Palladium TPPTS catalyst in water: C-allylation of phenol and guaiacol with allyl alcohol and novel isomerisation of allyl ethers of phenol and guaiacol

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Abstract

The use of allylic alcohols for the direct synthesis of alkenylphenols instead of allylic halides is highly attractive. However, such phenol allylations mainly lead to the production of phenyl ethers (O-allylation). We introduce herein the potential of palladium TPPTS complexes in water for a selective C-allylation of phenol and guaiacol by allyl alcohol into allylphenols and eugenols ($0.8 < para/ortho < 2$). With the same reaction conditions, in presence of an excess of phenol in basic conditions, allyl phenyl ether is isomerised into C-allylated compounds through a catalytic allyl transfer from the allyl ether to the phenate which is present in excess in the aqueous phase. A similar isomerisation reaction occurs with allyl guaiacyl ether. Intermolecular allyl transfers between allyl phenyl ether and guaiacol or between allyl guaiacyl ether and phenol were observed and also led to the production of C-allylated compounds. All these catalytic reactions are based on the well characterized cationic complex $[\pi\text{-allylpalladium(TPPTS)}_2]^+$ generated through the facile heterolytic cleavage of allyl alcohol or allyl phenyl ether by the Pd(0) TPPTS complex. This π-allylpalladium(II) TPPTS complex is stable in water at room temperature.
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1. Introduction

Alkenylphenols (propenyl and prenyl, etc.) make up a large family of natural products having a high economic attraction, including flavours and fragrances (isoeugenol, eugenol and anethole) [1] and Vitamins E and K [2]. The synthesis of these compounds usually requires the use of allyl halides and leads to the production of numerous by-products, especially allylic ethers. The addition of base is also necessary to neutralize the acid produced. Moreover, the separation of metallic catalysts is often difficult to achieve and not very efficient.

The allylation of phenol (a) or guaiacol (b) by allyl chloride or allyl bromide in water, without catalyst, leads to the production of ethers 1(a) and 1(b) (O-allylation) and allyl phenols 2(a), 3(a), 2(b) and 3(b) (C-allylation) (Fig. 1). Higher yields are obtained if the reaction is carried out in the presence of a base consumed by the acid released. Under optimal conditions, only 50% of C-allylation (and 50% of O-allylation) is obtained with phenol [3–5] or guaiacol [6]. Under these conditions, only phenols with a higher electron density increase the C-allylation up to 80–90%. For example, with 3,5-dimethylphenol C-allylation selectivity is 82% [7].

The use of allylic alcohols for the direct synthesis of C-allylated compounds is still highly attractive. This path would limit by-product formation and base consumption. Therefore, it is important to be able either to control the C-allylation or to turn the ether produced into a C-allylated compound under conditions smoother than those of the Claisen transposition usually carried out at a temperature greater than 150 °C.

If only the reaction between phenol and allyl alcohol is taken into consideration, an interesting perspective is offered by catalysis with the palladium triphenylphosphine catalyst (Pd TPP catalyst) according to the Tsuji–Trost reaction (Fig. 2) [8].
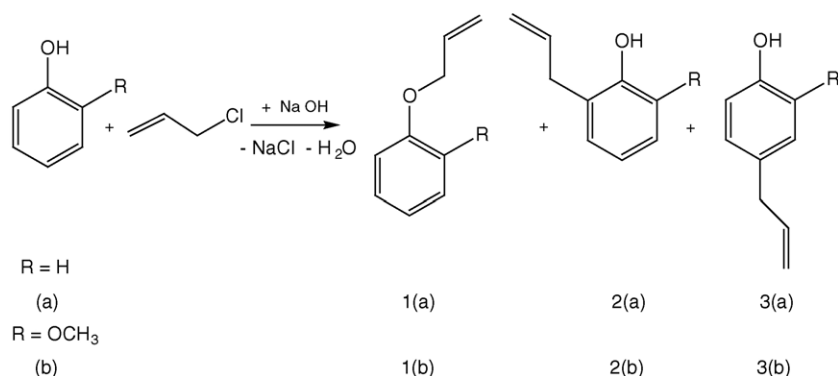
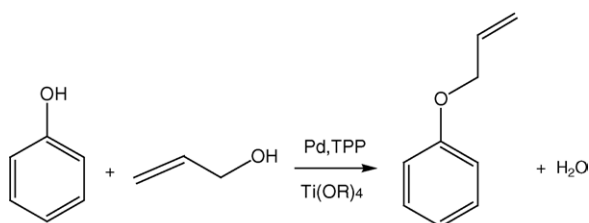Fig. 1. Allylation of phenol and guaiacol with allyl chloride in water.

Fig. 2. Allylation of phenol with allyl alcohol.

Phenol is allylated by allyl alcohol into allyl ether 1(a) (87% of yield) in benzene in the presence of the Pd TPP catalyst and titanium(IV) isopropoxide and molecular sieves in large amounts [9]. Without titanium(IV) isopropoxide no reaction was reported. Under similar reaction conditions, the ether 1(a) is stable, as already observed in 1974 with the platinum complex Pt (TPP)$_4$ or Pd TPP catalyst [10–12]. In the 1970s, the exchange of allyl groups between phenols catalysed by Pd TPP catalyst were reported, which are other examples of O-allylation reaction (Fig. 3) [13,14]. Thus, the C-allylation of phenol by allyl alcohol has never been revealed with palladium complexes. Only O-allylation has been reported.

With the same catalytic system based on palladium, a large range of phenols, among them phenol and guaiacol, were allylated into ethers usually by the means of allylic acetates or allylic carbonates [11].

However, different authors pointed out the C-allylation of electron-rich phenols by the Pd TPP catalyst (Fig. 4). 3,5-dimethoxyphenol was turned into 4-allyl-3,5-dimethoxyphenol
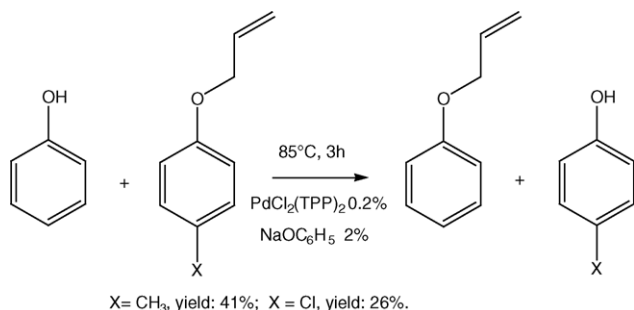

X= CH$_3$, yield: 41%; X = Cl, yield: 26%.

Fig. 3. Exchange of allyl group of phenols (Hata) [13,14].

(yield 82%) by reaction with allyl alcohol (A) [9]. Later, the C-allylation of phloroglucinol was observed by reaction with cinnamaldehyde diacetil acylal or cinnamyl acetate, but with yields less than 30% (B) [15]. Other C-allylations were also observed: the C-allylation of 1-naphtol by allyl alcohol at 100 °C (78%) (C) [16], the C-allylation of 2-naphtol by methyl (or ethyl) allylcarbonate (54%) (D) [11] and by isomerisation the C-allylation of the cinnamyloxy-2-naphthalene into 1-cinnamyl-2-naphtol (40%) [11] or 1-naphthoxyocta-2,7-diene into 1-(octa-2,7-dienyl)-2-naphthol (90%) (E) [17]. As early as 1967, Smutny observed with the use of the Pd TPP catalyst the degradation of 1-(octa-2,7-dienyl)phenyl ether into phenol and octa-1,3,7-triene together with small amounts of 2- and 4,1-(octa-2,7-dienyl)phenol [18].

A recent study on phenol allylation by allyl acetate and catalysed by a Hβ zeolite highlighted the limitations of acid catalysis as only 62% of C-allylation was achieved in the best conditions (25% of ethers and 13% of dimers) [19].

In conclusion, the allylation of phenols by allylic compounds catalysed by palladium systems generally leads to the production of ethers (O-allylation). However, C-allylation was observed with some electron-rich phenols, unfortunately with non-quantitative yields. With the same catalytic system, the isomerisation of allylic ethers of naphtol into C-allylated compounds was also observed, but with non-quantitative yields. Moreover, whatever the conditions, the separation of the catalyst remains a problem.

