Ultrasonics Sonochemistry 20 (2013) 826–832

Contents lists available at SciVerse ScienceDirect

Ultrasonics Sonochemistry

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

# Indium-mediated regioselective synthesis of ketones from arylstannanes under solvent-free ultrasound irradiation

Marcos J. Lo Fiego, Mercedes A. Badajoz, Claudia Domini, Alicia B. Chopa *,[1], María T. Lockhart *

*Instituto de Química del Sur (CONICET-UNS), Departamento de Química, Universidad Nacional del Sur, Avenida Alem 1253, Bahía Blanca B8000CPB, Argentina*

ARTICLE INFO

*Article history:*
Received 3 July 2012
Received in revised form 26 October 2012
Accepted 31 October 2012
Available online 22 November 2012

*Keywords:*
Ultrasound
Solvent-free
Aromatic ketones
Arylstannanes
Indium

ABSTRACT

The solvent-free indium-promoted reaction of alkanoyl chlorides with sterically and electronically diverse arylstannanes is a simple and direct method for the regioselective synthesis of primary, secondary and tertiary alkyl aryl ketones in good to excellent isolated yields (42–84%) under mild and neutral conditions. The protocol is also adequate for the synthesis of aryl vinyl ketones. Reaction times are drastically reduced (from 3–32 h to 10–70 min) under ultrasonic irradiation. Evidences for the involvement of a homolytic aromatic *ipso*-substitution mechanism, in which indium metal acts as radical initiator, are presented. It is possible the transference of two aryl groups from tin, thus improving effective mass yield, working with diarylstannanes as starting substrates.



## 1. Introduction

Ketones are vital building blocks in organic synthesis as well as an important functionality found in several natural products and pharmaceutical compounds. The Friedel–Crafts (F–C) acylation of aromatic compounds is the most common route for the synthesis of aromatic ketones [1]. Nevertheless, intrinsic limitations of F–C reactions are the substituent-directing effects, the reactivity substrate requirements and the fact that recovery and recycling of the catalyst is seldom possible after aqueous work-up and a large amount of toxic waste is generated. On the other hand, Pd-catalyzed cross-coupling reactions of acyl halides with organometallic reagents provide a direct procedure for the synthesis of isomeric ketones [2]; a drawback is that Pd-catalysts are expensive and that it is usually necessary to find the appropriate catalytic protocol for each pair of reactants. We have been involved in the synthesis of arylstannanes as well as in their application as intermediates in organic synthesis [3]; recently, based on the exceptional leaving group ability of the trialkylstannyl group in electrophilic aromatic substitutions we have developed new straightforward procedures for the regiospecific [4] mono-, bi- and triaroylation of aromatic rings by the reaction of mono-, bi- and tristannylarenes with different aroyl chlorides [5]. Moreover, we have proposed an efficient catalyst-free route (*o*-dichlorobenzene, 180 °C) for the selective synthesis of tertiary alkyl aryl ketones in good to high yields, without the generation of alkylbenzenes as by-products, by the reaction of arylstannanes with tertiary aliphatic acyl chlorides [6]. Unfortunately, under a similar protocol acyl chlorides bearing α-hydrogens lead only to protodestannylated products due to the presence of HCl generated under the reaction conditions, probably, by a β-elimination of the alkanoyl chloride [6]. In recent years, the development of indium-mediated synthetic methods has grown up in the literature due to the special properties of indium metal [7]. Thus, it is unaffected by air, moisture or oxygen at ambient temperature and, most importantly, the element itself is without any apparent toxicity. In this respect, we have established that indium metal is a promoter of the solvent-free reaction of aroyl chlorides with arylstannanes applied to the synthesis of hindered benzophenones [5c]. Based on this experience we considered interesting to explore the application of a similar protocol for the synthesis of alkyl aryl ketones, specially taking into account the above mentioned limitation found in our catalyst-free route [6].

In the last decades, ultrasound irradiation has emerged as an eco-environmental technology in green chemistry [8]. It has been increasingly used as an alternative energy source to promote several organic transformations in higher yields, shorter reaction times and milder conditions, being considered a clean and useful protocol compared with traditional methods [9]. A literature survey demonstrates that many synthetic protocols using metals or organometallic reagents could be promoted by ultrasonic irradiation [10]. Thus, it has beneficial effects on indium-mediated reactions [10,11], and the existence of SET pathways may be

* Corresponding authors. Tel.: +54 291 4595101/3537; fax: +54 291 4595187 (M.T. Lockhart).
*E-mail address:* lockhart@criba.edu.ar (M.T. Lockhart).
[1] Member of CIC.

1350-4177/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ultsonch.2012.10.018

probable in these type of reactions [7]. Additionally, many solvent-free protocols can be conducted smoothly by sonication [12].

On the base of these antecedents we considered really interesting to study the effect produced by ultrasonic irradiation on our protocol.

Thus, we report herein the synthetic potential of the ultrasound irradiated, solvent-free, indium-promoted reaction of acid chlorides with arylstannanes; we have checked the reusability of the indium metal and a special work-up was carried out to recover the organotin by-products. The study resulted in an attractive process for the synthesis of alkyl aryl ketones under mild and neutral conditions.

## 2. Results and discussion

We started our study by synthesizing a series of sterically and electronically diverse arylstannanes (**1a–h**) which were then subjected to the reaction with different acid chlorides (**2a–g**) under the conditions we have previously established, that is, solvent-free, in the presence of indium powder [5c].

An analysis of the results summarized in Table 1 shows that electronic effects have a notable influence in the reaction; thus, arylstannanes bearing electron-releasing groups gave the corresponding ketones even at room temperature meanwhile the presence of electron-withdrawing groups made it necessary to work at higher temperatures (for example, compare entry 2 with 3 and 4). Moreover, the reaction of **2a** with **1h**, bearing a *p*-cyano substituent, was negative even after 72 h at 80 °C and the starting substrate was almost recovered (entry 7). On the other hand, the substitution pattern of the aromatic ring did not greatly affect the reaction and *ortho*-, *para*- and *meta*-substitution were well tolerated. In general, the reactions gave, as a single product, the corresponding ketones resulting from the strict *ipso*-substitution of the stannyl group, allowing the synthesis of ketones with high specificity. Thus, even the more sterically hindered 2,6-dimethylphenylstannane (**1g**) was also successfully *ipso*-acyldestannylated giving the corresponding ketones **3ga**, **3gb**, **3gf** and **3gg** in good isolated yields (47–75%). It should be mentioned that in experiments 6, 14 and 22 traces of an isomeric ketone were detected (GC), generated by direct acylation of the aromatic ring followed by protodestannylation. On the other hand, the negative reaction between **1g** and **2c** is probably due to steric effects (entry 19). Unfortunately, it was not possible to overcome the strong *para*-directing effect of the OMe group producing, whatever the acyl chloride employed, high amounts of the ketone generated by direct acylation of the ring (entries 1 and 18), being these results consistent with those obtained previously in the aroylation of arylstannanes [5c].

