

## Ultrasonic activation of the arylation reaction of styrene catalyzed by transition metals

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Received: 12.01.2017

Accepted/Published Online: 22.03.2017

Final Version: 05.09.2017

**Abstract:** The arylation reaction of styrene was tested in the presence of different transition metal-based catalysts, mainly iron-based, given its low cost and its nonpolluting and nontoxic characteristics. The study of the effect of sonochemical activation on the evolution of the selectivity of the reaction is also proposed. Higher efficiency was observed for a very short period of time of just a few minutes. Furthermore, an improvement of the selectivity of the arylation of the external carbon of styrene was observed.

**Key words:** Stilbene, iron, ultrasound, arylation, selectivity

### 1. Introduction

In recent years, there has been a strong tendency to develop new methods to activate the C-H bond and the application of these methods in the synthesis of target molecules such as natural products and pharmaceutical compounds. Thus, new C-C bond formation reactions based on transition metal catalysis have been discovered. These have offered new synthesis perspectives and have allowed researchers to access increasingly complex molecules that were inaccessible through conventional methods. The Heck coupling reaction<sup>1,2</sup> is one of the most important methods used for C-C bond formation with transition metals as catalysts.<sup>3-10</sup>

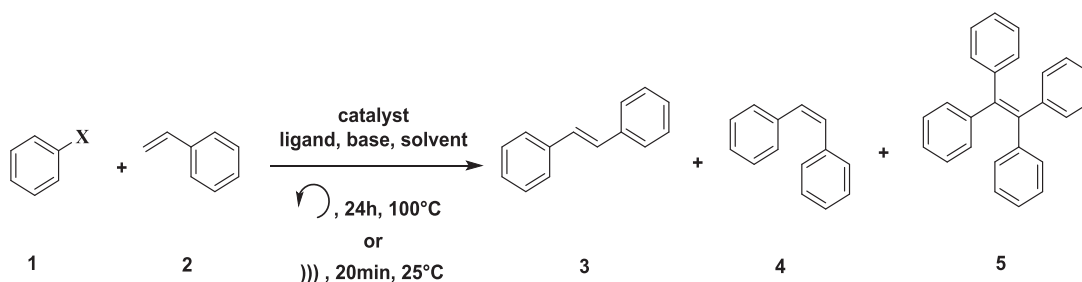
Among the various transition metals used, palladium has proven to be the metal of choice for performing C-C coupling reactions. However, the use of this type of palladium complex has a major disadvantage for this method given the high cost of the complex and given that several scientific studies show that it has harmful effects on health and the environment.<sup>11-13</sup> For these reasons, the search for new more cost-effective and green routes for the formation of C-C bonds has become a major problem for industrial and academic research teams.

In this regard, we have tested the arylation reaction of styrene in the presence of a new iron-based catalyst, which has the advantage of being less expensive, nonpolluting, and nontoxic.<sup>14,15</sup> The aim of this work was to study the effect of the reaction parameters and the effect of ultrasonic activation on the evolution and selectivity of the reaction by comparing the results obtained with those obtained through the conventional (thermal) method.

### 2. Results and discussion

Different conditions were studied for the arylation reaction of styrene under thermal conditions (24 h at 100 °C) or under ultrasonic irradiation (20 min at 25 °C), during which several products were detected (Scheme).

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Scheme. The arylation reaction of styrene.

## 2.1. Thermal activation

### 2.1.1. Effect of the nature of the solvent

Table 1 summarizes the conversions and yields obtained in various solvents. From all the solvents tested, it appears that an aprotic polar solvent such as DMF is the most suitable for carrying out the arylation of styrene  $\beta$ -carbon. The yield reached in this case is 55% for the trans form and 17% for the cis form. The use of n-hexane, chloroform, THF, acetic acid, and water instead of DMF makes it possible to improve the arylation of styrene by forming tetraphenylethylene in yields reaching up to 91% when using THF. However, in a polar protic medium, the results show lower reactivity with slightly lower yields of 89% in water, which decreases to 29% in acetic acid. This seems to be due to the secondary reactions that take place in a polar protic medium.<sup>16</sup> However, the most plausible explanation seems to be the polarity of the environment.

**Table 1.** Influence of the nature of the solvent on the arylation reaction of styrene.

Product	Solvent	Dipole moment (D)	Conversion (%) <sup>a</sup>		Yield (%) <sup>b</sup>	
			5	3/4	5	3/4
1	DMF	3.82	-	57/18	-	55/17
2	n-Hexane	0.00	> 99	-	88	-
3	Chloroform	1.04	95	-	85	-
4	THF	1.75	> 99	-	91	-
5	Acetic acid	1.74	31	-	29	-
6	Water	1.85	98	-	89	-

**Procedure A:** FeCl<sub>3</sub>·6H<sub>2</sub>O (0.025 mmol), PPh<sub>3</sub> (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.125 mmol), iodobenzene (2.5 mmol), styrene (2.25 mmol), solvent (3 mL), 100 °C, 24 h. <sup>a</sup>The conversions were determined by HPLC on the basis of area percentage, <sup>b</sup>isolated yield.

In the ground state, the two  $\pi$  electrons of an alkene are symmetrically located with regards to the two carbon atoms and there is no charge excess or charge defect. The movement of an electron from the  $\pi$  orbital to the  $\pi^*$  orbital results in the destruction of the  $\pi$  bond in the excited state. The two electrons are then located in the two 2p atomic orbitals of each carbon atom, which are now perpendicular. These orbitals then interact with the nonbinding orbital of the oxygen in DMF, resulting in two interactions with three weakly bonding electrons: the  $\pi^*$  level moves down.<sup>17,18</sup> This state with separated electrons is more stable, with stronger interactions, and so the solvent is more polar.

