

Anionic activation of the Wittig reaction using a solid-liquid phase transfer: examination of the medium-, temperature-, base- and phase-transfer catalyst effects

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Abstract

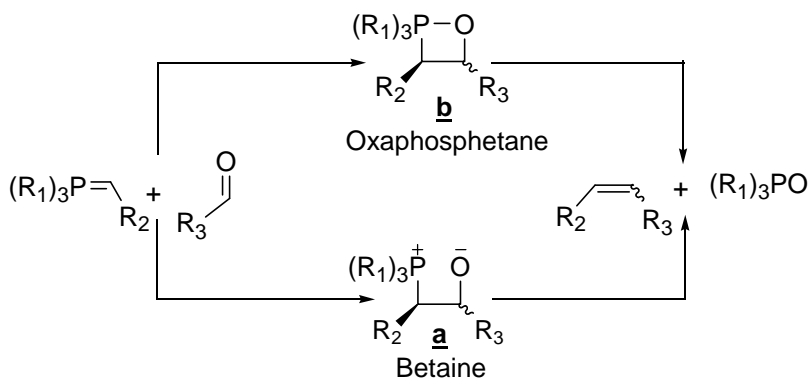
Potassium carbonate is a remarkable base in the Wittig reaction. It promotes the formation of ethylenic compounds in excellent yields, by a biphasic solid-liquid process. There is modest reactivity in the presence of hydroxides. The *Z*-isomer is the major product in aprotic media whereas the *E*-isomer is promoted in protic media. The addition of phase-transfer agents accelerates the reaction. However sodium hydroxide on alumina can be used as the basic system for the Wittig reaction.

Keywords: Wittig reaction, anionic activation, phase transfer catalysis .

Introduction

The Wittig reaction has been from its infancy a very important method for the formation of carbon-carbon double bonds.^{1,2} It is seen as the key step for the synthesis of many natural products.³ The basic reagent in the Wittig process is prepared via deprotonation of the corresponding phosphonium salt obtained by quaternization of a phosphine with a halo compound.⁴ The synthesis of phosphonium salts often requires harsh conditions. It is usually necessary to heat the phosphine-halo compound mixture under reflux for several hours, even days. A better methodology would obviously be welcome.⁵

The mechanism of the Wittig reaction has been abundantly studied. The betaine **a** was formerly considered to be the main intermediate.⁶ In 1973, Vedejs and Snoble⁷ detected only oxaphosphetane **b** by NMR spectroscopy during the course of the reaction.



Both intermediates are unstable and decompose into alkene and phosphine oxide. The main advantage of the Wittig reaction is its stereoselectivity.⁸ The stereochemistry depends on several parameters: the structure of the phosphonium salt,⁹⁻¹⁵ the presence of metal cations,^{1,16,17} and the experimental conditions.¹⁸⁻²¹ From this point of view, phase-transfer catalysis in the Bayliss-Hillman, aldolization, ketoaldolization reactions,²² and in the synthesis of cyclopropanes,²³ often requires phase-transfer agents such as quaternary ammonium salts or crown-ethers. Although Wittig reactions in liquid-solid biphasic conditions do not necessarily require the presence of such compounds,^{24,25} the latter do, however, permit one to lower, or even impede, the rate of secondary reactions, *e.g.*, Knoevenagel²⁴ or Cannizzaro reactions.²⁶ We have shown that the use of hydroxides and carbonates in solid-liquid phase-transfer conditions in slightly hydrated organic mixtures^{27,28} or formamide²⁹ permits one to obtain alkenes from aldehydes with very good yield and selectivity ratios. However, in the Wittig olefination reactions of Garner's aldehyde³⁰ with non-stabilized ylides, the (*E*) alkenes could be produced as a major product by simply quenching the reaction with a large excess of methanol at -78°C .²¹ Without addition of methanol, the usual selectivity for the (*Z*) alkenes was obtained in ratio of 94:6.²¹

We report in this Paper a thorough study of several effects (solvent, base, temperature, addition of phase-transfer catalysts) in the Wittig reaction between propyltriphenylphosphonium bromide, pentyltriphenylphosphonium bromide, and various carbonyl compounds. In addition, a reaction mechanism is proposed to rationalize the results.