A global evaluation of the results indicates that the method can be used to produce ketones either from primary, secondary or tertiary alkanoyl chlorides.[2] By the way, due to its low boiling point, the reactions with acetyl chloride must be carried out in solution being benzotrifluoride chosen as solvent in view of its properties (entry 23) [13]. Furthermore, experiment 22 shows that by using cinnamoyl chloride (**2g**) afforded the desired ketone although in moderate yield (47%). On the other hand, electron withdrawing groups on the acyl chloride moiety showed a negative effect. Thus, while the reaction of pivaloyl chloride (**2d**) with **1b** produced the desired ketone in 55% yield (22 h, 60 °C), under analogous conditions the reaction of the similar acyl chloride **2e** with **1b** was negative and the starting substrate was almost recovered after 24 h of reaction (entries 20 and 21).

It should be mentioned that each reaction was, in principle, performed at the lowest temperature which allowed keeping the stirring of the reaction mixture during reaction time. Nevertheless, it is important to note that an increase in reaction temperature causes a sharp reduction of reaction times (entries 3 vs. 4; 8 vs. 9).

We carried out control experiments which showed that no reaction occurred in the absence of indium, indicating that the metal acts as a promoter of these reactions. On the other hand, the addition of galvinoxyl radical (0.5 equiv) to a couple of reactions produced a marked retardation effect and they did not proceed efficiently comparing with blank ones. Based on these results, we believe that these reactions proceed initially through a single-electron transfer (SET) from indium to the acyl chloride with generation of an acyl radical,[3] which reacts with the arylstannane through a homolytic *ipso* aromatic substitution affording the ketone. The selective *ipso*-substitution is a consequence of the enhanced hyperconjugation of the unpaired electron with the β-carbon-tin bond (β-effect) [14]. The tin radical should be rapidly lost and reacts with the alkanoyl chloride, regenerating the acyl radical (Scheme 1). It should be mentioned that the reaction also takes place using sub-stoichiometric amounts (0.2 equiv) of In(0) although the yield decrease from 84% to 71% (entries 9 and 10).

Next, since sonication is able to affect heterogeneous systems which include radical mechanisms [9], we studied the effect produced by ultrasonic irradiation over these reactions.

The optimal conditions for carrying out the irradiated reactions were found by the reaction of tributylstannyl-3-chlorobenzene (**1f**) and butanoyl chloride (**2a**) in the presence of indium (Table 2). The model reaction was carried out using an ultrasonic probe (from Cole-Parmer ultrasonic homogenizer-4710 of 20 kHz and 375 W) equipped with a 10 mm diameter titanium horn. Experiments were conducted in closed glass reactors along with the horn immersed in a bath. The first experiments were performed in a water/detergent bath [15] (60 °C initial temperature) working at 70% and 90% of output power and in a pulsed mode with different duty cycles (70% or 80%). The results indicated that the reaction proceeded similarly under the diverse conditions employed so, in the following, 70% of power out and 70% duty cycles were used. Moreover, as cavitation is dependent on temperature [16], one experiment was performed at 100 °C (initial temperature, oil bath); under these conditions product **3fa** was obtained in a similar yield but in really shorter reaction time (3 min). Probably, the increase in the reaction rate at 100 °C is due to the decrease of the reaction mixture viscosity (solvent-free) which improves the molecular diffusion [12a]. These results enable us to affirm that in comparison with the conventional method (Table 1, entry 5) the major advantage of ultrasound application is the significant decrease in the reaction time (from 5 h at 80 °C under classical conditions to 10 min at 60 °C or 3 min at 100 °C, under irradiation).

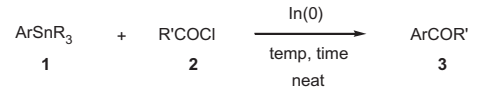
The optimized conditions were applied to a representative series of reactions, shown in Table 3, in order to compare with those reactions carried out by the conventional method (Table 1). It should be mentioned that the reactions were performed at the lowest temperature which kept a homogeneous mixture of substrate and reactant.

The results obtained show that, in all cases, sonication dramatically reduced the reaction times without significantly affecting the yields. Once more, ultrasound enhanced the rate of a reaction and, consequently, reduced energy consumption. Comparing experiments 4 and 5, the reaction took place even using sub-stoichiometric amounts of indium but giving lower yields of ketone (62% vs. 47%). On the other hand, experiments 7 and 9 show that it was possible to performed reactions, in a reasonable reaction time, without

[2] It was found that 2.0 equiv. of tertiary acyl chloride is required in order to shorten reaction times.

[3] Indium metal is capable of promoting SET processes. See Ref. [7].

**Table 1**
Indium-mediated reactions of arylstannanes with acid chlorides.



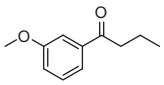
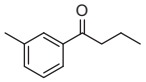
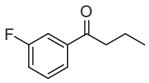
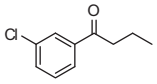
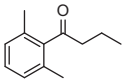
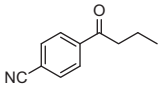
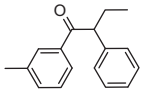
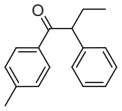
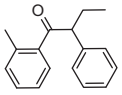
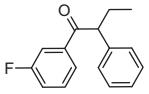
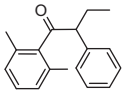
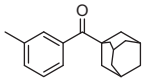
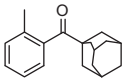
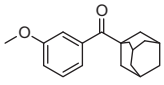
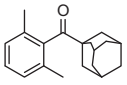
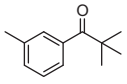
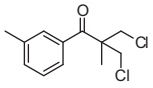
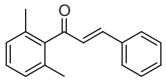
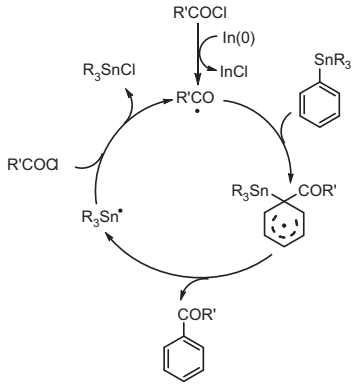