In order to explain the formation of the different products obtained, we propose the following reaction mechanism (Figure 1): the cycle begins with the reduction of Fe<sup>III</sup> by adding a phosphine as a reaction medium,<sup>19</sup> followed by an oxidative addition of the aryl halide to Fe<sup>I</sup>, which gives rise to an organo-iron product. A syn-insertion of styrene into this last complex (Ph-Fe-I) then results in the formation of a new

unstable C-C bond. This involves an internal rotation around this bond so that the  $\beta$ -hydrogen of the metal center is in the syn-position relative to the iron and thus leads to a  $\beta$ -elimination, which forms the new substituted alkene (stilbene) and the iron hydride. Finally, the presence of a base decomposes the iron hydride into  $\text{Fe}^I$  and traps the HI acid produced.

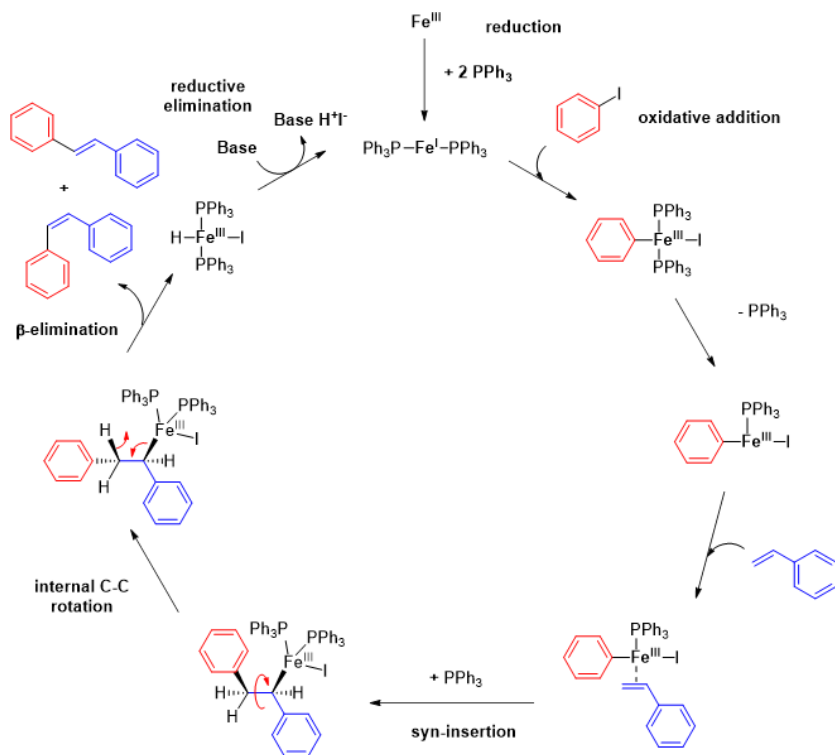


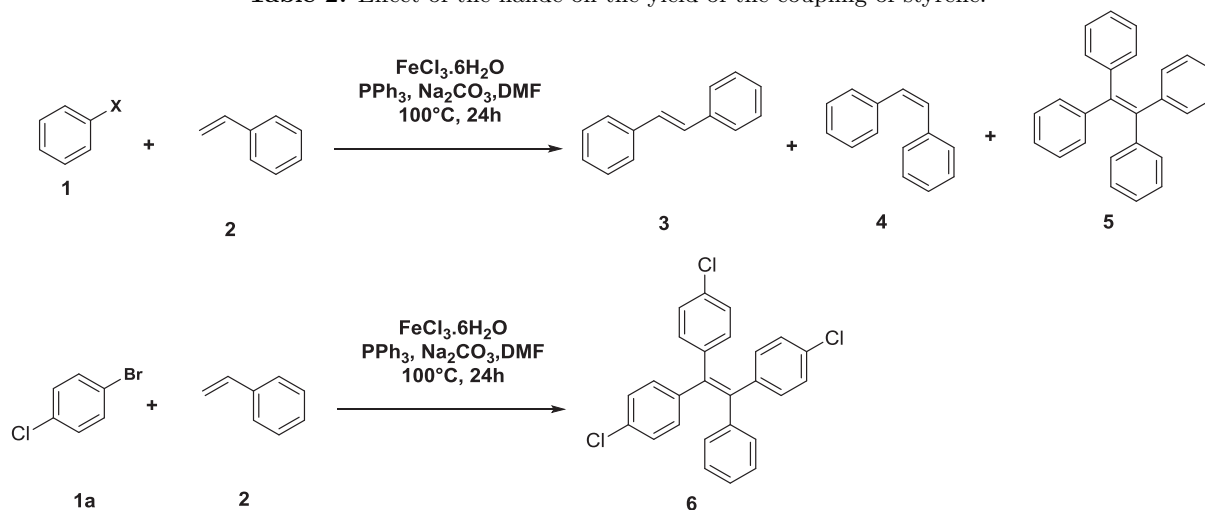
Figure 1. Proposed catalytic mechanism of the arylation reaction of styrene.

### 2.1.2. Effect of the nature of the halogen

The effect of the nature of the halogen in the arylation reaction of styrene is shown in Table 2.

In light of the results shown in Table 2, the effect of the halogen nature on the evolution of the arylation reaction of styrene is clearly seen. The analyses show that the use of iodobenzene generates the arylation of the styrene external carbon producing both the trans and the cis forms with yields of 55% and 17%, respectively. However, the use of bromobenzene, chlorobenzene, and 1-bromo-4-chlorobenzene involves the tri-arylation of styrene with yields of 85%, 80%, and 90%, respectively. The analyses show that the use of iodobenzene generates the arylation of the styrene external carbon, producing both the trans and the cis forms with yields of 55% and 17%, respectively. However, the use of bromobenzene, chlorobenzene, and 1-bromo-4-chlorobenzene involves the tri-arylation of styrene with yields of 85%, 80%, and 90%, respectively. This result was confirmed by Hajipour and Azizi,<sup>15</sup> who showed that iodobenzene was the only reagent participating in the reaction and bromobenzene was fully recovered after purification. On the other hand, 1-bromo-4-iodobenzene was converted into methyl-4-bromocinnamate as the only product.

In order to interpret the results obtained, we propose a reaction mechanism illustrating the styrene arylation reaction according to the nature of the halogen used (Figure 2). Thus, the regiochemistry of the final product depends on the reaction mechanism.