We introduce herein the potential of the palladium TPPTS (tris(*m*-sulfonatophenyl)phosphine trisodium salt) complexes in water for the reactions of allylation of phenol and guaiacol by allyl alcohol and the transformation of the allyl ethers of phenol 1(a) and guaiacol 2(a) into C-allylated compounds. This system potentially allows an easier separation of the catalyst system from the reaction products. Recently it was shown that allyl-palladium species can be readily formed from allyl alcohol and Pd(0) TPPTS in water at room temperature [20]. We have confirmed the easy heterolytic cleavage of allyl alcohol and allyl phenyl ether by the Pd(0) TPPTS complex with the formation of the cationic complex [π-allylpalladium(TPPTS)$_2$]$^+$ that plays a key role in the catalytic reaction. We have also reported some results about the C- and O-allylation of phenol by allyl alcohol in organic medium in the presence of the Pd TPP catalyst.
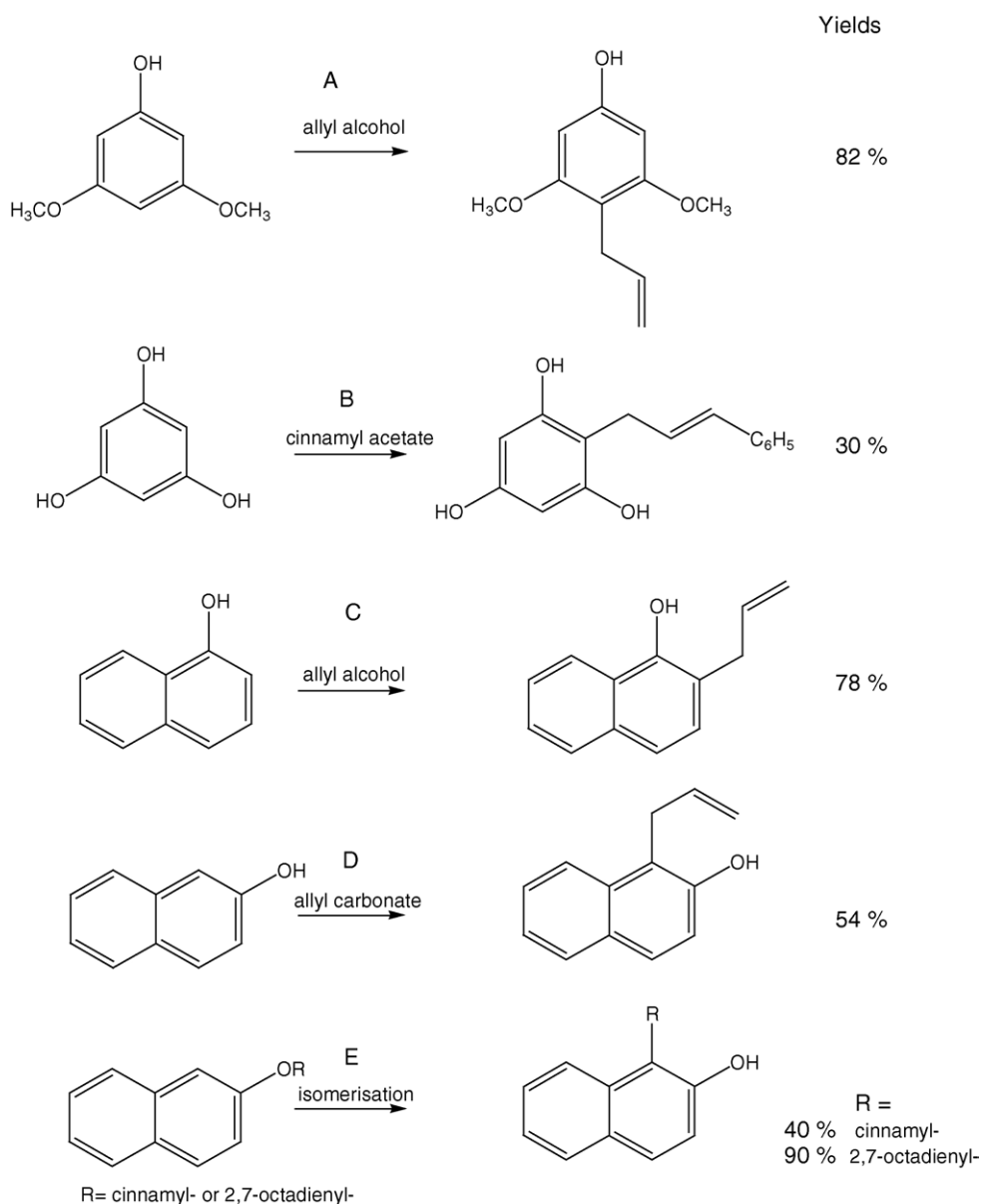
Fig. 4. C-allylation with electron-rich phenols (palladium catalyst).

2. Results and discussion

### 2.1. General information about the catalytic system in presence of the reagents

The allylation of phenol or guaiacol by allyl alcohol in water was carried out in the presence of the catalytic system in a neutral or slightly acidic medium, or in basic medium in the presence of sodium hydroxide. The allylation of phenol or guaiacol may lead to a range of O- and C-allylated products as described in Scheme 1a and b.

Generally, only one phase appeared at the beginning of the reaction at 80 °C with phenol or guaiacol and sodium hydroxide. Above 65 °C, phenol and water are miscible in all proportions. Guaiacol is less soluble and with too great a ratio of guaiacol/water the initial system may be biphasic. Depending

on the selectivity of the catalyst, various ethers and allylated phenols were produced (mono-, bi- and triallylation). Those products were also observed for the allylation of phenols by allyl chloride in basic media according to the Kornblum method [3,4,7].

Ethers have a low solubility in water, less than $1 \, \mathrm{g \, L^{-1}}$, but also C-allylated phenols, particularly if sodium hydroxide has too low a molar ratio. Thus, an organic phase appeared after half an hour of reaction even in the absence of the formation of ethers. In the case of guaiacol with of sodium hydroxide (molar ratio sodium hydroxide/guaiacol = 0.6), the organic phase essentially contains the *ortho* and *para* eugenols produced. This is because they have a low solubility. This phenomenon limited the formation of polyallylated compounds.

The Pd TPPTS catalyst was synthesized in situ in the deoxygenated mixture—water (neutral or acidic), allyl alcohol, phe-
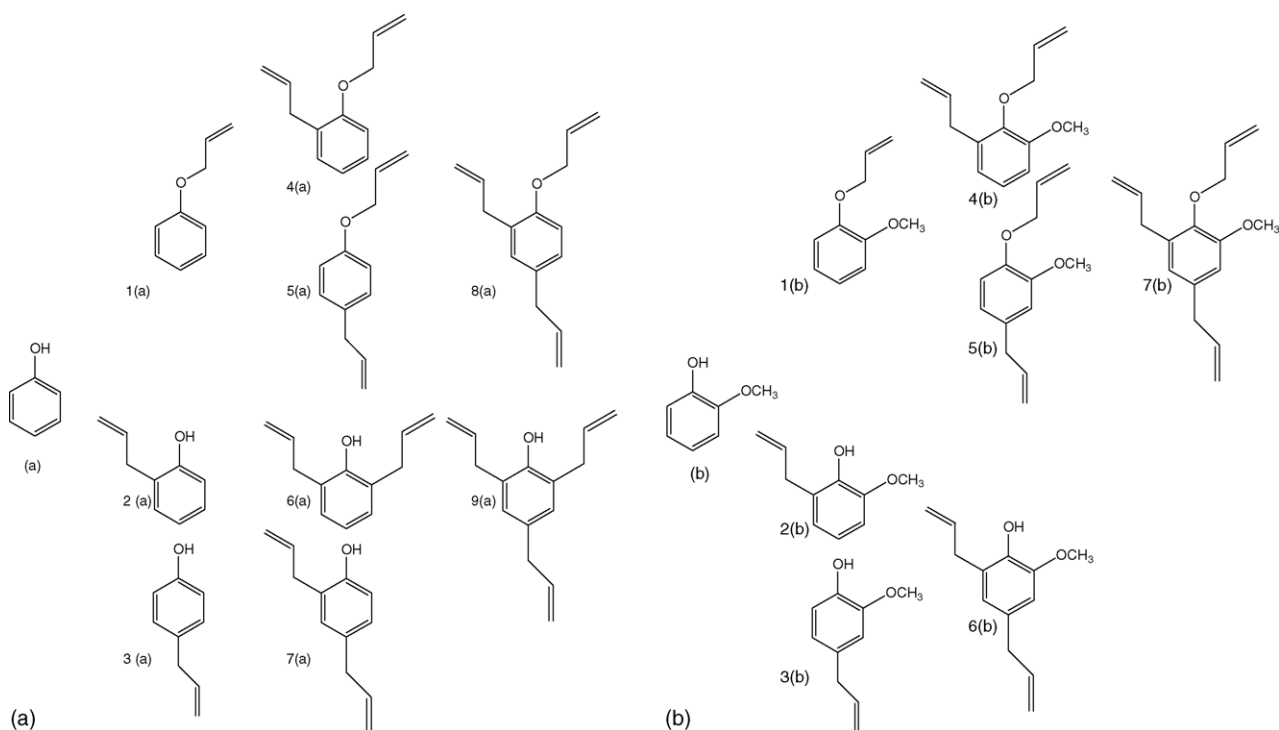
Scheme 1. (a) Phenol and its allylated compounds and (b) guaiacol and its allylated compounds (*o*-eugenol 2(b) and *p*-eugenol 3(b)).

nol, TPPTS and palladium acetate, which was dissolved by TPPTS, and then reduced by a reagent or by TPPTS in excess. Sodium hydroxide was added last.

However, a palladium TPPTS complex in aqueous solution could be introduced last to the deoxygenated reagents in the two following cases: the Pd(0) TPPTS complex prepared from palladium acetate and TPPTS in excess at adjusted pH [21], or the [π-allylpalladium(II)TPPTS$_2$]$^+$ complex prepared from TPPTS and allyl palladium chloride dimer [20].

To analyse the reaction products by GC–MS, the biphasic reaction medium was neutralised by an acid and then subjected to an extraction by toluene.

2.2. Evidence for a C-selective allylation

Phenol and guaiacol were allowed to react with allyl alcohol (0.5 eq.) either in the absence of a base or in the presence of sodium hydroxide (1.05 eq.). The results are summarized in Table 1.

Phenols were turned (4%) into allyl ethers 1(a) and 1(b). No C-allylated phenols were observed. On the contrary, in the presence of sodium hydroxide, C-allylation of phenol and guaiacol was observed with a selectivity of 97.5% and 99.7%. The main products were allylated phenols with a selectivity of 90% 2(a), 3(a) *ortho* and *para* allylphenol and 2(b), 3(b) (eugenols). The *para* allylation selectivity $p/(o + p)$ was 45% for phenol and 64% for guaiacol.

O-allylation was observed: 2.5% of three ethers 1(a), 4(a) and 5(a) with phenol and 0.13% of 1(b) with guaiacol.

The influence of the amount of sodium hydroxide was studied on similar reaction conditions with guaiacol, 15 min of reaction, which gave us the required low conversion (Table 2). The previous results with an excess of sodium hydroxide (1.05 eq.) or without sodium hydroxide were confirmed. The use of sodium hydroxide at 0.6 eq. decreased the C-allylation selectivity to 95.6% with a higher reaction rate. The *para* allylation of guaiacol was close to 62% for all these experiments.

Table 1
Allylation of phenol and guaiacol at 80 °C, 1 h reaction time

	NaOH/phenols	Conversion (%)	O-allylation (%)	C-allylation (%)	$p/(o + p)$ (%)	Mono C-allylation (2) + (3) (%)
Phenol	0	4	100	0	–	–
Phenol	1.05	8	2.5	97.5	45	90.5[a]
Guaiacol	0	4	100	0	–	
Guaiacol	1.05	18	0.13	99.7	64	90[b]

Conditions: water 4.08 g; phenol 0.542 g, 5.75 mmol or guaiacol 0.715 g, 5.75 mmol; molar ratios Pd(OAc)$_2$/TPPTS/NaOH/allyl alcohol/phenol or guaiacol: 1/4/0 or 105/50/100.