| Entry[a] | 1 | Ar | 2 | R' | Temp. (°C) | Time (h) | 3 | ArCOR′ | Yield (%)[b] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | 3-$MeOC_6H_4$ | **2a** | Pr | r.t. | 6 | **3aa** |  | Traces[c] |
| 2 | **1b** | 3-$MeC_6H_4$ | **2a** | Pr | r.t. | 6 | **3ba** |  | 49 |
| 3 | **1e** | 3-$FC_6H_4$ | **2a** | Pr | r.t. | 24 | **3ea** |  | 5[d] |
| 4 | **1e** | 3-$FC_6H_4$ | **2a** | Pr | 80 | 5 | **3ea** | | 55 |
| 5 | **1f** | 3-$ClC_6H_4$ | **2a** | Pr | 80 | 5 | **3fa** |  | 49 |
| 6 | **1g** | 2,6-$Me_2C_6H_3$ | **2a** | Pr | 80 | 6 | **3ga** |  | 72[e] |
| 7 | **1h** | 4-$CNC_6H_4$ | **2a** | Pr | 80 | 72 | **3ha** |  | 0[f] |
| 8 | **1b** | 3-$MeC_6H_4$ | **2b** | —CH(Ph)$CH_2CH_3$ | r.t. | 100 | **3bb** |  | 64 |
| 9 | **1b** | 3-$MeC_6H_4$ | **2b** | —CH(Ph)$CH_2CH_3$ | 80 | 6 | **3bb** | | 84 |
| 10[g] | **1b** | 3-$MeC_6H_4$ | **2b** | —CH(Ph)$CH_2CH_3$ | 80 | 6 | **3bb** | | 71 |
| 11 | **1c** | 4-$MeC_6H_4$ | **2b** | —CH(Ph)$CH_2CH_3$ | 80 | 3 | **3cb** |  | 76 |
| 12 | **1d** | 2-$MeC_6H_4$ | **2b** | —CH(Ph)$CH_2CH_3$ | 80 | 3 | **3db** |  | 65 |
| 13 | **1e** | 3-$FC_6H_4$ | **2b** | —CH(Ph)$CH_2CH_3$ | 80 | 7 | **3eb** |  | 61 |
| 14 | **1g** | 2,6-$Me_2C_6H_3$ | **2b** | —CH(Ph)$CH_2CH_3$ | r.t. | 32 | **3gb** |  | 75[e] |
| 15 | **1b** | 3-$MeC_6H_4$ | **2c** | 1-Ad | 80 | 25 | **3bc** |  | 42[d] |
| 16[h] | **1b** | 3-$MeC_6H_4$ | **2c** | 1-Ad | 80 | 5 | **3bc** | | 69 |
| 17[h] | **1d** | 2-$MeC_6H_4$ | **2c** | 1-Ad | 80 | 14 | **3dc** |  | 51 |
| 18[h] | **1a** | 3-$MeOC_6H_4$ | **2c** | 1-Ad | 60 | 10 | **3ac** |  | 0[c] |
| 19[h] | **1g** | 2,6-$Me_2C_6H_3$ | **2c** | 1-Ad | 80 | 24 | **3gc** |  | Traces[f] |
| 20[h] | **1b** | 3-$MeC_6H_4$ | **2d** | *t*-Bu | 60 | 22 | **3bd** |  | 55 |
| 21[h] | **1b** | 3-$MeC_6H_4$ | **2e** | —C($CH_2Cl$)$_2CH_3$ | 60 | 24 | **3be** |  | 0[f] |

**Table 1** (*continued*)

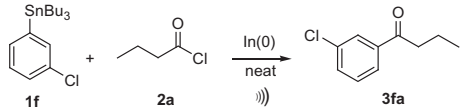
| Entry[a] | 1 | Ar | 2 | R' | Temp. (°C) | Time (h) | 3 | ArCOR′ | Yield (%)[b] |
|---|---|---|---|---|---|---|---|---|---|
| 22 | **1g** | 2,6-$Me_2C_6H_3$ | **2g** | —CH=CHPh | 60 | 3 | **3gg** |  | 47[e] |
| 23[i] | **1g** | 2,6-$Me_2C_6H_3$ | **2f** | —$CH_3$ | r.t. | 8 | **3gf** |  | 57 |

[a] All reactions were conducted in solventless conditions using 1.0 equiv of **1**, 1.2 equiv of **2** and 1.0 equiv of indium metal, unless otherwise stated.
[b] Isolated yields from 1.0 mmol scale experiment (column chromatography).
[c] High yield of para-isomer (GC).
[d] Together with starting substrate (GC).
[e] Together with traces of isomer.
[f] Starting substrate was almost recovered.
[g] In presence of 0.2 equiv of In(0).
[h] 2.0 equiv of **2** were used.
[i] In solution of $CF_3C_6H_5$ (1.0 M in **1**).




**Scheme 1.** Proposed mechanistic pathways for the indium-mediated homolytic aromatic *ipso*-substitution of aryltins.

**Table 2**
Optimizing conditions for ultrasound.



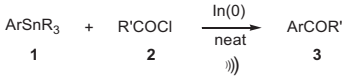

| Entry | Power (%) | Duty cycles (%) | Temp.[a] (°C) | Time (min) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | 70 | 70 | 60 | 10 | 53 |
| 2 | 90 | 70 | 60 | 10 | 49 |
| 3 | 90 | 80 | 60 | 10 | 52 |
| 4 | 70 | 70 | 100 | 3 | 54 |

[a] Water/detergent bath (60 °C); oil bath (100 °C).
[b] Isolated yields.

using an excess of tertiary alkanoyl chlorides (compare with entries 6 and 8), thus improving the traditional method (minimization of the reagents correspondingly minimized waste).

In order to evaluate the role of ultrasound in the reaction system we repeated experiments 6 and 7 (Table 3) but in the absence of indium, that is, under homogeneous conditions. After the same reaction times (20 min and 53 min, respectively) the corresponding ketones were obtained (23% and 36%, respectively) together with starting substrate. The presence of ketone supports the

**Table 3**
Indium-mediated reactions of arylstannanes with acid chlorides under ultrasonic irradiation.



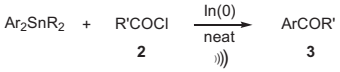

| Entry[a] | 1 | 2 | Temp.[b] (°C) | Time (min) | 3 | Yield[c] (%) |
|---|---|---|---|---|---|---|
| 1 | **1b** | **2a** | 60 | 10 | **3ba** | 47 |
| 2 | **1e** | **2a** | 60 | 10 | **3ea** | 55 |
| 3 | **1b** | **2b** | 80 | 30 | **3bb** | 79 |
| 4 | **1e** | **2b** | 80 | 45 | **3eb** | 62 |
| 5[d] | **1e** | **2b** | 80 | 45 | **3eb** | 47 |
| 6[e] | **1b** | **2c** | 80 | 20 | **3bc** | 70 |
| 7 | **1b** | **2c** | 80 | 53 | **3bc** | 70 |
| 8[e] | **1b** | **2d** | 80 | 40 | **3bd** | 55 |
| 9 | **1b** | **2d** | 80 | 70 | **3bd** | 52 |

[a] All reactions were conducted in solventless conditions using 1.0 equiv of **1**, 1.2 equiv of **2** and 1.0 equiv of indium metal, unless otherwise stated.
[b] Water/detergent bath (60 °C); oil bath (80 °C).
[c] Isolated yields.
[d] In(0) (0.2 equiv).
[e] **2** (2.0 equiv).

existence of a chemical ultrasound enhancement [9a,b]. The intense local temperature and high pressure produced during cavitation promoted the cleavage of the carbon-halogen bond of the acid chloride (sonolysis) generating an acyl radical and initiating the radical process to give the corresponding ketone, although in lower yields compared with the indium-catalyzed reaction. Ultrasound exerts a dual effect on the indium-assisted reaction (heterogeneous system); on the one hand, it favors the radical reaction and, on the other hand, it enhances the activity of the metal. In this way, cavitation generates microinjects of liquid which bombard the solid surface, removing contaminating coatings. It is known that clean metal surfaces favor the single-electron transfer (SET) from metals (indium) to an organic compound (the acyl chloride) increasing the reaction rate [9a,c].