Results and Discussion

Solvent effect

According to Table 1, the yield depends on the solvent. A higher dielectric constant is associated with an improved yield. Such solvents enhance the base strength through the dissociation of the cation-anion link of the basis, the activation of the basic entity opposite the acidic hydrogen of the phosphonium salt and facilitates desorption of the formed ylide.

In aqueous media the rate is lowered and, even more in water-hexane mixtures. These results are due to the low solubility of the aldehyde in water and strong stability of reaction

intermediates (betaine and oxaphosphetane) through hydrogen bonds. The ylide solvation is a hydrolysis reaction leading to the formation of phosphine oxide and benzene as shown in the mechanism of the Wittig reaction between benzaldehyde and propyltriphenylphosphonium bromide in aqueous medium in the presence of potassium carbonate (Scheme 1).

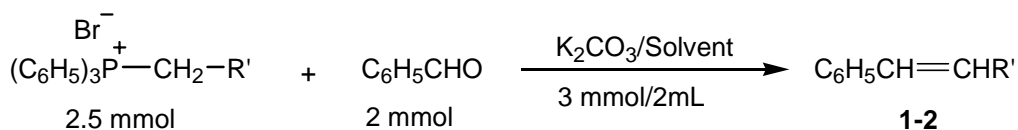
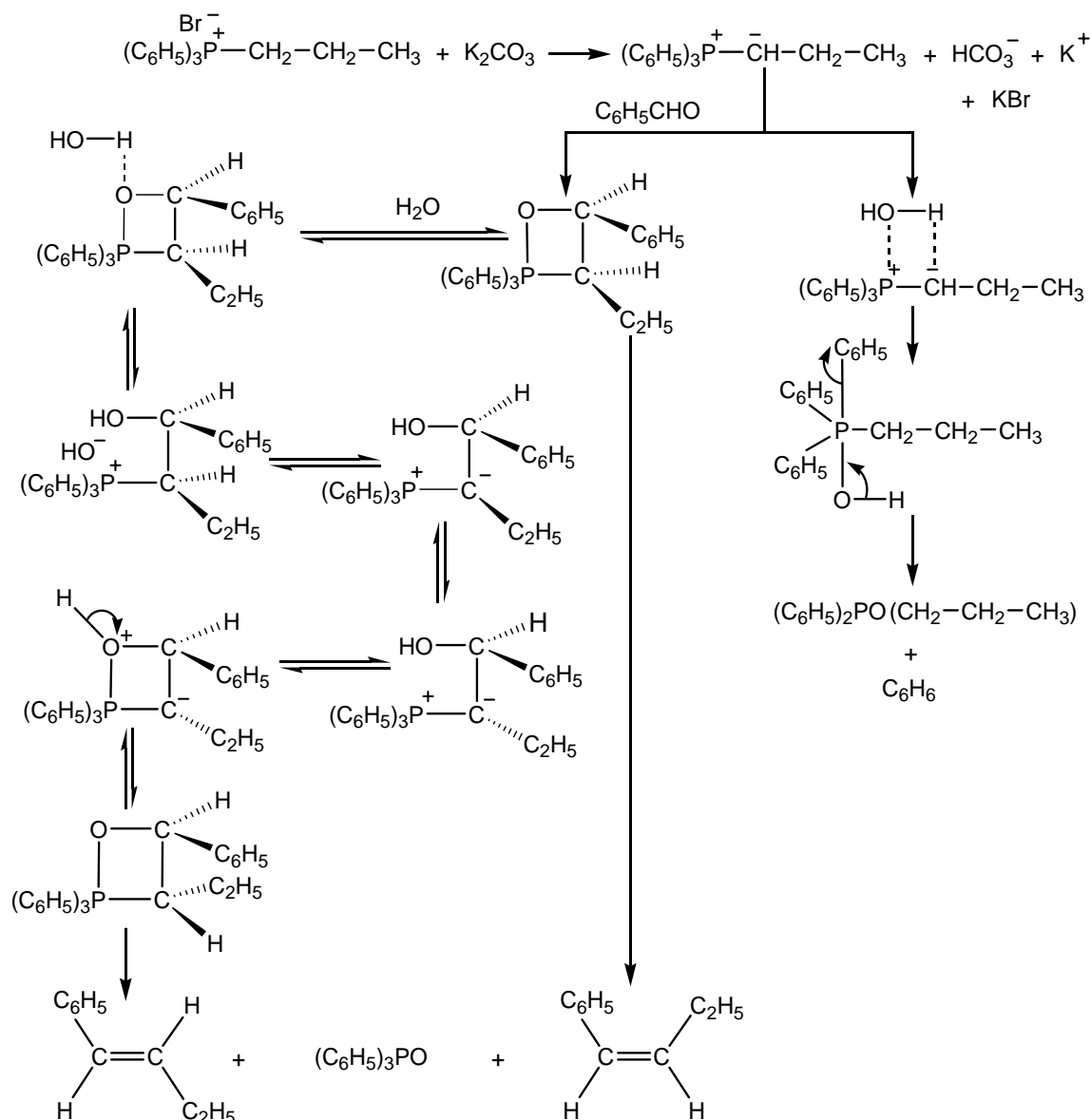