**Table 2.** Effect of the halide on the yield of the coupling of styrene.

Product	Aryl halide	Conversion (%) <sup>a</sup>			Yield (%) <sup>b</sup>		
		5	6	3/4	5	6	3/4
1	C <sub>6</sub> H <sub>5</sub> -I	-	-	57 /18	-	-	55/17
7	C <sub>6</sub> H <sub>5</sub> -Br	> 99	-	-	85	-	-
8	C <sub>6</sub> H <sub>5</sub> -Cl	> 99	-	-	80	-	-
9	Cl-C <sub>6</sub> H <sub>4</sub> -Br	-	100	-	-	90	-

**Procedure A:** FeCl<sub>3</sub>.6H<sub>2</sub>O (0.025 mmol), PPh<sub>3</sub> (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.125 mmol), aryl halide (2.5 mmol), styrene (2.25 mmol), DMF (3 mL), 100 °C, 24 h. <sup>a</sup>The conversions were determined by HPLC on the basis of area percentage, <sup>b</sup>isolated yield.

- In the case of iodine, the main mechanism seems to involve passing through the neutral intermediate. Indeed, the iron-halogen bond is a strong bond.
- In the case of Br or Cl, the iron-halogen bond is much more unstable and so a reaction proceeding through the cationic intermediate is more frequent.

This result is confirmed by the work of Ludwig et al.,<sup>20</sup> who showed the effect of the aryl halide on the regioselectivity of the Heck reaction when passing from X = I, OAc to BF<sub>4</sub>. In our case, the formation of TPE can be explained by the formation of 1,1-diphenylethylene while the arylation of the styrene external carbon leads to lower values of the steric hindrance and the electronic density.<sup>21</sup>

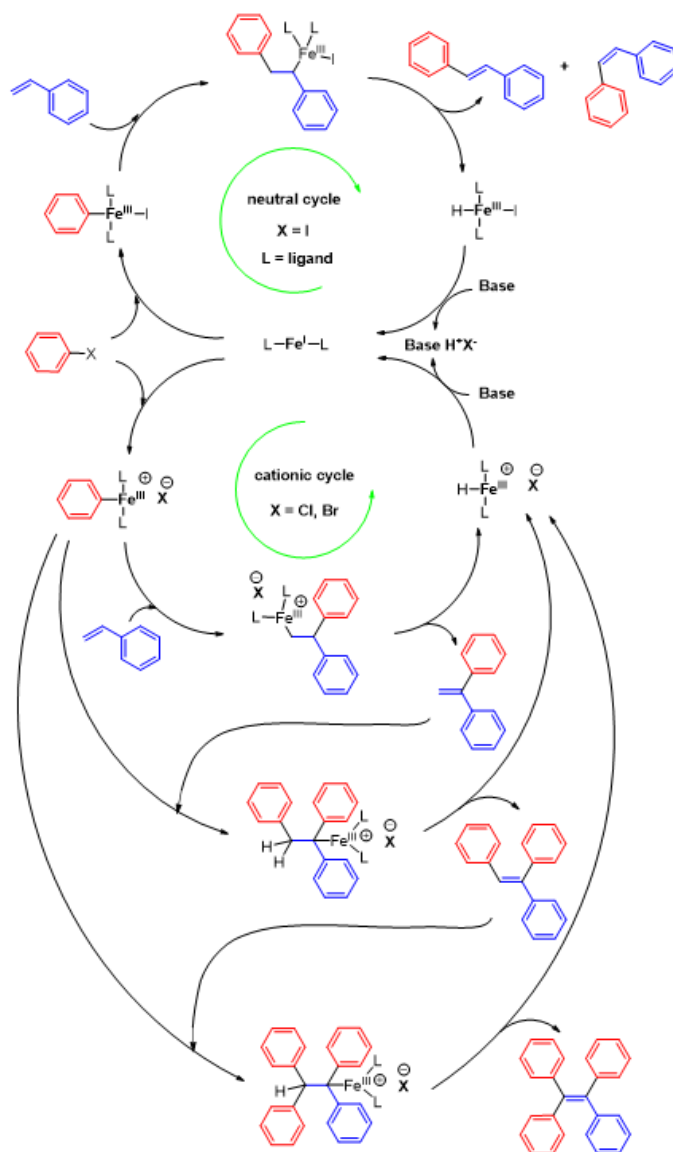
### 2.1.3. Effect of the nature of the ligand

The spectroscopic analyses show a difference in the nature of the adduct compound for each ligand used. Thus, the use of P(p-Ph-Cl)<sub>3</sub> results in the formation of two trans-stilbene and cis-stilbene isomers. However, the use of PPh<sub>3</sub>, P(p-Ph-CH<sub>3</sub>)<sub>3</sub>, and P(p-Ph-OCH<sub>3</sub>)<sub>3</sub> involves the formation of tetraphenylethylene.

Table 3 shows the conversions and yields obtained for each type of ligand used.

The results obtained show a better reactivity for all the reactions studied but different regioselectivities. The internal arylation of styrene has already been explained above with the use of bromobenzene, which favors a cationic mechanism.<sup>20</sup>

The use of P(p-Ph-Cl)<sub>3</sub> results in arylation at the styrene β-position. This result can be explained at



**Figure 2.** Neutral and cationic mechanisms of the arylation reaction of styrene according to the nature of the aryl halide.