A drawback of the synthetic protocol is the generation of an equimolecular amount of triorganotin chlorides. Because of the environmental problems caused by the well-known toxicity of triorganotin residues, we considered really important to trap them and applied a special work up in order to recover the trialkyltin chlorides produced (see Section 3). With the main goal of decreasing the level of pollution we also considered interesting to study the possibility of transferring more than one aryl group attached

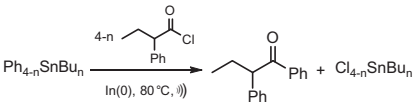
**Table 4**
Indium-mediated reactions of diarylstannanes with acid chlorides under ultrasonic irradiation.




| Entry[a] | Ar | 2 | Temp.[b] (°C) | Time (min) | 3 | Yield[c] (%) |
|---|---|---|---|---|---|---|
| 1 | 3-$MeC_6H_4$ | **2a** | 60 | 6 | **3ba** | 36 |
| 2 | 3-$MeC_6H_4$ | **2b** | 80 | 15 | **3bb** | 61 |
| 3 | 3-$MeC_6H_4$ | **2c** | 80 | 25 | **3bc** | 60 |
| 4 | 3-$ClC_6H_4$ | **2a** | 60 | 6 | **3fa** | 33 |
| 5 | 3-$FC_6H_4$ | **2a** | 60 | 6 | **3ea** | 41 |
| 6 | 3-$FC_6H_4$ | **2b** | 80 | 10 | **3eb** | 42 |

[a] All reactions were conducted in solventless conditions using 1.0 equiv of $Ar_2SnR_2$, 2.0 equiv of **2** and 1.0 equiv of indium metal.
[b] Water/detergent bath (60 °C); oil bath (80 °C).
[c] Isolated yields referred to stoichiometric equation.

to the metal. For this purpose, we applied the ultrasound protocol to the reaction of acyl chloride **2b** with tributylphenylstannane, dibutyldiphenylstannane, butyltriphenylstannane and tetraphenylstannane, as model systems. The results are summarized in Eq. (1) and the yields are referred to the stoichiometric equation.




| n | | |
|---|---|---|
| 3 | 50 min | 84 % |
| 2 | 30 min | 52 % |
| 1 | 15 min | 25 % |
| 0 | 7 min | 5 % |

(1)

The results obtained showed that while diphenylstannane is a suitable substrate giving the ketone in an acceptable yield (52%), tri- and tetraphenylstannanes afforded only 25% and 5% of ketone, respectively, together with large amounts of protodestannylation product.

Next, we synthesized a series of diarylstannanes in order to study their reactivity towards different alkanoyl chlorides (Table 4).

It can be seen that, in general, diarylstannanes are appropriate substrates as the corresponding ketones are obtained in acceptable yields implying the use of sub-stoichiometric amounts of organotin compounds. In addition, from a sustainable point of view, the byproduct to be separated is $Bu_2SnCl_2$ which is less toxic than $Bu_3SnCl$ and easily converted into insoluble $(Bu_2SnO)_n$ (see Section 3).

Moreover, it is important to mention that indium metal is stable under both reaction conditions employed and we were able to recover (ca. 90%)[4] and reuse it without significant changes in the yield of the following reactions. This is really significant taking into account that indium has been defined as a rare metal and that, due to the many uses of indium in technology, there has been an increasing demand and, consequently, significantly increased costs.In conclusion, the method provides a facile and specific access to a wide range of alkyl aryl ketones via arylstannanes. These partners are attractive due to their availability, air- and moisture-stability, and their compatibility with a variety of functional groups. Moreover, the transfer of two aryl groups from tin reduced the amount of non-benign organotin subproducts. The difficulties connected with organotin removal were largely solved in the workup and, in addition, these by-products were recovered and not rejected.The striking advantages of the method are (i) energy saving by sonication; (ii) the use of no solvent; (iii) readily available, non-toxic and reusable metal catalyst; (iv) accessible substrates and reactants; (v) improved effective mass yield [17]; (vi) specificity of the reaction; and (vii) simplicity in the isolation of the products. These characteristics make this procedure very attractive.

[4] Purity and identity proof of indium metal were obtained by differential scanning calorimetric (DSC) analysis.

## 3. Experimental

### 3.1. General methods

All reactions were carried out under a dry nitrogen atmosphere. Acid chlorides were commercially available and fractionally distilled under nitrogen before use. Aryltributylstannanes **1a–f** were prepared by transmetallation of the appropriate Grignard reagents with tributyltin chloride in anhydrous THF. Aryltrimethylstannanes **1g** and **1h** were obtained by photostimulated reaction with $Me_3SnNa$ in liquid ammonia, according to the literature procedures; the former from the corresponding commercial aryl chloride [18] and the latter from the synthesized (4-cyanophenyl) trimethylammonium methylsulfate [3b]. Reactions were monitored by thin-layer chromatography carried out on silica gel plates (60F-254) and visualized under UV light or using 5% phosphomolybdic acid in ethanol. Column chromatography was performed over silica gel 60 (70–230 mesh) doped with 10% of potassium fluoride [5a]. The NMR spectra were recorded on a 300 MHz spectrometer (300.1 MHz for $^1H$, 75.5 MHz for $^{13}C$). Chemical shifts ($\delta$) are reported in ppm downfield from tetramethylsilane, with residual non deuterated solvent resonance as internal reference ($CDCl_3$: $\delta$ 7.27 for $^1H$ and $\delta$ 77.0 for $^{13}C$) and coupling constants ($J$) are in Hz. Identity and purity of the products (crude or purified) were established using a GC/MS instrument (HP5-MS capillary column, 30 m × 0.25 mm × 0.25 μm) equipped with 5972 mass selective detector operating at 70 eV (EI). Program: 50 °C for 2 min with increase 10 °C/min to 280 °C. For gas–liquid chromatography (GC) an instrument equipped with a flame-ionization detector and a HP5 capillary column (30 m × 0.25 mm × 0.25 μm) was used. External sonication was carried out using an ultrasonic probe (from Cole-Parmer 4710 series ultrasonic homogenizer of 20 kHz and 375 W) equipped with a 10 mm diameter titanium horn, which was immersed either in a water–detergent [15] or in an oil bath.