[a] Selectivity ethers: 1(a) 1%, 4(a) 0.5%, 5(a) 1%; selectivity phenols: 6(a) 2%, 7(a) 4%, 9(a) 1%.

[b] Selectivity ether 1(b) 0.3%, selectivity 6(b) 10%.

Table 2
Allylation of guaiacol at low conversions at 80 °C, 15 min reaction time

NaOH/guaiacol molar ratio ($x/100$)	Guaiacol conversion (%)	C-allylation selectivity (%)	$p/(o+p)$ selectivity (%)	TON	TOF (h^{-1})
1.05	3.7	100	62.2	3.7	14.8
0.60	6.8	95.6	61.5	6.8	27.2
0.20	2.3	70	62.5	2.3	9.2
0	3.7	0	–	3.7	14.8

Conditions: water 2.75 g; guaiacol 0.434 g, 3.5 mmol; molar ratios Pd(OAc)$_2$/TPPTS/NaOH/allyl alcohol/guaiacol: 1/4/x/200/100.

Table 3
Allylation of guaiacol at 80 °C with NaOH 1.05 eq.

Time (min)	Guaiacol conversion (%)	C-allylation Selectivity (%)	$p/(o+p)$ selectivity (%)	TON	TOF (h^{-1})
3	0[a]	–	–	0	0
5	0	–	–	0	0
10	0	–	–	0	0
15	0.3	100	33	0.3	0.3
30	4	100	62	4	4
60	8.6	100	62	8.6	8.6

Conditions: water 2.75 g; guaiacol 0.434 g, 3.5 mmol; molar ratios Pd(OAc)$_2$/TPPTS/NaOH/allyl alcohol/guaiacol: 1/4/105/200/100.

[a] Conversions cannot be compared to the previous experiments since the system was put out of the bath for taking.

2.3. Kinetic studies

Kinetic studies were carried out with guaiacol in the presence of sodium hydroxide (1.05 eq. and 0.60 eq.) (Tables 3 and 4). With 1.05 eq. of sodium hydroxide, no conversion was observed during the first 10 min. At 0.3% of conversion, no ether 1(b) was detected. Therefore, the anion was quantitatively C-allylated (Table 3).

With 0.60 eq. of sodium hydroxide at 0.1% of conversion in the first 3 min, the "initial" C-allylation selectivity was 88%. This selectivity quickly increased to reach 97.5% at 7.5% of conversion and 99.5% at 14% and 22% of conversion. The amount of ether 1(b) produced during the reaction time remained low (Table 4).

Under the same conditions in the presence of 0.6 eq. of sodium hydroxide, phenol led to an initial C-allylation selectivity of 44%. This selectivity quickly increased to reach 86% (1.4% of conversion) and 98.5% (4.6% of conversion) (Fig. 5).

We can consider that the allylation of phenol or guaiacol by allyl alcohol in aqueous phase is shared between the O-allylation of molecular phenol or molecular guaiacol and the C-allylation of the phenate or guaiacolate anion. Since the pK_a of
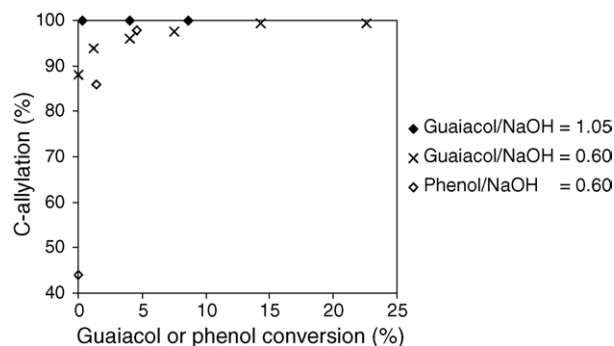

Fig. 5. Percentage of C-allylation of guaiacol and phenol at low conversion.

phenols is around 9.9–10, the ratio of the species (ArO$^-$/ArOH) is slightly different from the ratio (NaOH/ArOH) that controls the initial selectivity for C-allylation. However, with sodium hydroxide (0.6 eq.), the C-allylation selectivity very quickly reaches 98–99% at conversions less than 10% as though another phenomenon occurred. The hypothesis of a fast transformation of ethers produced into C-allylated compounds had to be studied.

Table 4
Allylation of guaiacol at 80 °C with NaOH 0.6 eq.

Time (min)	Guaiacol conversion (%)	C-allylation selectivity (%)	$p/(o+p)$ selectivity (%)	TON	TOF (h^{-1})	1(b)[a] (mmol L^{-1})
3	0.1	88	47	0.1	2	0.069
5	1.2	94.4	58	1.2	14.4	0.69
10	4	96	60	4	24	0.63
15	7.5	97.5	61	7.5	30	0.78
30	14	99.5	63	14	28.6	0.81
60[a]	22	99.5	64	22	22.6	1.29

Conditions: water 2.75 g; guaiacol 0.434 g, 3.5 mmol; molar ratios Pd(OAc)$_2$/TPPTS/NaOH/allyl alcohol/guaiacol: 1/4/60/200/100. Note that using the Pd(0)TPPTS complex or the Pd(II)TPPTS complex as catalyst the results were similar (conversion and selectivity).

[a] Calculated in mmol per litre of water (2.75 mL).

2.4. Isomerisation of allyl ethers on the allylation conditions: allyl phenyl ether 1(a) + phenol, allyl guaiacyl ether 1(b) + guaiacol

As ethers 1(a) and 1(b) are slightly soluble in water, the reaction was always biphasic. With the Pd(0) TPPTS catalyst without NaOH, allyl phenyl ether 1(a) was inert (80 °C, 15 h). After heating, the conversion was only 0.7% into phenol without the formation of C-allylated phenol. However, with sodium hydroxide and an excess of phenol (NaOH/1(a)/phenol = 0.6/0.5/1), 1(a) was turned at 97% conversion into phenols: 81% of monoallylated phenols 2(a) and 3(a), 7.5% of diallylated phenol 6(a) and 7(a), 0.3% of triallylated phenol 9(a) and 11% of phenol (Fig. 6). A part of 1(a) was converted into phenol by hydrolysis with the formation of allyl alcohol (3% of selectivity) on the one hand, and by successive allylation reactions with diallylated and triallylated compounds (7.8% of selectivity) on the other.

The ratio para/(ortho + para) was close to 50%. During the reaction, the amount of phenol was stable or increased slightly, so that the excess of phenol with an appropriate amount of NaOH allowed a low selectivity in diallylated phenol 6(a) and 7(a).

Under the same conditions in the presence of 6% of phenol and 5% of sodium hydroxide (NaOH/1(a)/phenol = 0.05/1/0.06), the conversion of 1(a) was 3% in 1 h and 6% in 2 h, mainly into 2(a), 3(a) and ethers 4(a) and 5(a). It was therefore essential to use an excess of phenol in the presence of sodium hydroxide to convert 1(a) into C-allylated compounds at a reasonable rate.

Under the same conditions, 2(a) was converted at 99.9%, including 80% of eugenols (para/(ortho + para) = 58%), 9% of C-diallylated product 6(b), 0.5% of eugenols O-allylated 4(b) and 5(b), and 10.5% of guaiacol (Fig. 7). The allyl alcohol obtained by the hydrolysis of ether 2(a) was produced with a selectivity of 1%.
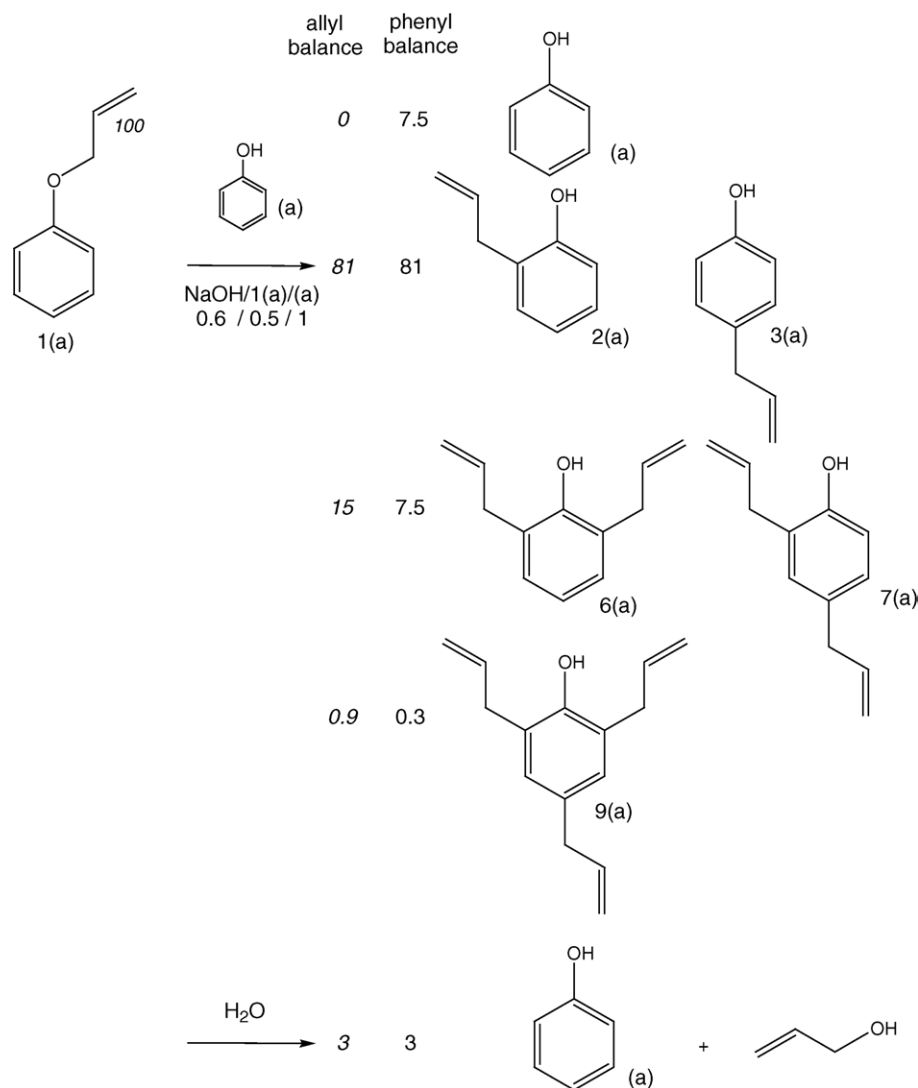