**Table 3.** Influence of the nature of the ligand of the arylation reaction of styrene.

Product	Ligand	Conversion (%) <sup>a</sup>		Yield (%) <sup>b</sup>	
		5	3/4	5	3/4
7	PPh <sub>3</sub>	> 99	-	85	-
10	P(p-Ph-CH <sub>3</sub> ) <sub>3</sub>	> 99	-	96	-
11	P(p-Ph-Cl) <sub>3</sub>	-	99/1	-	96/1
12	P(p-Ph-OCH <sub>3</sub> ) <sub>3</sub>	100	-	98	-

**Procedure A:** FeCl<sub>3</sub>.6H<sub>2</sub>O (0.025 mmol), ligand (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.125 mmol), (2.5 mmol) bromobenzene, styrene (2.25 mmol), DMF (3 mL), 100 °C, 24 h. <sup>a</sup>The conversions were determined by HPLC on the basis of area percentage, <sup>b</sup>isolated yield.

first by the presence of chlorine in the sphere of the complex formed after the oxidative addition step. Thus, it can modify the initial cationic nature and the neutral route will be favored. The electronic environment of the metal is easily adjusted by the appropriate choice of ligands, which influences both the reactivity and the selectivity of the reactions. The most plausible explanation seems to be due to the Tolman cone angle, which affects the reactivity of the ligands in the Heck coupling reaction.<sup>22</sup>

From the results collected in Table 4, it can be concluded that the yield depends on both the steric and the electrical effects of the ligand used.<sup>23</sup> Some studies state that the more cluttered the ligand is, the greater the metal–phosphorus distance will be, and therefore the more unstable the bond.<sup>24</sup> This was explained by the results obtained by Cooley et al.,<sup>25</sup> where they showed that the fastest reductive elimination was observed for the ligands with the largest cone angles.

**Table 4.** Variation of the steric and electrical characteristics of the different ligands.

Product	Ligand	Tolman cone angle (°)	Frequencies	Yield (%) <sup>b</sup>	
				5	3/4
7	PPh <sub>3</sub>	145	2068.9	95	-
10	P(p-Ph-CH <sub>3</sub> ) <sub>3</sub>	145	2066.7	96	-
11	P(p-Ph-Cl) <sub>3</sub>	176.6	2072.8	-	96/1
12	P(p-Ph-OCH <sub>3</sub> ) <sub>3</sub>	143.6	2066.1	98	-

<sup>b</sup>Isolated yield.

Similarly, Fu et al. showed that the combination of hindered and electron-rich phosphines with palladium sources generates a highly active species for coupling reactions.<sup>26–28</sup>

It can therefore be concluded from the results shown in Table 4 that the arylation of the external carbon in styrene, in the case where P(p-Ph-Cl)<sub>3</sub> is used, is due to the electronic and steric effects of this type of ligand.

#### 2.1.4. Effect of the nature of the base

The effect of the nature of the base in the arylation reaction of styrene is shown in Table 5.

**Table 5.** Influence of the nature of the base on the arylation reaction of styrene.

Product	Base	Conversion (%) <sup>a</sup>	Yield (%) <sup>b</sup>
		5	5
7	Na <sub>2</sub> CO <sub>3</sub>	> 99	85
13	NEt <sub>3</sub>		82
14	NBu <sub>3</sub>		91
15	NaOH		83
16	K <sub>2</sub> CO <sub>3</sub>		84

**Procedure A:** FeCl<sub>3</sub>·6H<sub>2</sub>O (0.025 mmol), PPh<sub>3</sub> (0.05 mmol), base (3.125 mmol), bromobenzene (2.5 mmol), styrene (2.25 mmol), DMF (3 mL), 100 °C, 24 h. <sup>a</sup>The conversions were determined by HPLC on the basis of area percentage, <sup>b</sup>isolated yield.

These results show total site-selectivity of the arylation of styrene in the  $\alpha$ -position due to the use of bromobenzene.<sup>20</sup> However, these bases did not kinetically affect the reactivity relative to the cationic complexes. Thus, the conversions obtained for the different bases used are almost identical. These results allow us to state that the base has no effect on the styrene insertion step.

### 2.1.5. Effect of the nature of the catalyst

The conversions and yields obtained are shown in Table 6.

**Table 6.** Influence of the nature of the catalyst on the arylation of styrene.

Product	Catalyst	Conversion (%) <sup>a</sup>		Yield (%) <sup>b</sup>	
		5	3/4	5	3/4
7	FeCl <sub>3</sub> .6H <sub>2</sub> O	> 99	-	85	-
17	Ag	> 99	-	83	-
18	CuO	77	-	74	-
19	ZrO <sub>2</sub>	> 99	-	90	-
20	Ni(OAc) <sub>2</sub>	98	2/<1	79	2/<1
21	Pd(OAc) <sub>2</sub>	-	59/41	-	55/35
22	Fe(OAc) <sub>2</sub>	-	99/<1	-	94/<1

**Procedure A:** Catalyst (0.025 mmol), PPh<sub>3</sub> (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.125 mmol), bromobenzene (2.5 mmol), styrene (2.25 mmol), DMF (3 mL), 100 °C, 24 h. <sup>a</sup>The conversion was determined by HPLC on the basis of area percentage, <sup>b</sup>isolated yield.

These results show that only palladium acetate, nickel acetate, and iron acetate lead to the formation of stilbene while the others involve the tri-arylation of styrene.

They show the efficiency of the catalytic system in the arylation reactions studied. However, the selective arylation at the styrene  $\alpha$  or  $\beta$  positions varies when the catalyst system is changed.

These results show that the type of transition metal is not responsible for the selectivity between the external and internal position of styrene but, in fact, is responsible for the type of ligand coordinated with it. Thus, the use of two forms of iron (FeCl<sub>3</sub>.6H<sub>2</sub>O and Fe(OAc)<sub>2</sub>) yields a change in the arylation position. Furthermore, the use of the acetate ligand (OAc) coordinated with different transition metals (Ni, Pd, Fe) always results in the external arylation of styrene. This was explained by Amatore et al.,<sup>29</sup> who found better reactivity of the PhPd(OAc)(PPh<sub>3</sub>)<sub>2</sub> species compared to PhPdI(PPh<sub>3</sub>)<sub>2</sub>. They deduced that the acetate ligand helped in the release of a coordination site, which favors the insertion of the alkene into the palladium.

## 2.2. Ultrasonic activation

### 2.2.1. Effect of the nature of the ligand

The influence of the sonochemical activation on the yields of the coupling reactions studied is shown in the results listed in Table 7. According to this table, it appears that activation by an ultrasonic probe greatly favors the reactions studied.

Comparing these yields with those obtained by thermal activation (Table 8) shows that the sonochemical activation improves the arylation of the styrene  $\beta$  carbon atom. Thus, the results obtained show that the arylation, in an irradiated medium, becomes more selective on styrene's external carbon.