The physical and spectroscopic characteristics of compounds **3bc**, **3dc** and **3bd** have been reported upon in a previous paper [5a].

Under silent conditions, indium-mediated reactions were carried out following the experimental procedure described in our latest work [5c].

### 3.2. Representative procedure for ultrasound assisted indium-mediated reactions. Synthesis of 1-(3-chlorophenyl)butanone (3fa; Table 2, entry 1) [19]

In a flame dried Schlenk tube (fitted with a Teflon plug valve) 1.2 mmol (0.127 g) of butanoyl chloride (**2a**) was added to a stirred mixture of 1.0 mmol (0.402 g) of tributyl(3-chlorophenyl)stannane (**1f**) and indium powder (0.148 g, 1.0 mmol) under a nitrogen gas stream. After purging the system with nitrogen by means of three pump-fill cycles, the tube was capped and immersed in a water–detergent bath at 60 °C. The ultrasonic titanium horn was placed into the bath to a distance of 10 mm to the wall and 5 mm from the bottom of the Schlenk tube and ultrasound was applied in a pulsed mode (duty cycle = 70%; output power = 70%) for 10 min. After addition of 10% (m/v) solution of NaOH (2 mL) and 10 μL of tetradecane (internal standard), the mixture was stirred at room temperature for 15 min and then diluted with DCM (5 mL). Once the stirring was stopped for about 5 min, the supernatant liquid

mixture was decanted into a separatory funnel. The silvery-white solid, settled at the bottom of the Schlenk tube, was washed with acetone (2 × 5 mL), deionized water (2 × 5 mL), and then vacuum-dried at room temperature. As indicated by DSC analysis, the dried sample (0.133 g) meant a 90% recovered yield of pure indium. On the other hand, the organic phase was successively washed with water and brine, dried over $Na_2SO_4$, filtered, analyzed by GC, and then concentrated *in vacuo*. Purification by column chromatography on silica gel (60 Å, 70–230 mesh) doped with 10% of KF (hexanes/DCM 8:2) gave 0.096 g (53%) of **3fa** as a colorless oil. $\nu_{max}/cm^{-1}$ 1692 (CO). **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.92 (m, 1H), 7.82 (m, 1H), 7.52 (ddd, $J$ = 1.0 Hz, $J$ = 1.9 Hz, $J$ = 7.9 Hz, 1H), 7.39 (t, $J$ = 7.8 Hz, 1H), 2.92 (t, $J$ = 7.2 Hz, 2H), 1.77 (m, 2H), 1.00 (t, $J$ = 7.4 Hz, 3H); **$^{13}$C NMR** (75.5 MHz, $CDCl_3$) $\delta$ (ppm) 198.9 (CO), 138.7 (C), 134.9 (C), 132.7 (CH), 129.9 (CH), 128.2 (CH), 126.1 (CH), 40.6 ($CH_2$), 17.6 ($CH_2$), 13.8 ($CH_3$); **MS** *m/z* (% rel. intensity, ion) 182 (5, $M^{+\cdot}$), 139 [100, ($M^{+\cdot}$—Pr$^{\cdot}$)], 111 [56, ($ClPh^+$)]. (**3fa** is also found in Table 1, entry 5 and in Table 4, entry 4).

*3.2.1. 1-(3-Methylphenyl)butanone (3ba; Table 1, entry 2; Table 3, entry 1 and Table 4, entry 1) [20]*

Yellow oil. $\nu_{max}/cm^{-1}$ 1690 (CO). **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.79–7.74 (m, 2H), 7.38–7.30 (m, 2H), 2.94 (t, $J$ = 7.3 Hz, 2H), 2.42 (s, 3H), 1.78 (m, 2H), 1.02 (t, $J$ = 7.4 Hz, 3H); **$^{13}$C NMR** (75.5 MHz, $CDCl_3$) $\delta$ (ppm) 200.6 (CO), 138.3 (C), 137.2 (C), 133.5 (CH), 128.5 (CH), 128.4 (CH), 125.3 (CH), 40.6 ($CH_2$), 21.3 ($CH_3$), 17.8 ($CH_2$), 13.9 ($CH_3$). **MS** *m/z* (% rel. intensity, ion) 162 (18, $M^{+\cdot}$), 147 [3, ($M^{+\cdot}$—Me$^{\cdot}$)], 134 [5, ($M^{+\cdot}$—$CH_2CH_2$)], 119 [100, ($M^{+\cdot}$—Pr$^{\cdot}$)].

*3.2.2. 1-(3-Fluorophenyl)butanone (3ea; Table 1, entry 4; Table 3, entry 2 and Table 4, entry 5)*

Yellow oil. $\nu_{max}/cm^{-1}$ 1692 (CO). **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.74 (d, $J$ = 7.7 Hz, 1H), 7.64 (m, 1H), 7.45 (m, 1H), 7.23 (m, 1H), 2.93 (t, $J$ = 7.3 Hz, 2H), 1.78 (m, 2H), 1.01 (t, $J$ = 7.4 Hz, 3H). **$^{13}$C NMR** (75.5 MHz, $CDCl_3$) $\delta$ (ppm) 197.6 (d, $^4J_{CF}$ = 1.5 Hz, CO), 163.1 (d, $^1J_{CF}$ = 247 Hz, C), 139.0 (C), 130.2 (d, $^3J_{CF}$ = 7.7 Hz, CH), 123.7 (d, $^4J_{CF}$ = 3.0 Hz, CH), 119.8 (d, $^2J_{CF}$ = 22 Hz, CH), 114.7 (d, $^2J_{CF}$ = 22 Hz, CH), 40.6 ($CH_2$), 17.6 ($CH_2$), 13.8 ($CH_3$); **MS** *m/z* (% rel. intensity, ion) 166 (12, $M^{+\cdot}$), 138 [11, ($M^{+\cdot}$—$CH_2CH_2$)], 123 [100, ($M^{+\cdot}$—Pr$^{\cdot}$)]. **Anal. Calcd.** for $C_{10}H_{11}FO$: C 72.27, H 6.67. Found: C 71.99, H 6.79.