Fig. 6. Allyl phenyl ether isomerisation at 80 °C, 2 h. *Conditions:* water 4.08 g, 1(a) 0.386 g, 2.9 mmol; molar ratios Pd(OAc)$_2$/TPPTS/NaOH/1(a)/phenol: 1/4/60/50/100. Selectivity 6(a) 2% and 7(a) 5%.
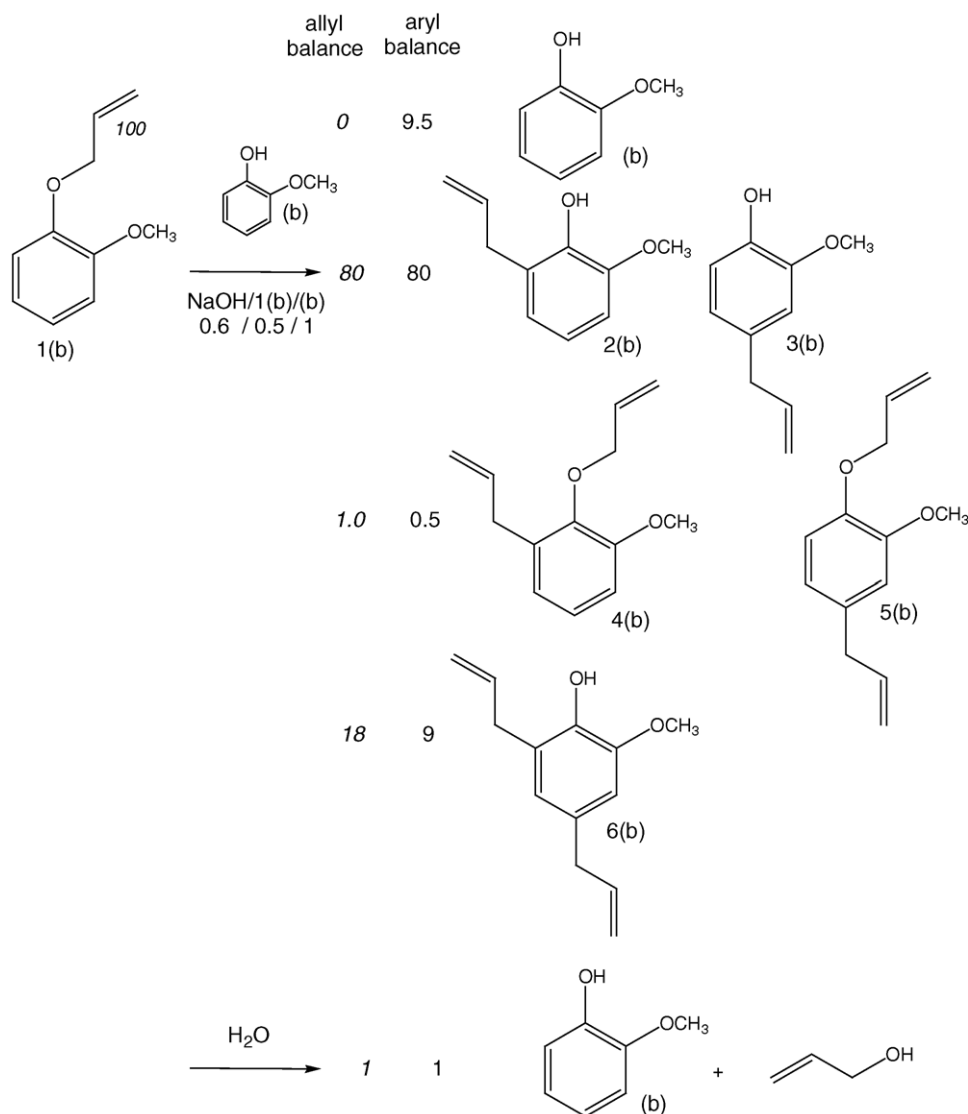
Fig. 7. Allyl guaiacyl ether isomerisation at 80 °C, 2 h. *Conditions:* water 4.08 g, 1(b) 0.472 g, 2.9 mmol; molar ratios Pd(OAc)$_2$//TPPTS/NaOH/1(b)/guaiacol: 1/4/60/50/100.

2.5. Intermolecular allyl transfer: allyl phenyl ether 1(a) + guaiacol, allyl guaiacyl ether 1(b) + phenol

At 80 °C, 1(a) was allowed to react with a large excess of guaiacol, whereas 1(b) was allowed to react with a large excess of phenol (molar ratios NaOH/1(a) or 1(b)/phenol or guaiacol = 6/1/10).

In the case of allyl phenyl ether 1(a) and guaiacol, the allyl group transfer leads to the production of eugenols 2(b) and 3(b) (97.5% and $p/(o+p) = 58\%$) and C-allylphenols 2(a) and 3(a) (2.5%) as described in Fig. 8. No ether 2(a) was detected and the conversion of 1(a) was 99.9%.

In the case of 1(b) and phenol, 1(b) was turned into C-allylated products with 99.5% of conversion. The allyl group was converted into C-allylphenols 2(a) and 3(a) (86.5%, $p/(o+p) = 50\%$), eugenols (13%, $p/(o+p) = 50\%$). 1(a) was produced with a selectivity of 0.5%, so in this case some O-allyl transfer from 1(b) to phenol was observed.

These results involve a cleavage of ethers by the catalyst in aqueous solution that releases the phenoxy group either as an anion or as phenol according to the pH. The catalyst reacts on nucleophiles in solution in function of their reactivity: guaiaco-late anion > phenate anion ≫ water. For example, in the reaction of allyl transfer between 1(a) and guaiacol in a molar ratio guaiacol/1(a) = 10, the phenol concentration in the solution is null at the beginning of the reaction and then increases to reach about 10% of the quantity of guaiacol at the end of the reaction. Its average value is about 5% of the quantity of guaiacol. About 2.5% of C-allylated phenols were obtained because the reactivity of phenate is less than that of guaiacolate (about two or three times less if all the results are taken into consideration). Thus, for the same reasons, at the end of the reaction between 1(b) and phenol in the same molar ratio (1(b)/phenol = 0.1), 13.5% of C-allylated guaiacol were obtained because the reactivity of guaiacolate was greater than that of phenate.
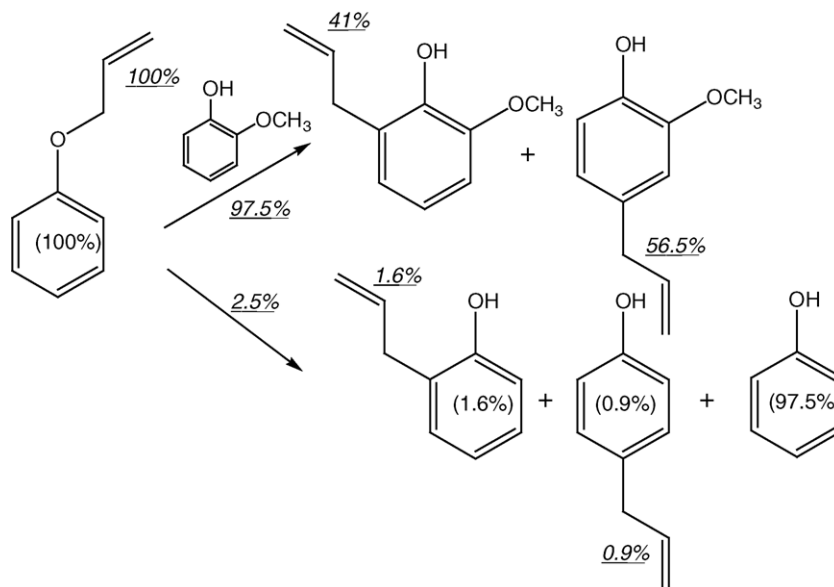
Fig. 8. Allyl transfer from allyl phenyl ether 1(a) to guaiacol in large excess at 80 °C, 15 min. *Conditions:* water 2.5 g; 1(a) 0.134 g, 1 mmol; molar ratios Pd(OAc)$_2$/TPPTS/NaOH/1(a)/guaiacol: 1/4/120/20/200. *100%*, allyl balance; (100%), phenyl balance.

It is worth noting that the formation of allyl alcohol is low (from 1 to 3%) in those reactions involving ethers. The catalyst preferentially reacts with the phenate anion instead of water or the hydroxide ion. Moreover, the thermodynamic equilibrium of hydrolysis is favored towards ether, and allyl alcohol may react with the catalyst. All these considerations explain the low production of allyl alcohol observed for those allyl transfers. However, some O-allyl transfer from 1(b) to phenol was observed. Does O-allylation occur simultaneously at the beginning of the reaction?