The ultrasound effects observed for the styrene arylation reaction are due to the cavitation phenomenon.<sup>30</sup> Thus, when the ultrasound propagates through the reaction medium, the molecule oscillations form compression and decompression zones due to the creation of acoustic pressure. These pressure variations involve the movement of the molecules, thus causing the molecular groups to move closer and further apart (Figure 3).

- During the rarefaction cycle, the distance increases.
- During the compression cycle, the distance decreases.

**Table 7.** Influence of ultrasonic activation on ligand reactivity.

Product	Ligand	Conversion (%) <sup>a</sup>		Yield (%) <sup>b</sup>	
		5	3/4	5	3/4
23	PPh <sub>3</sub>	60	12/1	46	52/1
24	P(p-Ph-CH <sub>3</sub> ) <sub>3</sub>	10	32/7	9	30/6
25	P(p-Ph-Cl) <sub>3</sub>	15	13/18	13	13/16
26	P(p-Ph-OCH <sub>3</sub> ) <sub>3</sub>	64	9/16	62	8/14

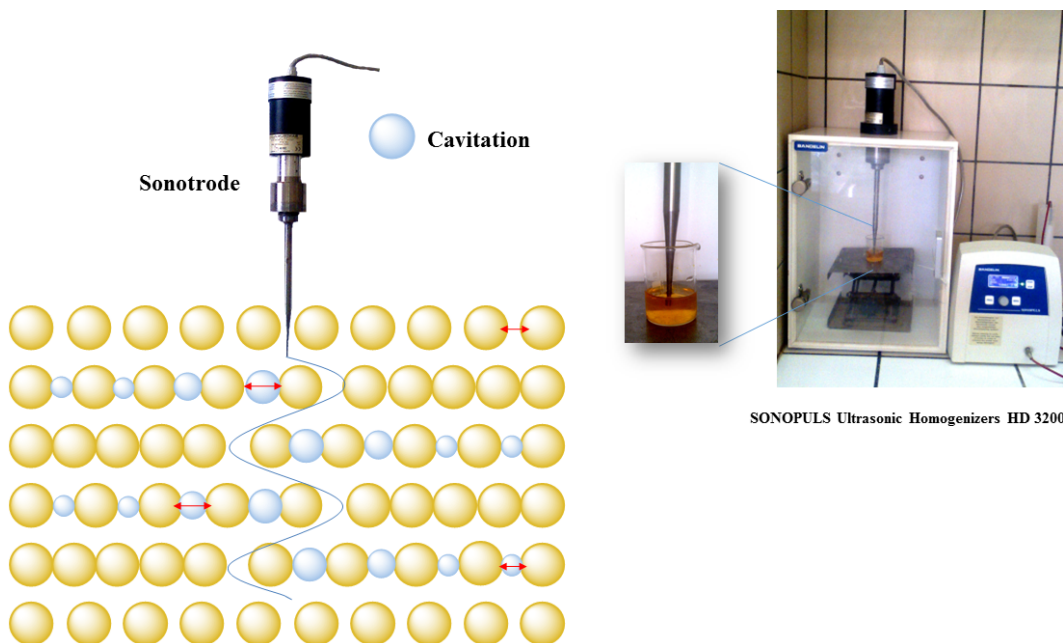
**Procedure B:** FeCl<sub>3</sub>.6H<sub>2</sub>O (0.025 mmol), ligand (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.125 mmol), bromobenzene (2.5 mmol), styrene (2.25 mmol), DMF (3 mL), 25 °C, 20 min. <sup>a</sup>The conversions were determined by HPLC on the basis of area percentage, <sup>b</sup> isolated yield.

**Table 8.** Effect of the ligand on the reactivity of the arylation reaction of styrene under thermal activation and ultrasonic irradiation.

Ligand	Yield (%) <sup>*b</sup>		Yield (%) <sup>**b</sup>	
	5	3/4	5	3/4
PPh <sub>3</sub>	85	-	46	52/1
P(p-Ph-CH <sub>3</sub> ) <sub>3</sub>	96	-	9	30/6
P(p-Ph-Cl) <sub>3</sub>	-	96/1	13	13/16
P(p-Ph-OCH <sub>3</sub> ) <sub>3</sub>	98	-	62	8/14

**\*Procedure A:** FeCl<sub>3</sub>.6H<sub>2</sub>O (0.025 mmol), ligand (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.125 mmol), bromobenzene (2.5 mmol), styrene (2.25 mmol), DMF (3 mL), 100 °C, 24 h. <sup>b</sup> Isolated yield.

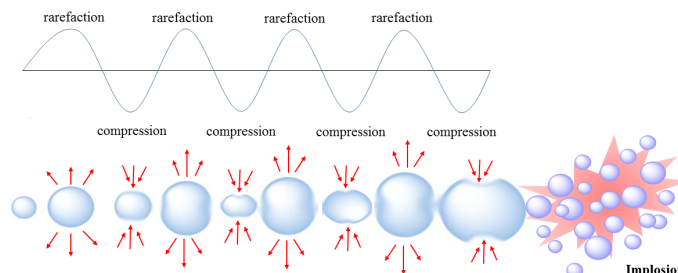
**\*\*Procedure B:** FeCl<sub>3</sub>.6H<sub>2</sub>O (0.025 mmol), ligand (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.125 mmol), bromobenzene (2.5 mmol), styrene (2.25 mmol), DMF (3 mL), 25 °C, 20 min. <sup>b</sup> Isolated yield.

**Figure 3.** Propagation of the ultrasonic wave in the reaction medium.

Each liquid medium has a critical molar distance. Above this characteristic threshold, the cohesive forces in the liquid are overcome and cavitation microbubbles, containing the liquid's vapor and dissolved gases,



appear. With the growth of these bubbles, very high temperatures and pressures are produced inside them to the point where they become unstable. As a result, their collapse produces enormous amounts of energy within the reaction medium (Figure 4). This favors the formation of high yields of stilbene for a very short time.<sup>31</sup>



**Figure 4.** Creation of bubbles followed by their implosion.

### 2.2.2. Effect of the nature of the catalyst

Table 9 shows the conversions and yields for the styrene arylation reaction activated by sonochemical irradiation when applying different transition metal-based complexes.