*3.2.3. 1-(2,6-Dimethylphenyl)butanone (3ga; Table 1, Entry 6)*

Yellow oil. $\nu_{max}/cm^{-1}$ 1693 (CO). **$^1$H NMR** (300 MHz, $CDCl_3$) 7.04 (t, 1H, $J$ = 7.6), 6.9 (d, 2H, $J$ = 7.6 Hz), 2.59 (t, 2H, $J$ = 7.3 Hz), 2.13 (s, 6H), 1.66 (m, 2H), 0.92 (t, $J$ = 7.4 Hz, 3H); **$^{13}$C NMR** (77.0 MHz, $CDCl_3$) 210.3 (CO), 142.5 (C), 132.3 (C), 128.3 (CH), 127.6 (CH), 46.5 ($CH_2$), 19.0 ($CH_3$), 16.7 ($CH_2$), 13.7 ($CH_3$); **MS** *m/z* (% rel. intensity, ion) 176 (4, $M^{+\cdot}$), 133 [100, ($M^{+\cdot}$—Pr$^{\cdot}$)], 105 [39, ($Me_2Ph^+$)]. **Anal. Calcd.** for $C_{12}H_{16}O$: C 81.77, H 9.15. Found: C 81.95, H 9.13.

*3.2.4. 2-Phenyl-1-(3-methylphenyl)butanone (3bb; Table 1, entry 9 and Table 3, entry 3)*

White solid; m.p. 70–71 °C. $\nu_{max}/cm^{-1}$ 1690 (CO). **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.77–7.74 (m, 2H), 7.31–7.20 (m, 6H), 7.17 (m, 1H), 4.44 (t, $J$ = 7.2 Hz, 1H), 2.33 (s, 3H), 2.21 (m, 1H enantiotropic), 1.85 (m, 1H enantiotropic), 0.90 (t, $J$ = 7.3 Hz, 3H); **$^{13}$C NMR** (75.5 MHz, $CDCl_3$) $\delta$ (ppm) 200.3 (CO), 139.7 (C), 138.2 (C), 137.2 (C), 133.5 (CH), 129.1 (CH), 128.7 (CH), 128.3 (CH), 128.2 (CH), 126.8 (CH), 125.8 (CH), 55.4 (CH), 27.1 ($CH_2$), 21.3 ($CH_3$), 12.2 ($CH_3$); **MS** *m/z* (% rel. intensity, ion) 238 (1, $M^{+\cdot}$), 119 [100, ($MePhCO^+$)], 91 [58, ($PhCH_2^+$)]. **Anal. Calcd.** for $C_{17}H_{18}O$: C 85.67, H 7.61. Found: C 85.38, H 7.58.

*3.2.5. 2-Phenyl-1-(4-methylphenyl)butanone (3cb; Table 1, Entry 11) [21]*

Colorless oil. $\nu_{max}/cm^{-1}$ 1692 (CO). **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.80 (d, $J$ = 8.2 Hz, 2H), 7.22–7.14 (m, 4H), 7.10–7.06 (m, 3H), 4.33 (t, $J$ = 7.2 Hz, 1H), 2.22 (s, 3H), 2.11 (m, 1H enantiotropic), 1.76 (m, 1H enantiotropic), 0.80 (t, $J$ = 7.4 Hz, 3H); **$^{13}$C NMR** (75.5 MHz, $CDCl_3$) $\delta$ (ppm) 199.6 (CO), 143.4 (C), 139.9 (C), 134.6 (C), 129.1 (CH), 128.7 (CH), 128.2 (CH), 126.8 (CH), 55.3 (CH), 27.1 ($CH_2$), 21.4 ($CH_3$), 12.3 ($CH_3$); **MS** *m/z* (% rel. intensity, ion) 238 (2, $M^{+\cdot}$), 119 [100, ($MePhCO^+$)], 91 [51, ($PhCH_2^+$)].

*3.2.6. 2-Phenyl-1-(2-methylphenyl)butanone (3db; Table 1, entry 12)*

Colorless oil. $\nu_{max}/cm^{-1}$ 1693 (CO). **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.74 (m, 1H), 7.50–7.36 (m, 8H), 4.50 (t, $J$ = 7.3 Hz, 1H), 2.54 (s, 3H), 2.46 (m, 1H enantiotropic), 2.07 (m, 1H enantiotropic), 1.16 (t, $J$ = 7.4 Hz, 3H); **$^{13}$C NMR** (75.5 MHz, $CDCl_3$) $\delta$ (ppm) 204.4 (CO), 139.2 (C), 138.9 (C), 137.7 (C), 131.5 (CH), 130.6 (CH), 128.6 (CH), 128.4 (CH), 127.7 (CH), 126.9 (CH), 125.3 (CH), 58.8 (CH), 26.5 ($CH_2$), 20.5 ($CH_3$), 12.3 ($CH_3$); **MS** *m/z* (% rel. intensity, ion) 238 (1, $M^{+\cdot}$), 119 [100, ($MePhCO^+$)], 91 [59, ($PhCH_2^+$)]. **Anal. Calcd.** for $C_{17}H_{18}O$: C 85.67, H 7.61. Found: C 85.90, H 7.63.

*3.2.7. 2-Phenyl-1-(3-fluorophenyl)butanone (3eb; Table 1 entry 13; Table 3, entry 4 and Table 4, entry 6)*

White solid, m.p. 55 °C. $\nu_{max}/cm^{-1}$ 1689 (CO). **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.64 (d, $J$ = 7.6 Hz, 1H), 7.54 (d, $J$ = 9.5 Hz, 1H), 7.30–7.06 (m, 7H), 4.29 (t, $J$ = 7.2 Hz, 1H), 2.12 (m, 1H enantiotropic), 1.78 (m, 1H enantiotropic), 0.83 (t, $J$ = 7.3 Hz, 3H); **$^{13}$C NMR** (75.5 MHz, $CDCl_3$) $\delta$ (ppm) 198.8 (d, $J$ = 1.9 Hz, CO), 162.8 (d, $J$ = 248 Hz, C), 139.3 (C), 139.2 (CH), 130.1 (d, $J$ = 7.5 Hz, CH), 128.9 (CH), 128.2 (CH), 127.1 (CH), 124.3 (d, $J$ = 2.7 Hz, CH), 119.7 (d, $J$ = 21.7 Hz, CH), 115.4 (d, $^2J_{CF}$ = 22 Hz, CH); 115,4 (d, $^2J_{CF}$ = 22 Hz, CH); 55,8 ($CH_2$); 27,0 ($CH_2$); 12,2 ($CH_3$). **MS** *m/z* (% rel. intensity, ion) 242 (9, $M^{+\cdot}$), 183 [5, ($M^{+\cdot}$—EtCO$^{\cdot}$)], 123 [100, ($FPhCO^+$)], 91 [92, ($PhCH_2^+$)]. **Anal. Calcd.** for $C_{16}H_{15}FO$: C 79.32, H 6.24. Found: C 79.10, H 6.21.

