium, other metals were screened as potential dehydrogenation catalysts. Heating α-terpinene in combination with different metal salts at 140 °C always resulted in some *p*-cymene being formed (Table 1). The reaction between α-terpinene and various palladium species gave a comparable yield of *p*-cymene after 1 h to that obtained from the action of K-10 montmorillonite clay and 10 wt% Pd/C on limonene. Again the reaction principally proceeds *via* a disproportionation mechanism to give *p*-menthane as a co-product (Scheme 3). These results suggest that the acidic clay mediated isomerisation of limonene to α-terpinene is quite satisfactory and it is the action of the metal catalyst that is responsible for the less than complete selectivity towards *p*-cymene. It was decided to proceed using Pd/C in combination with K-10 montmorillonite clay as

**Table 1**
Dehydrogenation of α-terpinene (analysed by $^1$H NMR spectroscopy).

| Catalyst | Loading | Conversion | Selectivity |
|---|---|---|---|
| 10 wt% Pd/C | 5% | 100% | 82% |
| PdCl$_2$ | 5% | 100% | 72% |
| Pd(OAc)$_2$ | 5% | 91% | 70% |
| PtCl$_2$ | 5% | 61% | 66% |
| FeCl$_3$ | 5% | 55% | 31% |
| Ni(OAc)$_2$·4H$_2$O | 5% | 52% | 68% |
| CuCl$_2$ | 5% | 52% | 26% |
| ZnCl$_2$ | 5% | 51% | 46% |
| Blank | 0% | 41% | 49% |



**Scheme 3.** Disproportionation of α-terpinene.

co-catalysts to aid any potential recycling of the palladium. Steam distillation can be used to retrieve the *p*-cymene prior to sulphonation although unfortunately *p*-menthane is also observed in the distillate.

In the optimisation of the final sulphonation stage, the reaction of *p*-cymene (Sigma–Aldrich®) with concentrated sulphuric acid was found to be unsatisfactory; after stirring with 2 equivalents of concentrated sulphuric acid at 100 °C for 4 h a yield of only 30% was obtained upon cooling and subsequent solidification of the reaction mixture. The use of 20% fuming sulphuric acid at room temperature increased the yield significantly [4]. The crude product could be isolated from the reaction by the addition of water, which induces the solidification of the product [3,7]. Recrystallisation from concentrated hydrochloric acid results in a white solid, previously described in the literature as the dihydrate of *p*-CSA in yields exceeding 90% of the theoretical maximum [4,5].

Once the individual stages of the synthesis had been demonstrated, the complete synthesis of *p*-CSA from citrus waste was explored. Two methods for the isolation of citrus oil were attempted. Steam distillation of orange peel afforded the essential oil in yields equating to a little over 1 g of essential oil for every three fruits. The alternative process was based on microwave assisted oil extraction [26]. Processing of food waste with microwave irradiation may prove useful for creating further valuable products within a bio-refinery as previously demonstrated for wheat straw [27]. However the procedure resulted in lower than anticipated yields of citrus oil and significant colourisation. Furthermore yields of *p*-cymene were lower when the citrus oil was obtained by microwave assisted extraction, most probably due to trace impurities interfering with the mode of catalysis (Table 2).

The citrus oil obtained by steam distillation was dried and reacted with K-10 montmorillonite clay and 10 wt% Pd/C at 100 °C for 1 h, after which the mixture was cooled then steam distilled to give the crude *p*-cymene. The extent of aromatisation was similar to the optimisation studies using pure limonene. Unfortunately the sulphonation of the crude *p*-cymene distillate was much poorer than the analogous procedure on pure *p*-cymene. In both circumstances the quantity of 20% fuming sulphuric acid added was proportional to the amount of *p*-cymene present in the substrate, and the reaction stirred at room temperature for 4 h. Despite this the yield of *p*-CSA dropped to 27%. Nevertheless the product was identical to *p*-CSA made from pure *p*-cymene. $^1$H NMR and $^{13}$C NMR spectroscopy techniques were used to establish the regioselectivity of the sulphonation on the isolated product. As expected only the 2-isomer was present after recrystallisation.