**Table 9.** Influence of the catalytic system on the arylation of styrene under ultrasonic irradiation.

Product	Catalyst	Conversion (%) <sup>a</sup>		Yield (%) <sup>b</sup>	
		5	3/4	5	3/4
23	FeCl <sub>3</sub> .6H <sub>2</sub> O	46	12/1	46	52/1
27	Ag	8	77/10	7	77/10
28	CuO	6	89/3	5	88/2
29	ZrO <sub>2</sub>	5	91/2	4	89/2
30	Ni(OAc) <sub>2</sub>	48	25/7	40	25/7
31	Pd(OAc) <sub>2</sub>	42	17/6	40	16/6

**Procedure B:** Catalyst (0.025 mmol), PPh<sub>3</sub> (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.125 mmol), bromobenzene (2.5 mmol), styrene (2.25 mmol), DMF (3 mL), 25 °C, 20 min. <sup>a</sup> The conversions were determined by HPLC on the basis of area percentage, <sup>b</sup> isolated yield.

The results shown in this table depict excellent selectivity of external styrene arylation while using FeCl<sub>3</sub>.6H<sub>2</sub>O, Ag, CuO, and ZrO<sub>2</sub>. The yields reached were 52%, 77%, 88%, and 89%, respectively. These are better yields than those obtained when using nickel or palladium, the metal of choice for the Heck reaction.

In order to clearly visualize the effect of sonochemical activation on the reactivity of the catalytic system, Table 10 lists the yields resulting from the two activation methods used.

It follows that the sp<sup>2</sup> hybridized carbon selective arylation is improved in the irradiated medium. Furthermore, certain catalytic systems that are less active during the thermal activation are more efficient in producing stilbene and, more specifically, the trans form. These results are confirmed by those obtained by Srinivosans et al.,<sup>32</sup> who observed that applying sonochemical irradiation to the arylation reaction of certain activated alkenes leads to both significant yields over a very short period of time and excellent selectivity for the E-form.

Similarly, Samant et al.<sup>33</sup> showed that Pd/C, when using ultrasound, can be used as a recyclable catalyst for this type of coupling reaction. As a result, it can reenter a new reaction cycle.

**Table 10.** Effect of the catalyst on the reactivity of the arylation reaction of styrene under thermal activation and ultrasonic irradiation.

Catalyst	Yield (%) <sup>*b</sup>		Yield (%) <sup>**b</sup>	
	5	3/4	5	3/4
FeCl <sub>3</sub> .6H <sub>2</sub> O	85	-	46	52/1
Ag	83	-	7	77/10
CuO	74	-	5	88/2
ZrO <sub>2</sub>	90	-	4	89/2
Ni(OAc) <sub>2</sub>	79	2/<1	40	25/7
Pd(OAc) <sub>2</sub>	-	55/35	40	16/6

**\*Procedure A:** Catalyst (0.025 mmol), PPh<sub>3</sub> (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.125 mmol), bromobenzene (2.5 mmol), styrene (2.25 mmol), DMF (3 mL), 100 °C, 24 h. <sup>b</sup> Isolated yield.

**\*\*Procedure B:** Catalyst (0.025 mmol), PPh<sub>3</sub> (0.05 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.125 mmol), bromobenzene (2.5 mmol), styrene (2.25 mmol), DMF (3 mL), 25 °C, 20 min. <sup>b</sup> Isolated yield.

### 2.3. Conclusions

The study of the sonochemical activation of the styrene arylation reaction has shown excellent efficiency for a very short period of just a few minutes. In addition, it has also shown an improvement of some catalytic systems that are less active in the conventional mode. Moreover, it has been shown that the coupling reactivity and selectivity are affected by the experimental conditions. Indeed, in an aprotic polar medium, the arylation becomes more selective on styrene's external carbon, and the more important the M-X bond is, the more selective the arylation becomes on the  $\beta$ -carbon of styrene. It has also been found that the evolution and selectivity of the reaction is affected by both electronic and steric effects of the ligand.

## 3. Experimental

### 3.1. General procedure

#### 3.1.1. Classical procedure

**Procedure A:** 0.025 mmol of catalyst, 0.05 mmol of ligand, and 3.125 mmol of base were introduced into a steel tube. Next, 2.5 mmol of halogenobenzene was added together with 2.25 mmol of styrene, and then 3 mL of the solvent was finally added. The steel reactor was placed in a thermostatic oil bath maintained at 100 °C for 24 h. After the reaction, the mixture was cooled and the organic phase was extracted three times with n-hexane or cyclohexane and then with the saturated NaCl solution. The adduct obtained was then dried using Na<sub>2</sub>SO<sub>4</sub>, filtered, and placed in a 25-mL ground flask. The solvent was evaporated using a rotary evaporator (Rotavapor). The final adduct was subjected to a TLC thin-layer chromatography test using n-hexane as an eluent and treated with silica gel column chromatography with the same eluent: n-hexane. Finally, the products obtained were analyzed using the usual analysis methods.

#### 3.1.2. Ultrasound procedure

**Procedure B:** The experimental procedure was the same as that of A, but the mixture obtained was subjected to ultrasonic irradiation for 20 min at room temperature (25 °C). At the end of the reaction the products obtained were analyzed using the usual analysis methods.

### 3.2. Characterization

Preparative column chromatography was carried out on 60 Å silica gel with a particle size of 5–14  $\mu\text{m}$ . The elution conditions are those described in the procedure.

The wavelengths used during the chromatographic analyses were measured with a HELIOS Omega UV-Visible apparatus, where the products were eluted in dichloromethane.

Chromatographic analyses were performed on a PerkinElmer HPLC equipped with a 200 series pump, to which a 20- $\mu\text{L}$  automatic loop injector and a UV-Vis detector were connected. The wavelength used was 235 nm. The column used was a C18-type column. The mobile phase used was a mixture of 80% acetone and 20% water with an initial 0.5 mL/min for 30 min. All analyses were processed using TotalChrom Navigator software.