*3.2.8. 2-Phenyl-1-(2,6-dimethylphenyl)butanone (3gb; Table 1, entry 14)*

Colorless oil. $\nu_{max}/cm^{-1}$ 1690 (CO) $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.26–7.19 (m, 3H), 7.16 (m, 2H), 7.09 (m, 1H), 7.53 (d, $J$ = 7.5 Hz, 2H), 3.91 (dd, $J$ = 5.5 Hz, $J$ = 9.5 Hz, 1H), 2.32–2.04 (m, 2H), 1.93 (s, 6H), 0.89 (t, $J$ = 7.4 Hz, 3H); **$^{13}$C NMR** (75.5 MHz, $CDCl_3$) $\delta$ (ppm) 209.1 (CO), 141.8 (C), 136.9 (C), 133.4 (C), 129.2 (CH), 128.5 (CH), 128.5 (CH), 127.7 (CH), 127.3 (CH), 62.1 (CH), 24.3 ($CH_2$), 19.2 ($CH_3$), 11.9 ($CH_3$); **MS** *m/z* (% rel. intensity, ion) 133 [100, ($Me_2PhCO^+$)], 105 [33, $Me_2Ph^+$)], 91 [20, ($PhCH_2^+$)]. **Anal. Calcd.** for $C_{16}H_{20}O$: C 85.67, H 7.99. Found: C 85.82, H 7.96.

*3.2.9. 1-(2,6-Dimethylphenyl)ethanone (3gf; Table 1, entry 23) [22]*

Yellow oil. $\nu_{max}/cm^{-1}$ 1690 (CO). **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.15 (t, $J$ = 7.1 Hz, 1H), 7.02 (d, $J$ = 7.1 Hz, 2H), 2.48 (s, 3H), 2.26 (s, 6H); **$^{13}$C NMR** (75.5 MHz, $CDCl_3$) $\delta$ (ppm) 208.0 (CO), 142.6 (C), 132.2 (C), 138.5 (CH), 127.8 (CH), 32.0 ($CH_3$), 19.1 ($CH_3$); **MS** *m/z* (% rel. intensity, ion) 148 (21, $M^{+\cdot}$), 133 [100, ($M^{+\cdot}$—Me$^{\cdot}$)], 91 [8, ($MePh^+$)], 77 [41, ($Ph^+$)].

*3.2.10. (E)-1-(2,6-Dimethylphenyl)-3-phenyl-2-propenone (3gg; Table 1, Entry 22)*

Yellow oil. $\nu_{max}/cm^{-1}$ 1680 (CO) and 1602 (C = C). **$^1$H NMR** (300 MHz, CDCl3) $\delta$ (ppm) 7.40 (dd, $J$ = 3.0 Hz, $J$ = 6.6, 2H), 7.29–7.27 (m, 3H), 7.11 (dd, $J$ = 8.0 Hz, $J$ = 16 Hz, 2H), 6.97 (d, $J$ = 7.6 Hz, 2H), 6.85 (d, $J$ = 16 Hz, 1H), 2.14 (s, 6H); **$^{13}$C NMR** (75.5 MHz, CDCl3) $\delta$ (ppm) 200.9 (CO), 146.8(CH), 146.6 (C), 139.9 (C), 134.4 (C), 134.0 (CH), 130.8 (CH), 128.9 (CH), 128.4 (CH), 127.8 (CH), 127.3 (CH), 19.4 (CH3); **MS** m/z (% rel. intensity,

ion) 236 (25, $M^{+\cdot}$), 221 [9, ($M^{+\cdot}$—$Me^{\cdot}$)], 159 [10, ($M^{+\cdot}$—$Ph^{\cdot}$)], 145 (100, $C_{10}H_9O^+$) 133 [20, ($Me_2PhCO^+$)], 103 [45, ($PhCHCH^+$)]. Anal. Calcd. for C17H16O: C 86.40, H 6.82. Found: C 86.71, H 6.80.

### 3.3. Recovering method for organotin chlorides

The recovery of trialkyltin chlorides was carried out using the methods resumed in our previous work [5c].

#### 3.3.1. Dibutyltin dichloride

After workup of the reactions carried out with diaryldibutylstannanes, the resulting cloudy organic phases (~5 mL for 1.0 mmol scale) were centrifuged. The amorphous off-white sediments of $(Bu_2SnO)_n$ were washed twice by centrifugation with DCM and reserved for its further conversion in $Bu_2SnCl_2$ [23].

## Acknowledgments

This work was partially supported by CONICET, CIC, ANPCYT and the Universidad Nacional del Sur, Bahía Blanca, Argentina. CONICET is thanked for a research fellowship to MJL F.