**Table 2**
Dependency of *p*-cymene production efficiency on limonene purity.

| Source of limonene | Yield | Selectivity |
|---|---|---|
| Purchased (Sigma–Aldrich®) | 89% | 71% |
| Citrus waste (steam distillation) | 88% | 70% |
| Citrus waste (microwave extraction) | 64% | 79% |

**Table 3**
Selected physical properties of *p*-TSA and *p*-CSA.

| Property | *p*-TSA | *p*-CSA |
|---|---|---|
| $T_m$ (°C) | 106–107 | 50–51 |
| $T_d$ (°C) | 206 | 203 |
| $H_0$ (80 mmol dm$^{-3}$) | 1.22 | 1.26 |

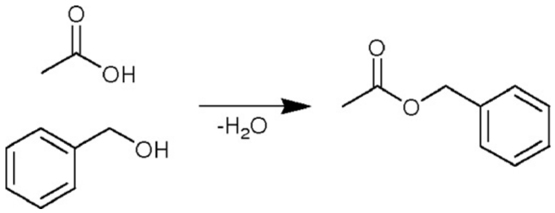
### 3.2. Characterisation of p-CSA

Prior to its application as an acid catalyst it was fitting to determine the acidity of *p*-CSA. The Hammett acidity function ($H_0$) is an equivalent measurement to pH for strong acids [28]. As a method of calculating the ability of strong acids to protonate a weak base by UV–visible spectroscopy, it is now routinely used as part of the characterisation of novel sulphonic acids [29]. As expected from electronic arguments, the acid strength of alkyl functionalised arenesulphonic acids is inversely proportional to the degree of substitution present, and so *p*-CSA is a slightly weaker acid than *p*-TSA. However the difference is less than that between *p*-TSA and benzenesulphonic acid ($H_0$ = 1.12 at 80 mmol dm$^{-3}$).

One benefit of using *p*-TSA as a catalyst in synthesis is that it can be easily washed out of an organic phase with water. Biphasic systems of ethyl acetate (20 mL) and water (20 mL) containing either 0.05 mmol of *p*-TSA or *p*-CSA were prepared to represent a post-reaction work-up. Neither organic layer contained any sulphonic acid in the organic layer after mixing as determined by $^1$H NMR spectroscopy. It is noticeable that the system containing *p*-CSA is slower to separate after agitation, but addition of sufficient water allowed the complete removal of the acid from the organic phase. The thermal stability of both sulphonic acids is also comparable. These observations are summarised in Table 3.

### 3.3. Application of p-CSA

Chosen from the most common uses of organic acids, esterification, aldol condensation, and acetal forming reactions were conducted to demonstrate the similar performances of *p*-TSA and *p*-CSA in the catalysis of these procedures. Firstly the kinetics of a model esterification were explored in a variety of different solvents (Scheme 4). The choice of solvent was found to have an influence on the catalysis of the reaction. In agreement with previous studies, solvents with low hydrogen bond accepting abilities, as measured on the Kamlet–Abbout–Taft β scale, accentuate the kinetic benefit provided by the catalyst to the esterification process [23]. Values of the β scale were calculated using a comparison of the UV–visible spectra of 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline in accordance with literature precedent [30]. Good examples of appropriate solvents are toluene and *p*-cymene, the precursors to the sulphonic acids evaluated in this work. Solvents that are able to accept hydrogen bonds are likely to interact with acid catalysts and hinder protonation of the reactants as required in the rate determining step. This effect can be represented by a linear free energy relationship (Fig. 1).



**Scheme 4.** Model esterification: Acetylation of benzyl alcohol to yield benzyl acetate.

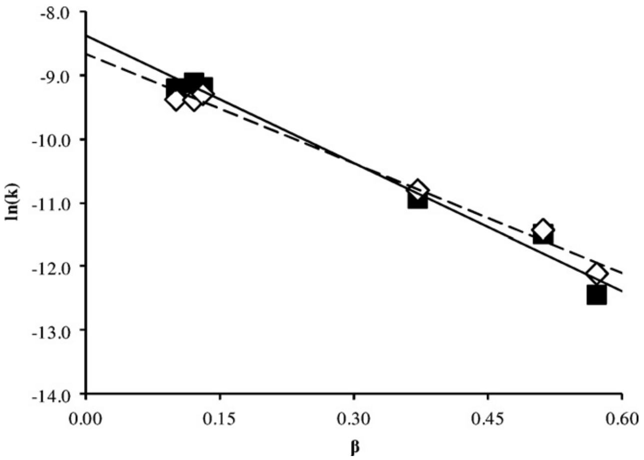


**Fig. 1.** Rates of esterification catalysed by *p*-TSA (diamonds/dashed line) and *p*-CSA (squares/solid line) in the following solvents (left to right): chloroform, toluene, *p*-cymene, acetonitrile, butanone, and 2-methyltetrahydrofuran (2-MeTHF).