Melting points were measured on a K ofler Bench after calibration with pure compounds, which had melting points similar to the expected values.

FT-IR spectra were recorded using a PerkinElmer Spectrum 100 apparatus. The absorption frequencies ( $\nu$ ) are expressed in  $\text{cm}^{-1}$ .

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the synthesized compounds were recorded on a Bruker AC 400 apparatus with Fourier transform and a nominal frequency of 100 MHz. Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane (TMS), used as an internal reference. The spectra were recorded in deuterated chloroform  $\text{CDCl}_3$ .

Irradiation was guaranteed by using an ultrasonic probe (Sonopuls HD 3200 model, 20 kHz, 200 W) with an ultrasonic generator (Sonics VC 505, 300 W). The ultrasonic probe ( $\Phi = 3$  mm) was immersed directly in the reactor (JENA<sup>er</sup> GLAS 25-mL beaker). The sonication was carried out at a low frequency of 20 kHz (amplitude of 45%) at room temperature for 20 min with a 3-s pulsation.

#### 3.2.1. (E)-Stilbene

Mp: 123–124  $^\circ\text{C}$ ; IR (KBr,  $\text{cm}^{-1}$ )  $\nu = 3020$  ( $\text{CH}_{\text{aro}}$ ), 1750 ( $\text{CH}_{\text{ethyl}}$ ), 1597 ( $\text{C}=\text{C}_{\text{ethyl}}$ ), 1490 ( $\text{C}=\text{C}_{\text{aro}}$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 7.51 (d, 4H,  $J = 6.4$  Hz), 7.35 (t, 4H,  $J = 6.4$  Hz), 7.25–7.29 (m, 2H), 7.09–7.13 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 137.4, 128.8, 127.7, 126.6.

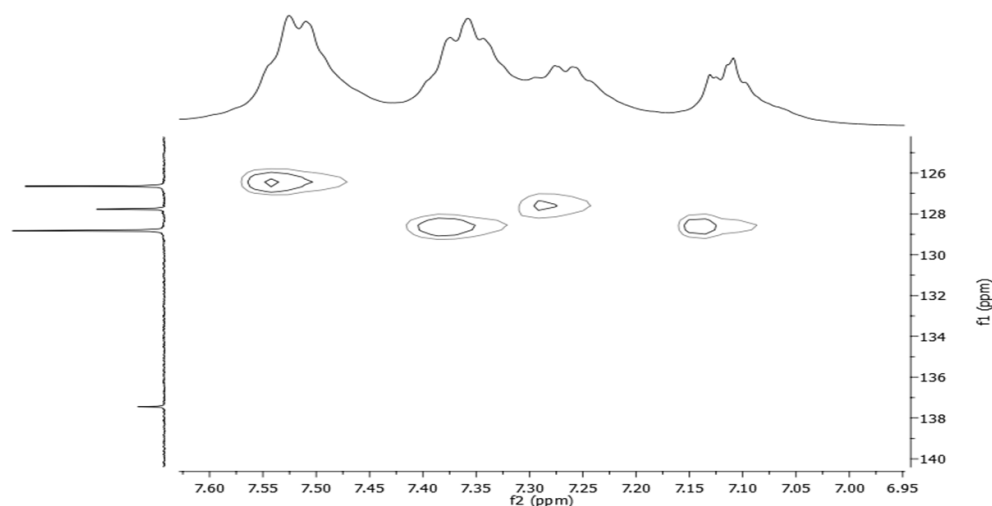
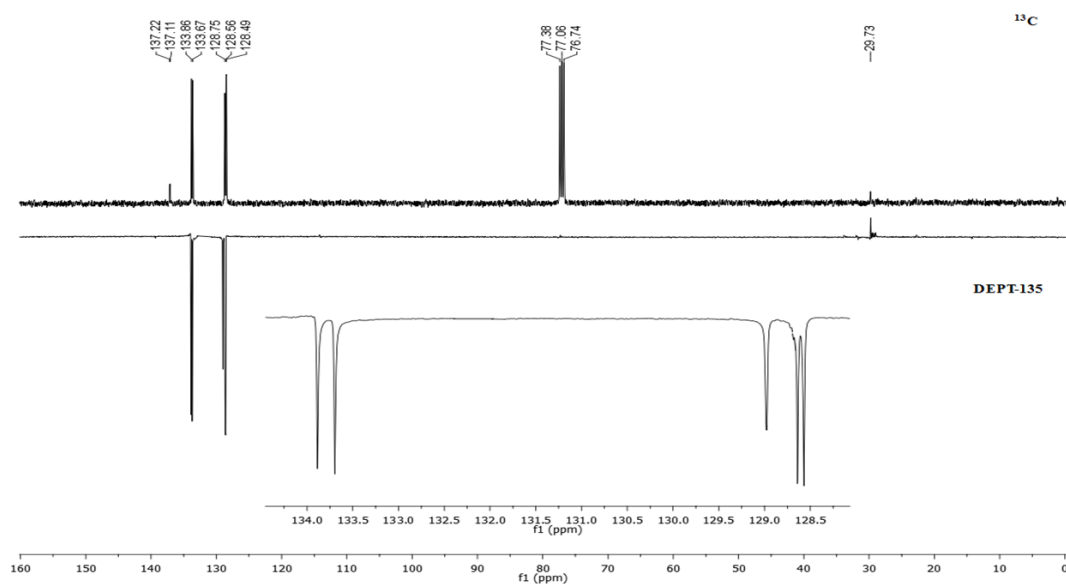


Figure 5. HSQC ( $\text{CDCl}_3$ ) spectrum of E-stilbene.