The selectivity of the reaction with 1(a) and guaiacol in the molar ratios NaOH/1(a)/guaiacol = 0.6/0.5/1 at a lesser temperature 55 °C was studied. The appearance of the various allylated products versus reaction time is shown in Fig. 9. The ether 1(b) was present after 15 min at 30% conversion of 1(a): O-allylation occurred at the beginning o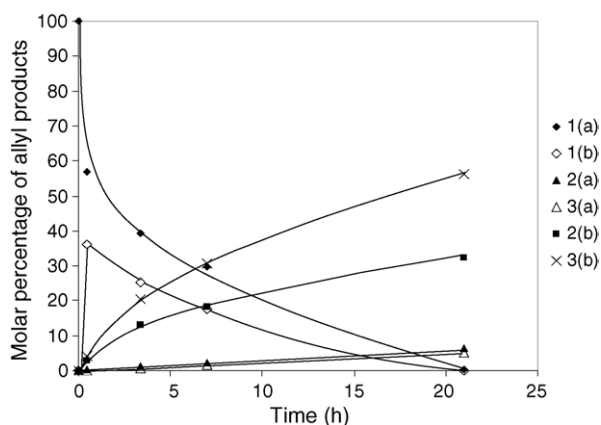f the reaction. Therefore, the molar ratio 1(b)/1(a) remained at the value of 0.6 during the reaction before their complete conversion. After 21 h, the conversion of 1(a) was 99.8% with a very low selectivity 0.04% to 1(b). The main products were eugenols 2(b) and 3(b) ($p/(o + p) = 64\%$) and C-allylphenols 2(a) and 3(a) ($p/(o + p) = 45\%$) in the percentages [2(b) + 3(b)] = 88% and [2(a) + 3(a)] = 12%. These values are in harmony with the previous results. The excess of guaiacol, and its greater reactivity compared to phenol limit the production of C-allylated phenols 2(a) and 3(a).

In conclusion, the intermolecular O → C allyl transfer from an allyl aryl ether to another phenol by C-allylation is accompanied by allyl exchange with ether formation (O → O allyl transfer). The ethers are then converted into C-allylated phenols.

2.6. Does C-allylation occur with phenol in organic medium?

In organic medium, allyl phenyl ether 1(a) was the only product identified during the allylation of phenol by allyl alcohol in the presence of the Pd TPP catalyst, titanium(IV) isopropoxide and molecular sieves at 80 °C [9].

We confirmed this result: C-allylation did not occur without a base and conversion reached 71% (Table 5). With 5% of sodium methoxide, conversion reached 51% with a selectivity of 16% for C-allylation (ratio $p/(o + p) = 9\%$).

However, without titanium(IV) isopropoxide and a base, our analyses established that the reaction was slower but C-allylation into 2(a) and 3(a) occurred with 23–28% of selectivity ($p/(o + p) = 23\%$) (Fig. 10 and Table 5).

The use of various bases was investigated, but it has not been possible to improve the selectivity (Table 5). The use of a polar aprotic solvent (DMSO, NMP) or pyridine with or without a base inhibited all C-allylation. Ethanol does not improve the results. The dilution in toluene or in tributylamine allows a slightly

Fig. 9. Allyl transfer from allyl phenyl ether 1(a) to guaiacol at 55 °C 21 h. *Reagents and conditions:* water 3.22 mL; NaOH 4 M 0.86 mL; Pd(0)TTPPTS catalyst 0.35 mL (Pd concentration 0.081 M); 1(a) 0.386 g, 2.88 mmol; (b) guaiacol 0.917 g, 5.76 mmol; molar ratios Pd(0)TPPTS/NaOH/1(a)/guaiacol: 1/120/100/200.

Table 5
Allylation of phenol in organic phase at 80 °C 2 h with Pd(OAc)$_2$TPP catalyst

Solvent	Base	Phenol conversion (%)	Selectivity		*para*-Selectivity 3(a)/(2(a) + 3(a))
			1(a) O-allylation	2(a) + 3(a) C-allylation	
No	No	12	77	23	23
No	Yes[b]	15	72	28	17
DMF	No	0	–	–	–
DMSO	Yes	3.5	100	0	–
NMP	Yes	1.1	100	0	–
Pyridine	Yes	1.2	100	0	–
Ethanol	Yes	2.0	100	0	–
Ethanol	No	2.37	100	0	–
Toluene	Yes	29	70	30	17
Tributylamine	No	17	62	38	0
No[a]	No	71	100	0	–
No[a]	Yes	51	75	16	9

[a] Titanium(IV) isopropoxide 10%/phenol. DMF: dimethylformamide; DMSO: dimethylsulfoxide; NMP: 1-methyl-2-pyrolidone. *Reagents and conditions:* solvent: none or 9 mL, 3 mL (2.91 g) of an equimolar solution of phenol (19.1 mmol) and of allyl alcohol (19.1 mmol); molar ratios Pd(OAc)$_2$/TPP/sodium methoxide or base/allyl alcohol/phenol: 1/4/0 or 5/200/200.

[b] Similar results with bases: LiOH, BaO, KOCH(CH$_3$)$_2$, NaOC$_2$H$_5$.

greater C-allylation (30% and 38%, respectively) with a ratio $p/(o+p)$ equal to 17% with toluene and 0% with tributylamine. No reaction was observed with DMF.

Allyl phenyl ether 1(a) had a very low reactivity at 90 °C in the presence of the Pd TPP catalyst at 0.5% molar ratio. A low conversion including only a low percentage into phenol (4%), *ortho*allylphenol 3(a) (1.5%), and diallylated compounds (0.5%) was obtained. The dilution in DMF or the addition of phenol fully inhibited the reaction.

In conclusion, the C-allylation of phenol with allyl alcohol occurs in an organic homogeneous medium with the Pd TPP catalyst, but the selectivity is limited to 30% and the *para*-selectivity to 23%. The ally phenyl ether 1(a) isomerisation into C-allylated compounds does not occur significantly.

2.7. The catalytic system: hydrosoluble cationic π-allylpalladium(II) complex formation

Since the discovery of the Pd(0) TPPTS system in 1974 [22], only a few analytical studies have been carried out on this system despite its numerous uses in organic synthesis [23]. Studies were essentially focused on the preparation of the Pd(0) TPPTS catalyst in aqueous solution by the reduction of palladium(II) by TPPTS [24–26].

During the course of the work presented here, there was a publication reporting the evidence of the [π-allylpalladium(TPPTS)$_2$]$^+$ species [20]. Those species are formed from Pd(OAc)$_2$, TPPTS, allyl alcohol and Na$_2$CO$_3$ in water or D$_2$O or from allyl palladium chloride dimer reaction with TPPTS.

We showed also the heterolytic scission of allyl alcohol and allyl phenyl ether in water, but under neutral conditions. The addition of allyl alcohol to aqueous solution of the Pd(0) (TPPTS)$_3$ complex ([Pd] = 0.0055 M) at pH 7.2 and room temperature produced an immediate increase of the pH value. The pH was kept at 7.2 by the addition of perchloric acid 0.2 M: 2 eq. of perchloric acid per mole of complex were added. The initial dark red colour progressively turned yellow. The same phenomenon was observed on the addition of allyl phenyl ether to a solution of Pd(0) (TPPTS)$_3$.

The ^{31}P NMR analysis of the aqueous solutions having 20% of D$_2$O showed the complete disappearance of the signal of the PdL$_3$ complex at +23.85 ppm and the appearance of signals at +22.31 ppm and at +25.60 ppm (Fig. 11). The signal at +22.31 ppm corresponded to the allylphosphonium TPPTS cation. The allylphosphonium TPPTS chloride was prepared by the reaction of allyl chloride with TPPTS and presented the same signal at +22.31 ppm (see Section 4.6 and Fig. 12a).
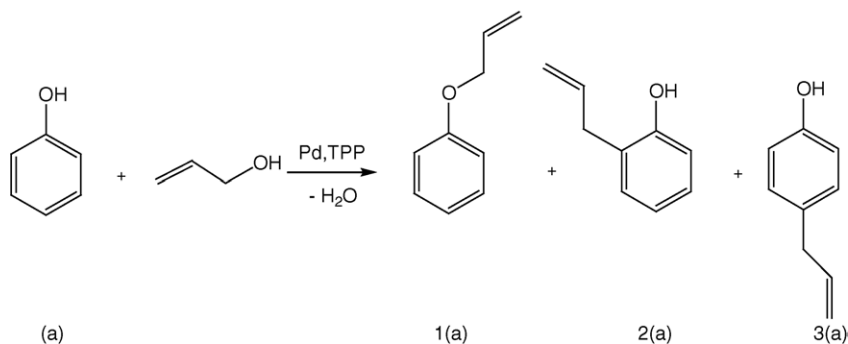
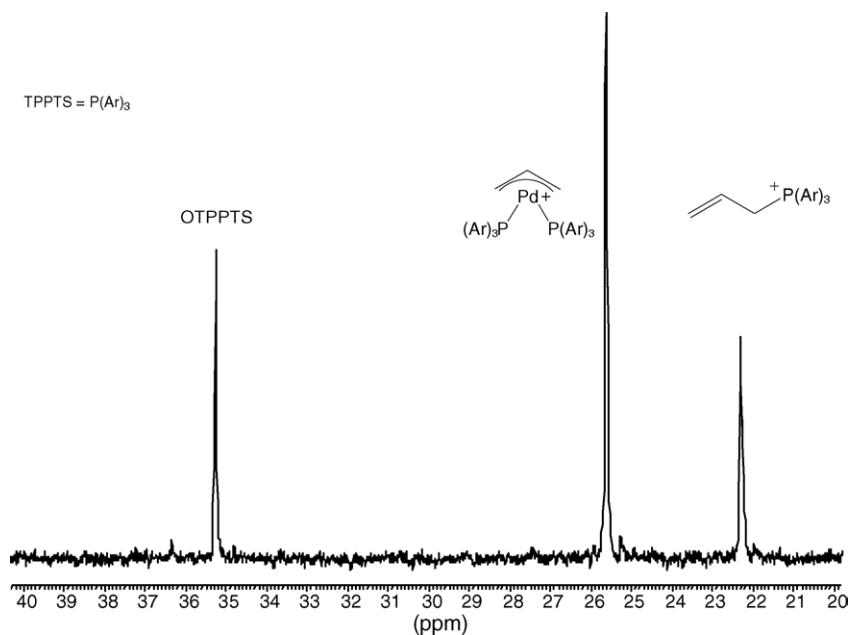

Fig. 10. Allylation of phenol in organic phase.

Fig. 11. ^{31}P NMR (300 MHz) spectrum. Aqueous solution having 20% of D$_2$O after allyl alcohol reaction with Pd(0) (TPPTS)$_3$ at pH 7.2, $\delta = +35.14$ ppm (OTPPTS), $\delta = +25.60$ ppm (complex [π-allylpalladium(TPPTS)$_2$]$^+$ and $\delta = +22.31$ ppm (allyl phosphonium of TPPTS).