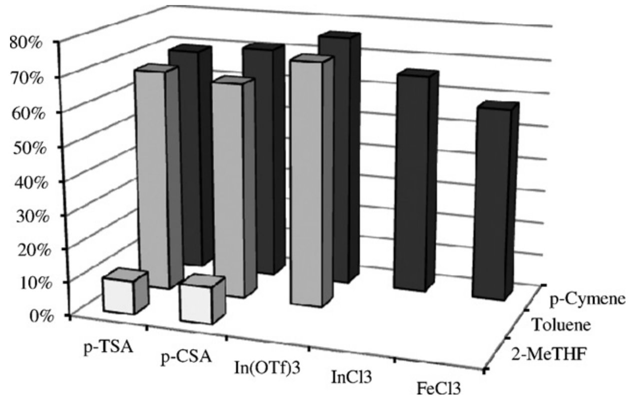
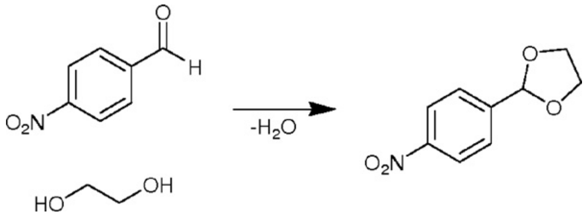


**Fig. 2.** Isolated yields of ethyl levulinate arising from different conditions. Reactions were performed overnight at 50 °C.



**Scheme 6.** Reaction B: Chalcone synthesis *via* the condensation of an aldehyde and a ketone to give 4-bromochalcone.

**Table 4**
Calculated acetylation yields.

| Solvent | Calculated conversion after 6 h | |
|---|---|---|
| | *p*-CSA catalysed | *p*-TSA catalysed |
| *p*-Cymene | 73% | 71% |
| Acetonitrile | 30% | 33% |
| 2-MeTHF | 10% | 12% |

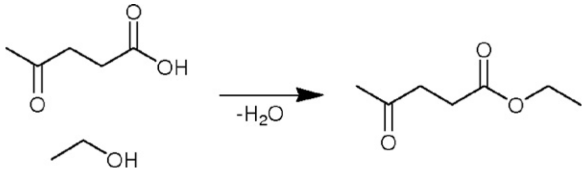
To a good approximation both *p*-TSA and *p*-CSA perform equally well as acid catalysts in this esterification at a 1 mol% loading, as shown by the following equations derived from Fig. 1:

$$p\text{-CSA catalysis}: \quad \ln(k) = -8.38 - 6.68\beta, \quad R^2 = 0.981$$

$$p\text{-TSA catalysis}: \quad \ln(k) = -8.67 - 5.72\beta, \quad R^2 = 0.988$$

However there is an indication that *p*-TSA is superior to *p*-CSA in high polarity solvents, while *p*-CSA marginally enhances reaction rates in low polarity solvents. Given the slighter superior acidity of *p*-TSA, the former observation is expected. The latter observation is most probably due to differences in the solubility of the catalysts, or more precisely the stability of their conjugate bases in solution during protonation of the reactive substrate. To alleviate any concern that in certain solvent systems *p*-CSA would be a significantly poorer catalyst than *p*-TSA, we have used the observed rate constants of this model reaction to calculate the expected conversion to the ester product after 6 h under the conditions explained in Section 2. There is a maximum of only 3% difference between conversions in any solvent system, three of which are shown in Table 4. Regardless, this reaction and similar carbonyl additions proceed much more efficiently in solvents without a strong tendency to accept hydrogen bonds, and in these instances *p*-CSA accelerates the reaction beyond the rates obtained by *p*-TSA catalysis.