Table 1. Influence of the solvent on Wittig reactions of benzaldehyde and various phosphonium salts

| Solvent / Time | ϵ (25°C) | T (°C) | R' | Product | Yield / % |
|---|-------------------|--------|-------------------------------|----------|-----------|
| H ₂ O 24 h | 87 | 100 | C ₂ H ₅ | 1 | 70 |
| | | | C ₄ H ₉ | 2 | 72 |
| CH ₃ OH (**) 2 h | 32.6 | 65 | C ₂ H ₅ | 1 | 84 |
| | | | C ₄ H ₉ | 2 | 86 |
| C ₂ H ₅ OH 2 h | 24.3 | 65 | C ₂ H ₅ | 1 | 60 |
| | | | C ₄ H ₉ | 2 | 64 |
| C ₃ H ₇ OH 2 h | 20.1 | 65 | C ₂ H ₅ | 1 | 58 |
| | | | C ₄ H ₉ | 2 | 61 |
| C ₄ H ₉ OH 2 h | 17.1 | 65 | C ₂ H ₅ | 1 | 55 |
| | | | C ₄ H ₉ | 2 | 55 |
| Acetonitrile (*) 2 h | 37.5 | 80 | C ₂ H ₅ | 1 | 66 |
| | | | C ₄ H ₉ | 2 | 68 |
| Hexane (*) 2 h | 1.9 | 65 | C ₂ H ₅ | 1 | 24 |
| | | | C ₄ H ₉ | 2 | 25 |
| Dichloromethane (*) 2 h | 9.08 | 40 | C ₂ H ₅ | 1 | 20 |
| | | | C ₄ H ₉ | 2 | 20 |
| 1,4-Dioxane 2 h | 2.21 | 95 | C ₂ H ₅ | 1 | 72 |
| | | | C ₄ H ₉ | 2 | 74 |
| Water: hexane = 1:1 48 h | | 65 | C ₂ H ₅ | 1 | 55 |
| | | | C ₄ H ₉ | 2 | 55 |

* Water (2 mmol) is added. ** 2mL methanol with 0.18 mmol water.



Scheme 1. Mechanism of the Wittig reaction between benzaldehyde and propyltriphenylphosphonium bromide in aqueous medium in the presence of potassium carbonate.