The signal at +25.60 ppm corresponded to the cationic complex [π-allylpalladium(TPPTS)$_2$]$^+$. After a few months, the ^{31}P NMR spectrum was still the same, which demonstrates a very good stability of the complex at room temperature.

The same complex was prepared by the quick dissolution of allyl palladium chloride dimer in an aqueous solution of TPPTS (water or deuterated water) strongly stirred at room temperature (molar ratio TPPTS/Pd = 2). The initial dark red solution turns yellow. The ^{31}P NMR analysis of the solution showed the main signal at +25.60 ppm, a signal at +35.14 ppm in a ratio of 3% due to TPPTS oxide present in the initial TPPTS, and

small signals at +23.85 ppm and +22.31 ppm corresponding to a low concentration of the palladium(0) TPPTS complex and the allylphosphonium of TPPTS. The ^{1}H NMR analysis of the solution in D$_2$O revealed a π-allylpalladium complex similar to that already published in D$_2$O [20] or in DMF from the oxidative addition of allyl acetate to a Pd(0) TPP complex (Fig. 12b) [27].

In conclusion, allyl alcohol or allyl phenyl ether 1(a) undergoes a heterolytic cleavage in the presence of palladium(0) at room temperature. Palladium(0) is transformed into a cationic π-allylpalladium(II) complex. The TPPTS released, reacts on the cationic complex to produce the phosphonium species by
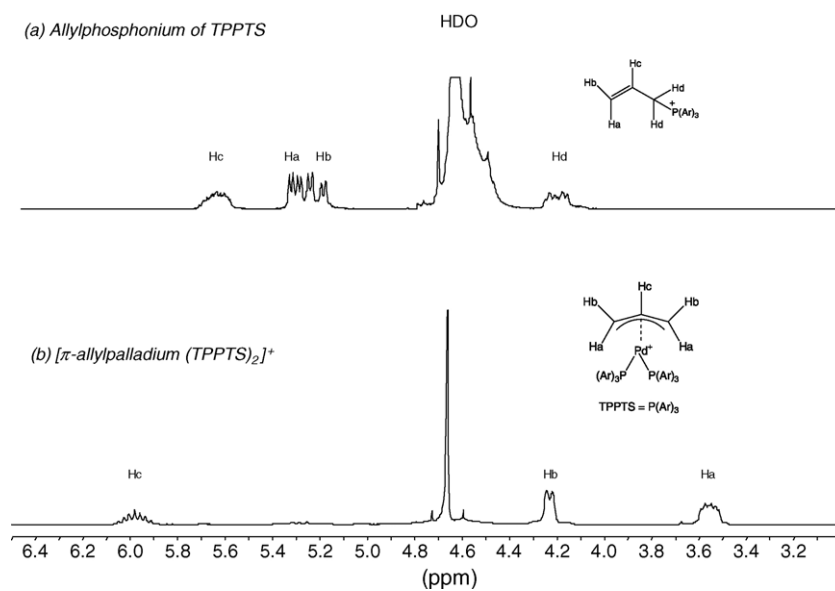

Fig. 12. ^{1}H NMR spectra in deutered water solution. (a) Allyl phosphonium of TPPTS, three sets of signals at $\delta = +5.63$, $\delta = +5.25$ and $\delta = +4.19$ and aromatic proton of TPPTS, (b) complex [π-allylpalladium(TPPTS)2]$^+$, three sets of signals at $\delta = +5.98$ (1H, Hc), $\delta = +4.23$ (2H, Hb), and $\delta = +3.58$ (2H, Ha) and aromatic proton of TPPTS.
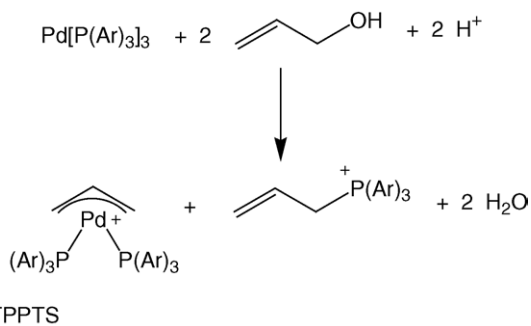
Fig. 13. Cationic complex [π-allylpalladium(TPPTS)$_2$]$^+$ and allyl phosphonium of TPPTS formations from allyl alcohol and Pd(TPPTS)$_3$ at pH 7.2.

releasing Pd(0) that reacts with allyl alcohol one more time (Fig. 13).

2.8. Mechanism in the organic phase

Before concluding on the mechanism describing the observed phenomena with the Pd(0) TPPTS catalyst, we reiterate the specificity of water used as solvent in the allylation reactions of phenol by allyl halides. Such allylation reactions have been known since the sixties through the works of Kornblum [3,4]. Water is the only common solvent allowing a significant C-allylation that remains limited to 50% by a massive solvation of phenate anion or guaiacolate anion reducing the O-allylation rate. However, the produced allyl ether, stable in the reaction conditions, accumulates.

In organic medium, the use of the catalytic system of the Tsuji reaction – Pd TPP catalyst – allowed the use of allyl alcohol instead of allyl halides in the allylation reaction of phenol. The mechanism of the Tsuji reaction based on a cationic π-allyl intermediate in organic medium mainly led to allyl phenyl ether because the C-allylation is controlled by the solvation of the phenol anion. By using reagents without a solvent with the Pd TPP catalyst, we have found that the O-allylation selectivity was 75% and the C-allylation selectivity was 25% with a ratio *para*/(*ortho* + *para*) less than 25%. The addition of organic solvents did not improve the C-alylation rate. We propose that the reaction mixture phenol + allyl alcohol allows generation of a Tsuji cationic π-allyl intermediate in ion pair with OH− that reacts with phenol to create phenate ions in an ion pair.

Phenate (or phenol in solution) reacts to produce mainly ether. However, the solvation by protic reagents (phenol, allyl alcohol or produced water) may play a role in the minor appearance of the C-allylation (Scheme 2).

The allyl phenyl ether alone in the presence of the Pd TPP catalyst is comparatively stable (only a few percent of phenol and 2(a) at 90 °C after 2 h of reaction). A π-allylpalladium phenate is probably formed, but the absence of solvation of the phenate oxygen atom limits the C-allylation, and the appearance of a low amount of phenol stops the reaction. The allyl exchange between phenols occurs according to the HATA reaction (Scheme 2) [13,14].

An interesting case is the C-allylation of electron-rich phenol by allylic compounds in the presence of solvents with the Pd TPP catalyst reported in the introduction of this article (Fig. 4). For example, 3,5-dimethoxyphenol was employed with allyl alcohol to give 4-allyl-3,5-dimethoxyphenol [9]. We think that the Pd TPP catalyst in organic medium, allows the oxidative addition of allyl alcohol by generating a basicity (OH−) in ion pair
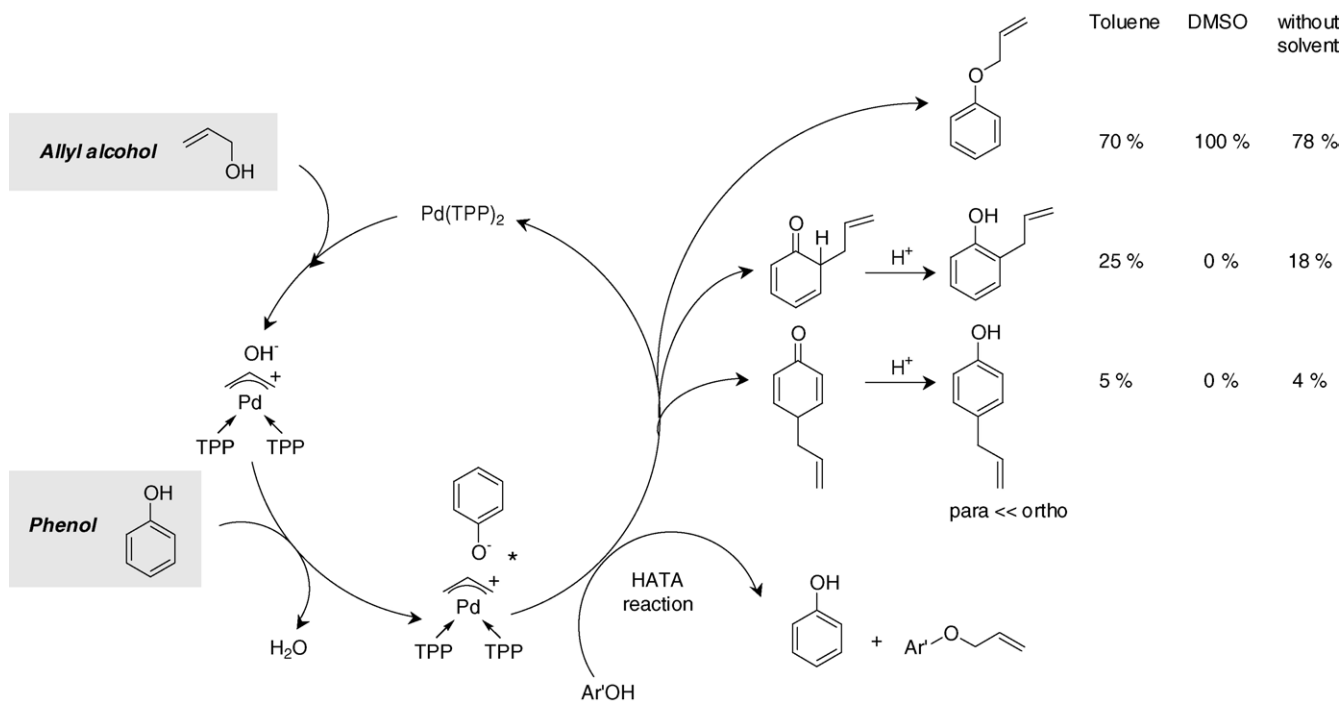
Scheme 2. Allylation of phenol in organic phase. *Solvatation by protic reagents (phenol, allyl alcohol or water) may play a role in the minor appearance of the C-allylation.
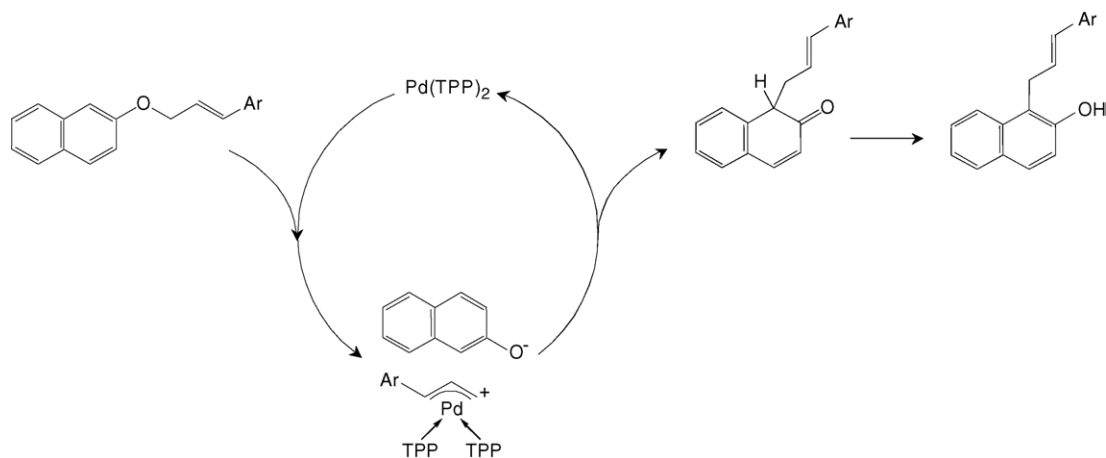
Scheme 3. Cinnamyloxy-2-naphthalene isomerisation to 1-cinnamyl-2-naphtol.