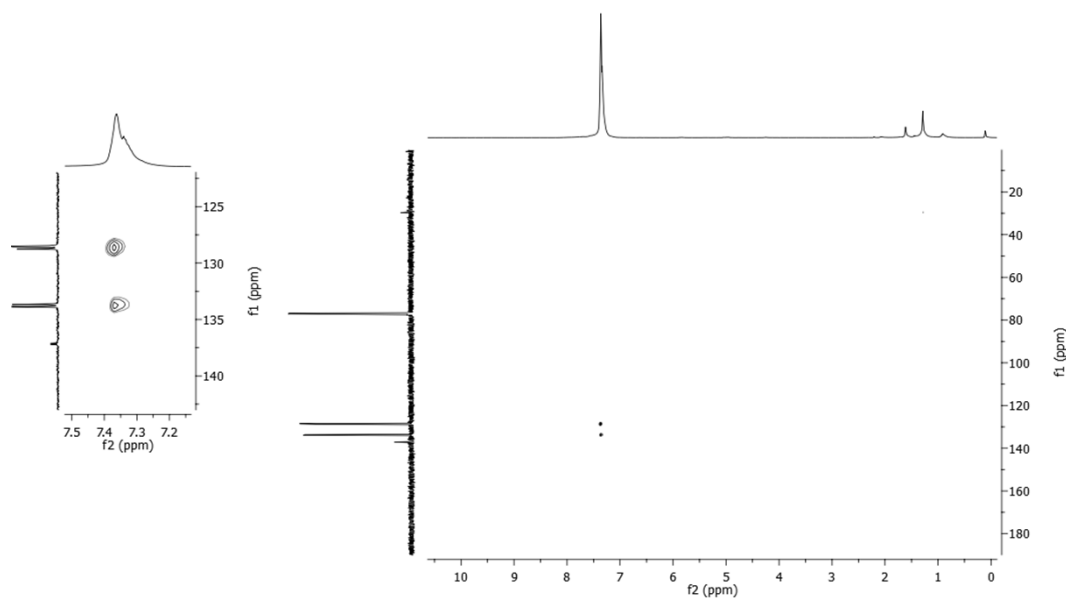


**Figure 6.** Comparison of  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) spectrum and DEPT-135 ( $\text{CDCl}_3$ ) spectrum of tetraphenylethylene (TPE).

The spectral study of the HSQC NMR (Figure 5) showed an agreement with the other structures under consideration. They are mainly characterized by the peak correlation at 128.8 ppm with the two signs relating to the protons at 7.11 ppm and 7.35 ppm.

### 3.2.2. Tetraphenylethylene (TPE)

Mp: 223–226 °C; IR (KBr,  $\text{cm}^{-1}$ )  $\nu = 3062$  ( $\text{CH}_{\text{aro}}$ ),  $\nu = 1642$  ( $\text{C} = \text{C}_{\text{ethyl}}$ ),  $\nu = 1469$  ( $\text{C} = \text{C}_{\text{aro}}$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 7.31–7.33 (m, 20H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 137.2, 137.1, 133.8, 133.6, 128.7, 128.5, 128.4.



**Figure 7.** HSQC ( $\text{CDCl}_3$ ) spectrum of tetraphenylethylene (TPE).

The DEPT-135 spectrum (Figure 6) confirms the assignment of the  $^{13}\text{C}$  NMR spectrum. Thus, a comparison of the two spectra shows the absence of two peaks at 137.1 ppm and 137.2 ppm, which proves that these two are proportional to the quaternary carbons.

The HSQC spectroscopy analysis (Figure 7) confirmed once more that the two peaks at 137.1 ppm and 137.2 ppm belong to the quaternary carbons due to the absence of correlation with an H proton. Moreover, this analysis verified that the other five peaks belong to the nonquaternary aromatic carbons.

The HMBC NMR spectra (Figure 8) showed an agreement with the expected structures. They are mainly characterized by the correlation of the peak at 137.1 ppm with the multiplet of the aromatic protons. This confirms that this peak is proportional to the aromatic quaternary carbons and not to the ethylenic carbons.

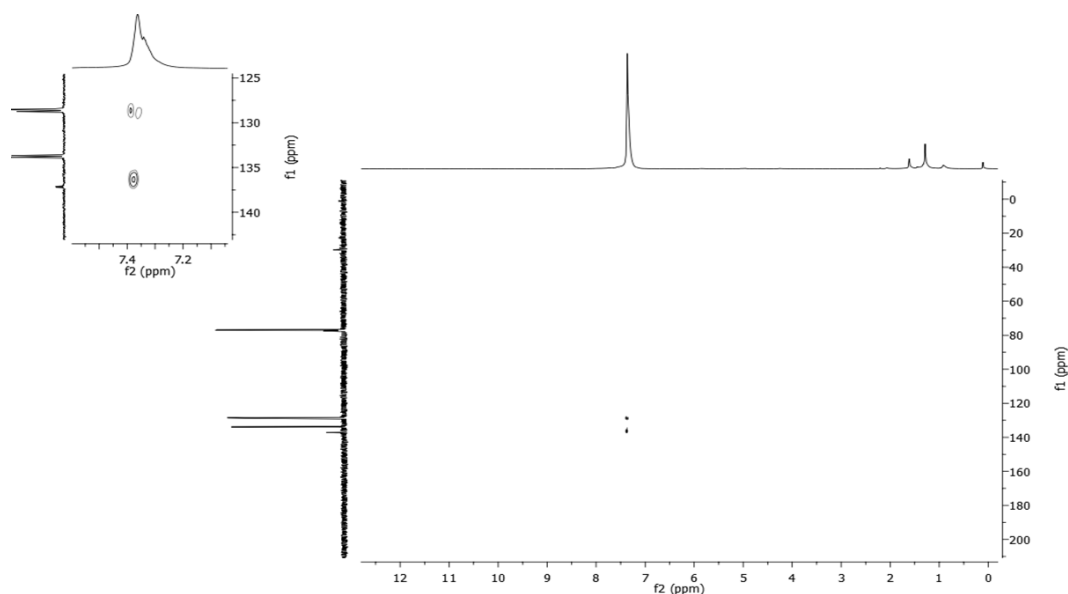


Figure 8. HMBC ( $\text{CDCl}_3$ ) spectrum of tetraphenylethylene (TPE).

## Acknowledgment

We gratefully acknowledge the financial support of the Ministry of Higher Education and Scientific Research of Tunisia.

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