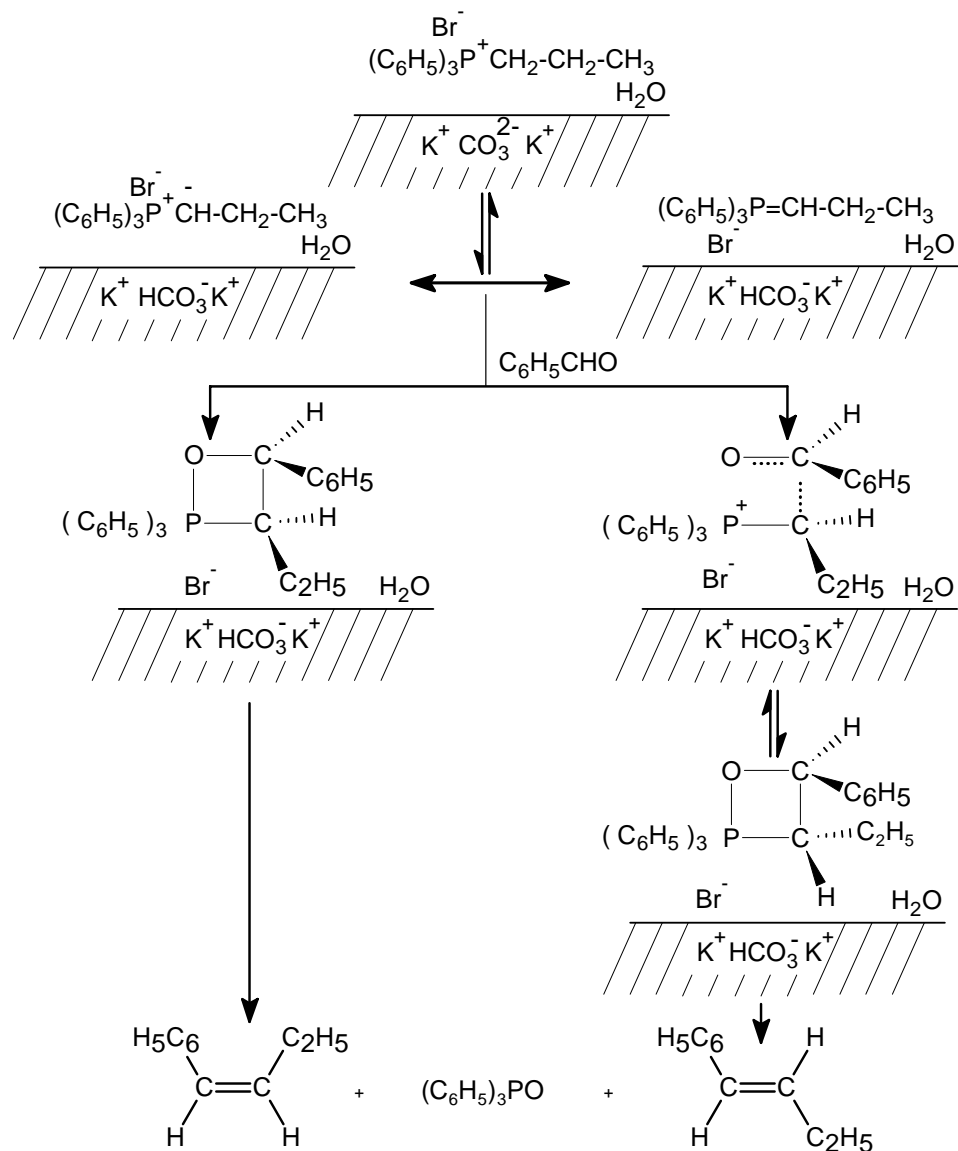
Table 2 reports that the addition of water to methanol decreases the alkene yield whereas the reactivity is increased in dioxane-water mixtures: a maximum is reached for water contents of 1-1.5 eq, the yield being decreased beyond. The “free” water content in methanol lowers the alkene yield owing to partial hydrolysis of the ylide into propyldiphenylphosphine oxide and benzene. Scheme 2 details the mechanism of the Wittig reaction between benzaldehyde and propyltriphenylphosphonium bromide in aprotic media.

Table 2. Effect of water and methanol on Wittig reactions of benzaldehyde and various phosphonium salts

| Solvent | Additive | R' | Yield / % |
|---------------|-------------------------------|-------------------------------|-----------|
| Dioxane | - | C ₂ H ₅ | 72 |
| | | C ₄ H ₉ | 74 |
| | 1mmol methanol | C ₂ H ₅ | 17 |
| | | C ₄ H ₉ | 18 |
| | 2mmol methanol | C ₂ H ₅ | 33 |
| | | C ₄ H ₉ | 33 |
| | 3mmol methanol | C ₂ H ₅ | 35 |
| | | C ₄ H ₉ | 36 |
| | 4mmol methanol | C ₂ H ₅ | 42 |
| | | C ₄ H ₉ | 44 |
| | 5mmol methanol | C ₂ H ₅ | 63 |
| | | C ₄ H ₉ | 65 |
| | 1mmol water | C ₂ H ₅ | 77 |
| | | C ₄ H ₉ | 78 |
| | 2mmol water | C ₂ H ₅ | 95 |
| | | C ₄ H ₉ | 97 |
| | 3mmol water | C ₂ H ₅ | 94 |
| | | C ₄ H ₉ | 94 |
| | 4mmol water | C ₂ H ₅ | 67 |
| | | C ₄ H ₉ | 67 |
| 6mmol water | C ₂ H ₅ | 56 | |
| | C ₄ H ₉ | 56 | |
| Methanol (**) | - | C ₂ H ₅ | 84 |
| | | C ₄ H ₉ | 86 |
| | 1mmol water | C ₂ H ₅ | 58 |
| | | C ₄ H ₉ | 59 |
| | 2mmol water | C ₂ H ₅ | 52 |
| | | C ₄ H ₉ | 55 |
| | 3mmol water | C ₂ H ₅ | 44 |
| | | C ₄ H ₉ | 48 |
| | 4mmol water | C ₂ H ₅ | 40 |
| | | C ₄ H ₉ | 40 |