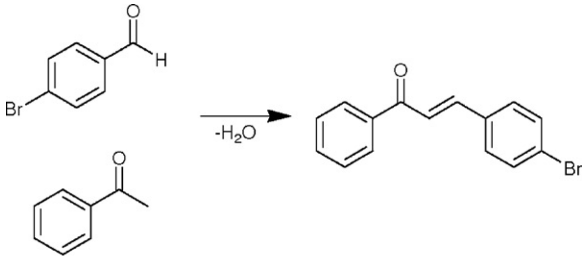
Another esterification (Reaction A) was attempted to confirm the similarity of the two acid catalysts and their activity compared to Lewis acids (Scheme 5). Ethyl levulinate was synthesised in *p*-cymene, toluene and 2-MeTHF using either *p*-TSA (1 mol%), *p*-CSA (1 mol%), In(OTf)$_3$ (5 mol%), InCl$_3$ (5 mol%), or FeCl$_3$ (5 mol%) as catalysts. The performances of the catalysts were fairly similar, although the Lewis acids had to be used in higher loadings to compete with the sulphonic acids. The comparable yields suggest that the equilibrium position of the reaction was being approached, which is not unreasonable given that equimolar quantities of the reactants were used. Both the Brønsted acid catalysts were effective (Fig. 2).



**Scheme 5.** Reaction A: The Fischer esterification of levulinic acid.

Furthermore, the synthesis of 4-bromochalcone *via* an aldol condensation (Reaction B, Scheme 6) and the acetal protection of 4-nitrobenzaldehyde with 1,2-ethanediol (Reaction C, Scheme 7) were performed as further demonstrations of acid catalysis by *p*-CSA. Both these types of procedure have been used previously as demonstrations of novel sulphonic acid catalysis and so were fitting in this context also [31,32]. Reaction B was performed without an auxiliary solvent, and the product recrystallised from ethanol. After refluxing in cyclohexane, the acetal product of Reaction C precipitated from the reaction mixture upon cooling.

A comparison of Reaction A, Reaction B, and Reaction C shows that *p*-TSA fairs no better than *p*-CSA in its role as an acid catalyst (Table 5). Reaction B and Reaction C appear to be less sensitive to the choice of catalyst than Reaction A. After performing each reaction in triplicate no difference in the mean yield of either reaction is



**Scheme 7.** Reaction C: Acetal protection using ethylene diol to give 2-(4-nitrophenyl)-1,3-dioxolane.

**Table 5**
Isolated product yields from acid catalysed condensation chemistries (esterification, aldol condensation, and acetal protection).

| Reaction | Yield | |
|---|---|---|
| | *p*-CSA catalysed | *p*-TSA catalysed |
| A (*p*-cymene) | 71% | 69% |
| A (toluene) | 65% | 67% |
| A (2-MeTHF) | 11% | 10% |
| B | 73% | 73% |
| C | 92% | 92% |

observed, unlike Reaction A in which up to 2% variation in yield is observed. Indeed within the context of a synthetic procedure no major allowances have to be made or additional considerations accounted for if replacing *p*-TSA with *p*-CSA.

## 4. Conclusion

The sulphonic acid derivative of *p*-cymene has been synthesised from limonene for the first time, and demonstrated as being equal to *p*-TSA in applications as an organic acid catalyst. The synthesis of *p*-CSA does not require organic solvents or rely on any other petrochemical auxiliaries. Although *p*-CSA has the undeniable benefit of being the product of a sustainable and cheap feedstock, it is not commercially available whereas *p*-TSA is supplied by many chemical manufacturers. Although a matter of inconvenience at present, if further chemistry is developed promoting the use of *p*-CSA the market pull may result in a commercial supply being available in the future. The necessity for sustainable chemical products will only increase with time, and as such *p*-CSA is an ideal candidate to fulfil this role in acid catalysis.

## Acknowledgements

The authors thank Mr. Paul Elliott for determining the thermal decomposition points of the sulphonic acids, Mr. Andrew Marriott for performing the mass spectrometry of *p*-CSA, and Dr. Thomas Farmer for proposing the concept of this article.

## References

[1] As of 30/11/11 the Scifinder® database cites 1,148,722 instances in which *p*-TSA or its monohydrate salt have been applied as a catalyst. By comparison sulfuric acid has been recorded as a catalyst in 251,064 different reactions.
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