that reacts with 3,5-dimethoxyphenol to give the ion pair *π-allylpalladium(II)–electron rich phenate* eventually solvated by allyl alcohol. The electronic effect of substituents is enough to spontaneously generate the C-allylated derivative through the release of the Pd(TTP)$_2$ complex since phenol itself leads partially to this C-allylation.

The ion pair *π-allylpalladium(II)–electron rich phenate* (Scheme 3) must also play a role in the isomerisation of the allylic ethers of electron-rich phenols. For example, the cinnamyloxy-2-naphthalene reacts with palladium(0) to give the 1-cinnamyl-2-naphtol (40%) (E) [11]. In this case, the absence of molecules able to solvate the ion pair and the low dielectric constant of the system must be noted. It must be assumed that the system has an electron density high enough to spontaneously generate the C-allylated derivative with a non-quantitative conversion, which could be due to the products of the reaction. The 1-cinnamyl-2-naphtol formed, the nucleophile present in the solution should limit the isomerisation according to the HATA mechanism of allyl exchange with phenols [13,14].

3. Mechanism in aqueous phase and conclusion

In the presence of allyl alcohol, Pd(0) TPPTS catalyst is mostly converted into [π-allylpalladium(TPPTS)$_2$]$^+$ cationic complex by the ionisation of allyl alcohol (Scheme 4, reaction (I)). This complex has a key role for the interpretation of the C- and O-allylation of phenol and guaiacol by allyl alcohol and the allyl transfer phenomena with allyl ethers.

By considering the case of guaiacol in basic medium, the fully dissociated cationic complex reacts on the one hand with guaiacolate solvated by water to produce *ortho* and *para* allylated compounds (eugenols) (Scheme 4, reaction (II)) and on the other hand, with molecular guaiacol to produce the allyl ether of guaiacol and a proton (Scheme 4, reaction (III)).

The reaction (II) is unusual in organic chemistry because it is a reaction of neutralization between two ions solvated by water: an organometallic cation and an organic anion. This neutralization transforms the cationic complex Pd(II) into Pd(0) TPPTS by releasing the C-allylated compounds as enone irreversibly turned into eugenols. The higher rate of the reaction (IV) with

respect to reaction (III) keeps the concentration of allyl ether low and allows the isomerisation of allyl guaiacyl ether into eugenols (Scheme 4, reactions (IV) and (II)).

The easy cleavage of allyl compounds by the catalyst at room temperature suggests that the slower step of this system essentially studied at 80 °C, is due to the nucleophilic nature of reagents present in the aqueous phase. This hypothesis could not have been proposed without the observation of the heterolytic cleavage of the allyl alcohol by palladium in aqueous solution.

Two points are clearly important: first, the selectivity of the formation of allylated compounds *para*/(*ortho* + *para*) that is 50% with phenol and 65% with guaiacol under the best conditions. Therefore, it seems difficult to improve this selectivity except by a large steric hindrance of the ligand located in the other half-space bordered by the plane of the allyl group. In fact, according to the Tsuji mechanism, the approach of a soft nucleophile on the allylic carbon is done in a space without interaction with the coordination sphere of palladium. The *para*-selectivity is then essentially controlled by the solvation of phenate or guaiacolate anion.

Second point is the stability of the catalytic system. The π-allylpalladium(II) (TPPTS) system is stable at room temperature in a neutral medium. However, in a basic medium, a light precipitate of metallic palladium appears after several weeks. This phenomenon of precipitation is also observed in the studies of the allylation of phenols at 80 °C in highly basic media. Supplementary fundamental studies of the π-allylpalladium(II) (TPPTS) complex are therefore necessary, including the equilibria concerned and their evolution under the reaction conditions are still under investigation.

4. Experimental

4.1. Chemical reagents

All the following reagents were used as supplied by the manufacturer: Pd(OAc)$_2$, PdSO$_4$, allyl palladium chloride dimer, phenol, guaiacol, allyl phenyl ether 1(a), eugenols 2(b) and 3(b), *ortho*allylphenol 2(a), allyl alcohol, allyl chloride (Aldrich);
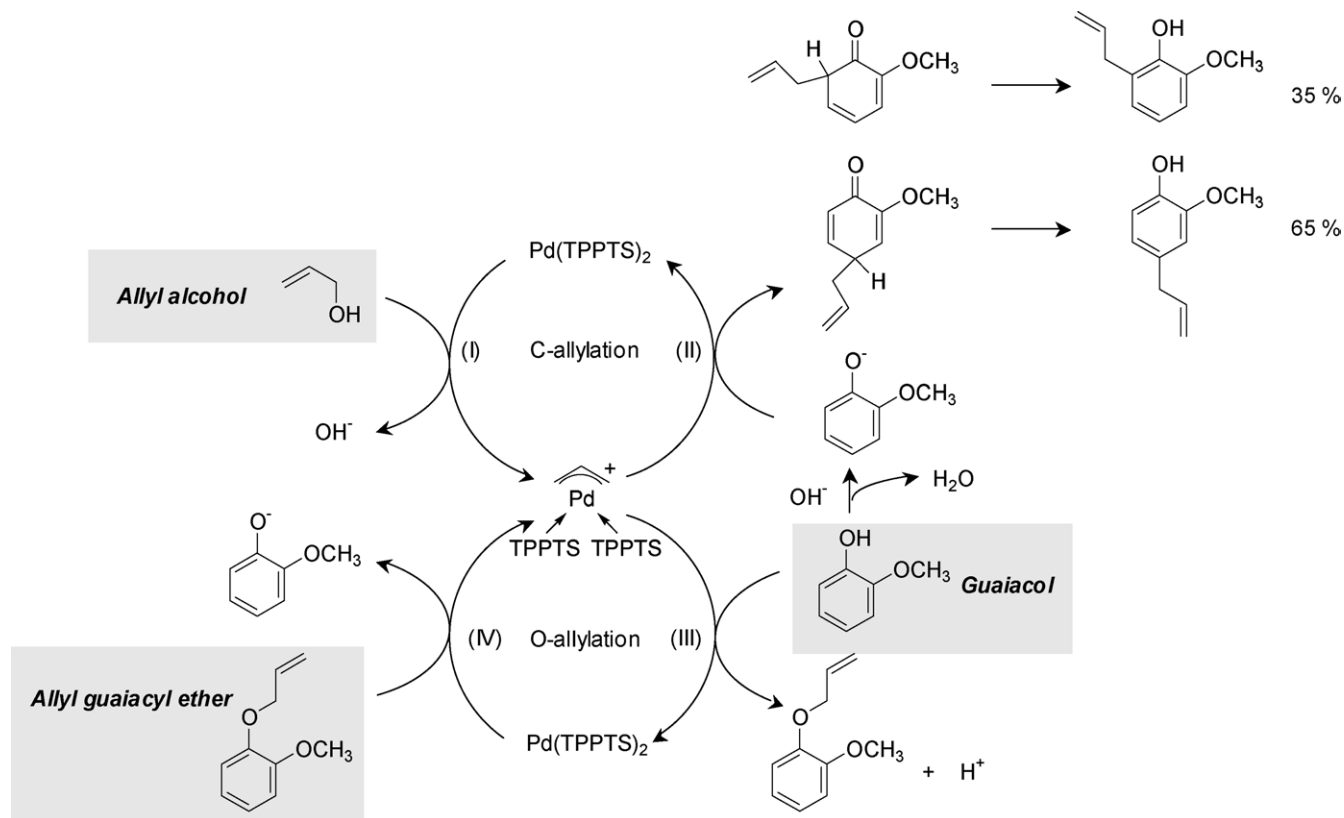
Scheme 4. Allylation of guaiacol in aqueous phase.

HClO$_4$, H$_2$SO$_4$, NaOH, NaOCH$_3$ (Laurylab). TPPTS was a gift from Hoechst (mixture of TPPTS 92%, TPPDS (sodium salt of di(metasulfophenyl)phenylphosphine) 5%, OTPPTS TPPTS oxide 3%.

Allyl guaiacyl ether 1(b) was prepared by condensation of guaiacol and allyl chloride in ethanol with 1 eq. of sodium hydroxide. After reaction, the sodium chloride was separated by filtration. The organic solution was then poured into water and the ether 1(b) was extracted with toluene and distilled. Purity: 98% (*ortho*eugenol 1.5%, *para*eugenol 0.4% and guaiacol 0.1%).