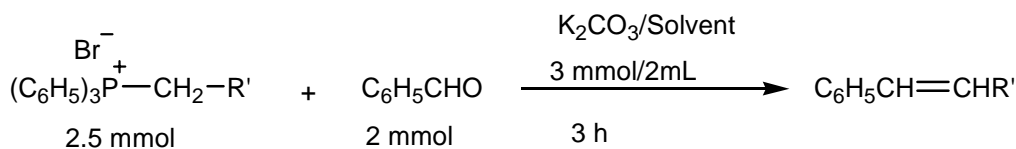
* Methanol (65°C), dioxane (95°C), time 3 h.

** Methanol, 2mL, with 0.18 mmol water.



Scheme 2. Mechanism of the Wittig reaction between benzaldehyde and propyltriphenylphosphonium bromide in 1,4-dioxane in the presence of potassium carbonate (solid-liquid phase-transfer process).

Base effect



The results of Table 3 show a modest reactivity in the presence of hydroxides. With carbonates such as K_2CO_3 and Cs_2CO_3 the yields are better (80 % in methanol and nearly quantitative in

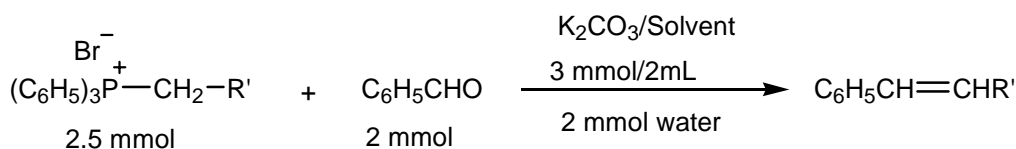
dioxane). The modest reactivity could be due to the formation of secondary products from the Cannizzaro reaction, or hydrolysis of the ylide in the presence of NaOH or KOH. This is no more the case when carbonates are present. The results are in agreement with those of Le Bigot.³¹ He proposed that secondary reactions are inhibited in the presence of carbonate ions. The formation of water when hydroxides are used favors solvation of the ylide in the first step of the Wittig process. In addition, the yield of alkene increases with the size of the cation, in relation to the cohesion energy density of the carbonates.

Table 3. Base effect on the Wittig reaction between benzaldehyde and propyltriphenylphosphonium bromide

| Base | Reticular energy Kj.mol ⁻¹ | Yield / % | |
|---------------------------------|--|-----------------------|---------------|
| | | Anhydrous dioxane (*) | Methanol (**) |
| CS ₂ CO ₃ | 1921 | 97 | 80 |
| K ₂ CO ₃ | 2084 | 95 | 79 |
| Na ₂ CO ₃ | 2301 | 13 | 15 |
| Li ₂ CO ₃ | - | 0 | 0 |
| KOH | - | 42 | 35 |
| NaOH | 824 | 40 | 32 |

* Water, 2 mmol, is added. ** Methanol (2mL) with 0.18 mmol water.

Temperature effect



| Solvent | Time (h) | T (°C) | Yield / % |
|---------------------------------|----------|--------|-----------|
| CH ₂ Cl ₂ | 3 | 40 | 20 |
| CH ₂ Cl ₂ | 18 | 40 | 92 |
| Dioxane | 3 | 95 | 95 |

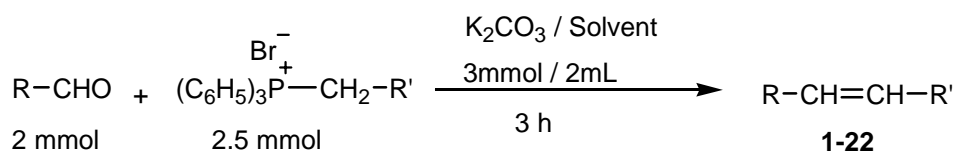
The reaction proceeds with quantitative yields in dioxane (95°C, 3h). Under otherwise identical conditions the yields are lowered in dichloromethane. Prolonged reaction times (18h) lead to 92% yield. The result is probably related to temperature and not solely traceable to the solvent used. To assess the hypothesis we carried out the Wittig reaction between benzaldehyde and propyltriphenylphosphonium bromide in dioxane in the presence of potassium carbonate at different temperatures (Table 4). A higher temperature results in higher alkene yields. This may be explained by enhanced basicity of the carbonate with increasing temperature which weakens

bonds between the potassium cation and carbonate anions, thereby reducing the cohesion energy density.