## References

[1] (a) M.B. Smith, J. March, March's Advanced Organic Chemistry, 6th. ed., John Wiley, New York, 2007;
(b) R.C. Larock, Comprehensive Organic Transformations, Wiley, VCH; New York, 1999.
[2] For a review of acylation of organometallic reagents with acid chlorides K. Dieter, Reaction of acyl chlorides with organometallic reagents: a banquet table of metals for ketone synthesis, Tetrahedron 55 (1999) 4177–4236.
[3] (a) Synthesis: A.B. Chopa, M.T. Lockhart, G.F. Silbestri, Two step synthesis of arylstannanes from phenols, Organometallics 19 (2000) 2249–2251;
(b) A.B. Chopa, M.T. Lockhart, G.F. Silbestri, Synthesis of arylstannanes from arylamines, Organometallics 20 (2001) 3358–3360;
(c) A.B. Chopa, M.T. Lockhart, V.B. Dorn, Phenols as starting materials for the synthesis of arylstannanes via SRN1, Organometallics 21 (2002) 1425–1429;
(d) A.B. Chopa, M.T. Lockhart, G.F. Silbestri, Synthesis of bis(trimethylstannyl) aryl compounds via SRN1 with intermediacy of monosubstitution products, Organometallics 21 (2002) 5874–5878;
(e) G.F. Silbestri, M.J. Lo Fiego, M.T. Lockhart, A.B. Chopa, Selective synthesis of mono- and distannylpyridines from chloropyridinols via an SRN1 mechanism, J. Organomet. Chem. 695 (2010) 2578–2585;
(f) . Applications:A.B. Chopa, G.F. Silbestri, M.T. Lockhart, Strategies for the synthesis of bi- and triarylic materials starting from commercially available phenols, J. Organomet. Chem. 690 (2005) 3865–3877.
[4] A. Davies, Organotin Chemistry, VCH Verlagsgesellschaft, Weiheim, Germany, 1997.
[5] (a) G.F. Silbestri, R. Bogel Masson, M.T. Lockhart, A.B. Chopa, A catalyst-free synthesis of asymmetric diaryl ketones from aryltins, J. Organomet. Chem. 691 (2006) 1520–1524;
(b) M.J. Lo Fiego, M.A. Badajoz, G.F. Silbestri, M.T. Lockhart, A.B. Chopa, Efficient catalyst-free bi- and triaroylation of aromatic rings in a single step, J. Org. Chem. 73 (2008) 9184–9187;
(c) M.J. Lo Fiego, G.F. Silbestri, A.B. Chopa, M.T. Lockhart, Selective synthetic routes to sterically hindered unsymmetrical diaryl ketones via arylstannanes, J. Org. Chem. 76 (2011) 1707–1714.
[6] M.J. Lo Fiego, M.T. Lockhart, A.B. Chopa, Catalyst-free alkanoylation of aromatic rings via arylstannanes. Scope and limitations, J. Organomet. Chem. 694 (2009) 3674–3678.
[7] (a) B.C. Ranu, Indium metal and its halides in organic synthesis, Eur. J. Org. Chem. (2000) 2347–2356;
(b) V. Nair, S. Ros, C.N. Jayan, B.S. Pillia, Indium- and gallium-mediated carbon–carbon bond-forming reactions in organic synthesis, Tetrahedron 60 (2004) 1959–1982;
(c) J. Augé, N. Lubin-Germain, J. Uziel, Recent advances in indium-promoted organic reactions, Synthesis (2007) 1739–1764;
(d) J.S. Yadav, A. Antony, J. George, B.V. Reddy, Recent developments in indium metal and its salts in organic synthesis, Eur. J. Org. Chem. (2010) 591–605.
[8] (a) T.J. Mason, P. Cintas, in: J. Clark, D. Macquarrie (Eds.), Handbook of Green Chemistry and Technology, Blackwell Science, Oxford, 2002;
(b) T.J. Mason, Sonochemistry and the environment – Providing a "green" link between chemistry, physics and engineering, Ultrason. Sonochem. 14 (2007) 476–483.
[9] (a) For reviews see: G. Cravotto, P. Cintas, Power ultrasound in organic synthesis: moving cavitational chemistry from academia to innovative and large-scale applications, Chem. Soc. Rev. 35 (2006) 180–196;
(b) R. Cella, H.A. Stefani, Ultrasound in heterocycles chemistry, Tetrahedron 65 (2009) 2619–2641;
(c) K.S. Suslick, Comprehensive Coordination Chemistry 2, Elsevier Science, NY, 2003 (Chapter 1.41, 731–739; Papers);
(d) A. Dandia, D.S. Bhati, A.K. Jain, G.N. Sharma, Ultrasound promoted clay catalyzed efficient and one pot synthesis of substituted oxindoles, Ultrason. Sonochem. 18 (2011) 1143–1147;
(e) E. Ruiz, H. Rodríguez, J. Coro, E. Salfrán, M. Suárez, R. Martínez-Alvarez, N. Martín, Ultrasound-assisted one-pot, four component synthesis of 4-aryl 3,4-dihydropyridone derivatives, Ultrason. Sonochem. 18 (2011) 32–36.
[10] P. Cintas, G. Palmisano, G. Cravotto, Power ultrasound in metal-assisted synthesis: from classical Barbier-like reactions to click chemistry, Ultrason. Sonochem. 18 (2011) 836–841.
[11] P.H. Lee, K. Bang, K. Lee, S.-Y. Sung, S. Chang, Ultrasound promoted synthesis of β-hydroxyesters by reformatsky reaction using indium metal, Synth. Commun. 31 (2001) 3781–3789.
[12] (a) M. Chtourou, R. Abdelhédi, M. Hédi Frikha, M. Trabelsi, Solvent free synthesis of 1,3-diaryl-2-propenones catalyzed by commercial acid-clays under ultrasound irradiation, Ultrason. Sonochem. 17 (2010) 246–249;
(b) I. Mohammadpoor-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, Z. Eskandari, Ultrasound promoted selective synthesis of 2-aryl-5,6-dihydro-4H-1,3-oxazines catalyzed by K-10 and KSF montmorillonite clays: a practical procedure under mild and solvent-free conditions, Ultrason. Sonochem. 17 (2010) 857–862;
(c) Z. Fu, H. Shao, An efficient synthesis of 3-substituted indole derivates under ultrasound irradiation, Ultrason. Sonochem. 18 (2011) 520–526.
[13] A. Ogawa, D.P. Curran, Benzotrifluoride: a useful alternative solvent for organic reactions currently conducted in dichloromethane and related solvents, J. Org. Chem. 62 (1997) 450–451.
[14] A.G. Davies, Metals as surrogates for hydrogen in organic chemistry: anything hydrogen can do, a metal can do better, J. Chem. Soc., Perkin Trans. 1 (2000) 1997–2010.
[15] (a) We added detergent to water (2.0% v/v) in order to facilitate ultrasound propagation. See: T.J. Mason, Sonochemistry, Oxford University Press, New York, 1999;
(b) C.C. Nascentes, M. Korn, C.S. Sousa, M.A.Z. Arruda, Use of Ultrasonic Baths for Analytical Applications: A New Approach for Optimization Conditions, J. Braz. Chem. Soc. 12 (2001) 57–63.
[16] J.C. de Souza-Barboza, C.P. Btrier, J-L. Luche, Ultrasound in organic synthesis. 13. Some fundamental aspects of the sonochemical Barbier reaction, J. Org. Chem. 53 (1988) 1212–1218.
[17] T. Hudlicky, D.A. Frey, L. Koroniak, C.D. Claeboe, L.E. Brammer, Towards a "reagent-free" synthesis, Green Chem. 1 (1999) 57–59.
[18] C.C. Yammal, J.C. Podestá, R.A. Rossi, Reactions of Triorganostannyl Ions with Haloarenes in Liquid Ammonia. Competition between Halogen-Metal Exchange and Electron-Transfer Reactions, J. Org. Chem. 571 (992) 5720–5725.
[19] F.I. Carroll, B.E. Blough, P. Abraham, A.C. Mills, J.A. Holleman, S.A. Wolckenhauer, A.M. Decker, A. Landavazo, K.T. McElroy, H.A. Navarro, M.B. Gatch, M.J. Forster, Synthetic and biological evaluation of bupropion analogues as potential pharmacotherapies for cocaine addiction, J. Med. Chem. 52 (2009) 6768–6781.
[20] P.J. Wagner, M.J. Thomas, E. Harris, Effects of methyl substitution on the photoreactivity of phenyl ketones. The applicability to Hammett sigma values in correlations of excitation energies, J. Am. Chem. Soc. 98 (1976) 7675–7679.
[21] T.P. Smyth, B.W. Corby, Toward a clean alternative to Friedel–Crafts acylation: in situ formation, observation, and reaction of an acyl bis(trifluoroacetyl)phosphate and related structures, J. Org. Chem. 63 (1998) 8946–8951.
[22] R.C. Fuson, H.O. House, Diacetylation of m-xylene, J. Org. Chem. 18 (1953) 496–500.
[23] R.K. Ingham, S.D. Rosenberg, H. Gilman, Organotin compounds, Chem. Rev. 60 (1960) 459–539.