4.2. Measurements

^{31}P NMR spectra and ^{1}H NMR spectra were recorded on a Brüker Avance 300 MHz spectrometer (external reference for phosphorous analyses: H$_3$PO$_4$ 85%). The samples of palladium TPPTS complexes or phosphorous compounds were dissolved in 0.5 mL of D$_2$O or 0.4 mL of water with 0.1 mL of D$_2$O.

The pH measurements were performed with a PHN 330 T pH meter and a combined electrode (Tacussel, France).

All experiments were performed under inert atmosphere using argon. The oxygen concentration in water was measured with a Bioblock Scientific 9071 oxymeter (Bioblock, France) and found to be less than 0.1 ppm.

The concentration of reaction products in the toluene phase (toluene was used to extract the organic products from the aqueous phase) was determined by GC analysis using an HP-5890

with an HP-5 capillary column (30 m × 0.25 mm) and an HP GCD series mass spectrometer.

Order of retention time: allyl alcohol, diallyl ether,[2] toluene, phenol, 1(a), 2(a), 3(a), 4(a), 5(a), 8(a), 6(a), 7(a), 9(a) and guaiacol, 1(b), 2(b), 3(b), 4(b), 5(b), 7(b), 6(b).

4.3. Pd(0) TPPTS catalyst preparation

The Pd(0) TPPTS catalyst was prepared from Pd(OAc)$_2$ + nTPPTS (3.7 < n < 4.5) by a redox process: the excess of TPPTS reduced palladium(II) to palladium(0). The pH was controlled by NaOH addition [21]. At the end of the reaction, the pH was brought to 7.0–7.2. [Pd concentration 0.06 M to 0.10 M, molar ratio OTPPTS/Pd = 1.2, TPPTS/Pd = 2.7–3.5].

4.4. Allyl alcohol (or allyl phenyl ether) reaction with Pd(0) TPPTS (TPPTS/Pd = 3.0) at 20 °C

A 20-mL Schlenk tube was equipped with a pH electrode. Five millilitres of an aqueous Pd(0) solution [Pd] = 0.0054 M at pH 7.2 were added in the Schlenk in an atmosphere of argon. Eighteen microlitres of allyl alcohol (molar ratio allyl alcohol/palladium = 10) were then added. In a few seconds, the pH

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[2] In these studies on phenol or guaiacol allylation with allyl alcohol in aqueous phase, only minor amounts of diallyl ether were observed. In organic phase, the amounts of diallyl ether were larger.

reached 8.5 and perchloric acid 0.2 M was added to keep the pH at 7.2. After 80 min, the pH became stable, and 0.026 mL of HClO$_4$ was then poured in (solution S).

^{31}P NMR spectrum: aqueous solution S (0.4 mL) + D$_2$O (0.1 mL) exhibited 2 new signals: + 25.61 ppm (see Section 4.5) and +22.31 ppm (see Section 4.6). The Pd(0)TPPTS signal at +23.85 ppm disappeared completely.

4.5. π-Allylpalladium(II) complex preparation in deutered water solution

Into a 20-mL Schlenk tube with a magnetic stirrer, 1.4 mL of deuterated water and 0.4 mmol of TPPTS were combined. The solution was deoxygenated by passing argon through it for an half an hour, 0.1 mmol of allyl palladium chloride dimer complex was then added with fast stirring. The complex was dissolved in the deuterated water in 2 min (the complex was not soluble in water without TPPTS).

^{31}P NMR spectrum of the solution exhibited a large signal at 25.60 ppm and small signals at +23.85 ppm and +22.31 ppm corresponding to a low concentration of the palladium(0) TPPTS complex and the allylphosphonium of TPPTS (Fig. 11).

^{1}H NMR spectrum of the solution is shown in Fig. 12.

These analyses were similar to those found in the recent publication [20] reporting the [π-allylpalladium(TPPTS)$_2$]$^+$ cation formation.

4.6. Synthesis of allylphosphonium of TPPTS chloride

In a stirred solution of TPPTS (6 mmol) in water (10 mL), 0.98 mL of allyl chloride (12 mmol) was added. After 5 h at 55 °C, evaporation of the water at 50 °C afforded 4.8 g of a white solid. The ^{31}P NMR spectrum in D$_2$O solution exhibited two signals: +22.31 ppm and +35.14 ppm (OTPPTS 3%) (Fig. 11). For the ^{1}H NMR spectrum of the solution (see Fig. 12).

Similar phosphonium species, such as, the allylphosphonium of TPPMS hydrogenocarbonate (TPPMS: metasulfophenyl(diphenyl)phosphine, in this case the lithium salt) were prepared. The ^{31}P NMR in sulfolane–water mixture resulted in a peak at +21.35 ppm [28].

4.7. Allylation of phenol or guaiacol with allyl alcohol

In a typical reaction, 4.08 mL of water, 5.75 mmol of phenol or guaiacol, 2.87 mmol of allyl alcohol, and 0.23 mmol of TPPTS^3 were put into a 20-mL Schlenk tube with a magnetic stirrer. The solution was deoxygenated by passing argon through it for an half an hour and 0.0575 mmol of Pd(OAc)$_2$ was added. Once the palladium salt dissolved in the liquid phase, 6.0 mmol of sodium hydroxide were added. After 2 h at 80 °C and cooling down to room temperature, 6.0 mmol of perchloric acid (4 M) were added. Three millilitres of toluene were added to extract the organic products (GC analysis).

4.8. Isomerisation of allyl phenyl ether 1(a) and allyl guaiacyl ether 2(a)

In a typical reaction, 4.08 mL of water, 2.9 mmol 1(a) or 2(a), 5.8 mmol of phenol or guaiacol and 0.232 mmol of TPPTS were put into a 20-mL Schlenk tube with a magnetic stirrer. The solution was deoxygenated and 0.058 mmol of Pd(OAc)$_2$ was added and dissolved in the aqueous phase. Then, 3.48 mmol of sodium hydroxide were added. After 2 h at 80 °C and cooling down at room temperature, 3.48 mmol of perchloric acid (4 M) were added. Three millilitres of toluene were added to extract the organic products (GC analysis).

Test without sodium hydroxide: Two millilitres of water and 8.1 mmol 1(a) (raw material with 0.03% of phenol) were put into a 20-mL Schlenk tube with a magnetic stirrer. The system was deoxygenated and 0.5 mL of Pd(0) TPPTS ([Pd] = 0.054 M) was added (0.027 mmol, molar ratio 1(a)/Pd complex = 300). After 15 h at 80 °C and cooling down to room temperature, the pH was 6.5. Three millilitres of toluene were added for analysis. Only 0.7% of phenol/1(a) was found, corresponding to the molar ratio phenol/Pd = 2.

4.9. Allyl transfer from 1(a) to guaiacol or 2(a) to phenol

At 80 °C: Experiments were carried out under inert atmosphere (argon). One mmol of 1(a) and 10 mmol of guaiacol were added to a stirred solution of TPPTS (0.2 mmol) in water (2.5 mL). The system was deoxygenated and 0.05 mmol of Pd(OAc)$_2$ was dissolved in the aqueous phase. Six millimoles of sodium hydroxide were then added. After 15 min at 80 °C and cooling down to room temperature, 6 mmol of HClO$_4$ perchloric acid (4 M) were added. Three millilitres of toluene were added to extract the organic products (GC analysis).

At 55 °C: 3.22 mL of water, 0.86 mL NaOH 4 M, 5.76 mmol of guaiacol and 2.88 mmol of 1(a) were put into a Schlenk tube with a magnetic stirrer. The system was deoxygenated and 0.35 mL of Pd(0)TTPPTS catalyst was added (Pd concentration 0.081 M, molar ratio Pd(0)/1(a) = 1/100). After 15 min at 55 °C, an aliquot of the organic phase was sampled (0.02 mL + 0.1 mL toluene for GC analysis), and then again at 45 min, 1 h 40 min, 2 h 40 min, 4 h and 21 h. We consider that the major part of the ethers, C-allylated phenols and eugenols were in the organic phase (>95%). During the reaction the major part of phenol and guaiacol were held in water by sodium hydroxide because the molar ratio (guaiacol + phenol)/NaOH is greater than one. Consequently the low solubility of eugenol and allylphenol in water limits their concentrations in the aqueous phase.

4.10. Allylation of phenol with allyl alcohol in organic medium

In a typical reaction, 3 mL (2.91 g) of an equimolar solution of phenol (19.1 mmol) and of allyl alcohol (19.1 mmol) (solution S) and 0.4 mmol of triphenylphosphine were put into a 20-mL Schlenk tube with a magnetic stirrer. The system was deoxygenated and 0.1 mmol of Pd(OAc)$_2$ was added and dissolved in the organic phase. After 1 h at 80 °C and cooling down to room

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^{3} Using a Pd(0) TPPTS catalyst solution or a π-allylpalladium(II) catalyst solution, these solutions were added last after the sodium hydroxide.

temperature, the organic products were flashed to separate the organic phase from the catalyst.

The solvents were added before solution S (volume ratio: solvent/S = 3). The base was added after Pd(OAc)$_2$ (molar ratio: 5%/phenol).

4.11. Allyl phenyl ether 1(a) in organic medium (Pd TPP catalyst)

Experiments were carried out under inert atmosphere (argon). In a typical reaction, 3 mL (22 mmol) of 1(a), 0.44 mmol of TPP, and solvent[4] were put into a 20-mL Schlenk tube with a magnetic stirrer. The system was deoxygenated and 0.11 mmol of Pd(OAc)$_2$ was added. After 2 h at 90 °C and cooling down to room temperature, the mixture was flashed to separate the organic phase from the catalyst.

Acknowledgements

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[4] After reaction with no solvent, the system contained products in the following molar ratio: 1(a) major product (93%), phenol (4%), 2(a) (0.5%), 4(a) (1.5%), non-identified products (1%). In the same conditions with DMF or phenol as solvent with a volume ratio solvent/1(a) = 3, no degradation product was found.