Table 4. Temperature effect on the Wittig reaction between benzaldehyde and propyltriphenylphosphonium bromide

| T °C | Time (h) | Yield / % |
|------|----------|-----------|
| 20 | 4 | 19 |
| 40 | 4 | 32 |
| 60 | 4 | 52 |
| 70 | 4 | 65 |
| 95 | 3 | 95 |

Reactivity of the carbonyl bond



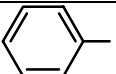
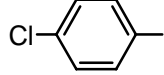
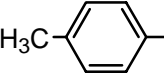
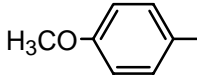
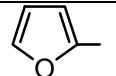
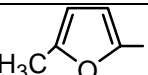
Aromatic aldehydes

Placing electron-donor substituents on the aromatic ring bearing the carbonyl group leads to a slowing down of the condensation between the ylide and the aldehyde in any medium, protic or aprotic, and therefore a decrease of the alkene yield. In fact, a group featuring either inductive (+I) or mesomeric (+M) effects on the aromatic ring of the carbonyl compound increases the charge density of the carbon atom of the CHO group, weakening thereby its electrophilicity toward the ylide. It should also be observed that (*E*)-alkenes are promoted in protic media compared to the major formation of (*Z*)-alkenes in aprotic media.

Aliphatic aldehydes

According to Table 6, the yields are higher when potassium carbonate is used in place of sodium hydroxide. The reactions proceed cleanly without formation of aldol products. The inhibition of the aldol reaction in the presence of potassium carbonate is ascribed to the absence of acid-base interactions between the enolizable hydrogen and the carbonate anion. In such conditions, the anion is not active enough to react. The solid state of K₂CO₃ promotes formation of an anion which could subsequently induce the formation of the ylide and not abstraction of the labile hydrogen at the interface. The formation of alkenes from aldehydes proceeds, therefore, according to a solid-liquid phase transfer. In addition, the reactivity decreases with increasing chain length of the aldehyde. The result can be explained by the donating effect of the alkyl group placed on the carbonyl bond, increasing thereby, the electronic density on the carbon of the carbonyl which is detrimental for the attack of the ylide.

Table 5. Condensation of aldehydes diversely substituted with propyltriphenylphosphonium and pentyltriphenylphosphonium bromide

| R | R' | Product | Dioxane1-4 (*) | | Methanol (**) | |
|---|---------------------------------|-----------|----------------|-------|---------------|-------|
| | | | Yield, % | E/Z | Yield, % | E/Z |
|  | C ₂ H ₅ | 1 | 95 | 19/81 | 84 | 76/24 |
| | n-C ₄ H ₉ | 2 | 97 | 16/84 | 86 | 80/20 |
|  | C ₂ H ₅ | 3 | 73 | 26/74 | 69 | 80/20 |
| | n-C ₄ H ₉ | 4 | 73 | 26/74 | 70 | 80/20 |
|  | C ₂ H ₅ | 5 | 42 | 27/73 | 52 | 68/32 |
| | n-C ₄ H ₉ | 6 | 44 | 24/76 | 55 | 66/34 |
|  | C ₂ H ₅ | 7 | 36 | 18/72 | 30 | 69/31 |
| | n-C ₄ H ₉ | 8 | 40 | 25/75 | 33 | 74/26 |
|  | C ₂ H ₅ | 9 | 93 | 25/75 | 68 | 70/30 |
| | n-C ₄ H ₉ | 10 | 95 | 20/80 | 70 | 77/23 |
|  | C ₂ H ₅ | 11 | 60 | 26/74 | 62 | 75/25 |
| | n-C ₄ H ₉ | 12 | 64 | 22/78 | 66 | 78/22 |

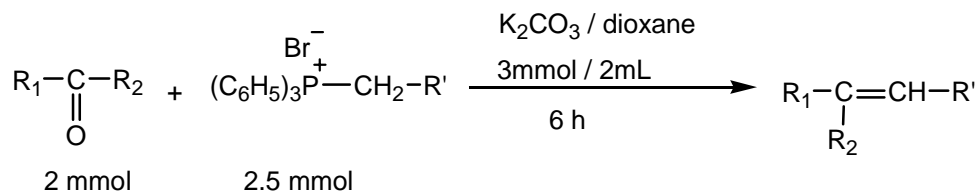
* Water (2 mmol) is added. ** 2 mL methanol with 0.18 mmol water.

Table 6. Effect of the aliphatic chain of the aldehyde on the Wittig reaction

| R | R' | Product | Yield / % | | | |
|----------------------------------|---------------------------------|-----------|---------------------------------------|-------------|--------------|------------|
| | | | Base = K ₂ CO ₃ | | Base = NaOH | |
| | | | 1,4-Dioxane* | Methanol ** | 1,4-Dioxane* | Methanol** |
| CH ₃ | C ₂ H ₅ | 13 | 72 | 68 | 30 | 20 |
| | n-C ₄ H ₉ | 14 | 74 | 68 | 28 | 20 |
| C ₂ H ₅ | C ₂ H ₅ | 15 | 70 | 68 | 28 | - |
| | n-C ₄ H ₉ | 16 | 70 | 66 | 30 | - |
| C ₃ H ₇ | C ₂ H ₅ | 17 | 68 | 60 | 26 | 18 |
| | n-C ₄ H ₉ | 18 | 72 | 62 | 26 | - |
| n-C ₇ H ₁₅ | C ₂ H ₅ | 19 | 64 | 54 | 22 | - |
| | n-C ₄ H ₉ | 20 | 70 | 54 | 28 | - |
| n-C ₈ H ₁₇ | C ₂ H ₅ | 21 | 58 | 50 | 26 | 18 |
| | n-C ₄ H ₉ | 22 | 60 | 52 | 26 | 18 |

* Water (2 mmol) is added. ** Methanol (2 mL) with 0.18 mmol water.

Ketones

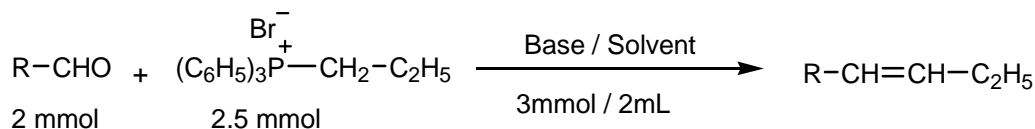


Wittig reactions involving acetophenone, 3-pentanone or cyclohexanone failed. Clearly, ketones are not reactive. The unreactivity is due to the low electrophilic character of the C=O bond and, very probably, steric effects. There is an exception, however, as a strong electron demanding group such as CF₃ increases the reactivity (95% yield). The results confirm the determining role of the electrophilicity of the carbon in the C=O bond toward the ylide.

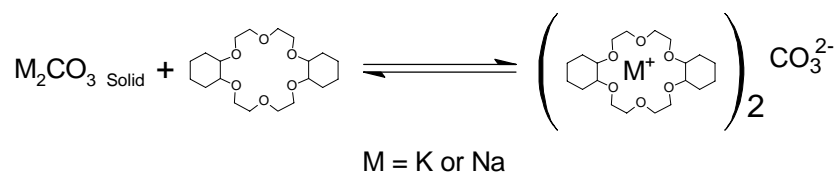
Table 7. Condensation of ketones with various phosphonium salts

| R ₁ | R ₂ | R' | Yield / % |
|--|-------------------------------|-------------------------------|-----------|
| C ₂ H ₅ | C ₂ H ₅ | C ₂ H ₅ | 0 |
| | | C ₄ H ₉ | 0 |
| -(CH ₂) ₅ - | | C ₂ H ₅ | 0 |
| | | C ₄ H ₉ | 0 |
| C ₆ H ₅ | CH ₃ | C ₂ H ₅ | 0 |
| | | C ₄ H ₉ | 0 |
| p NO ₂ -C ₆ H ₄ | CH ₃ | C ₂ H ₅ | 0 |
| | | C ₄ H ₉ | 0 |
| C ₆ H ₅ | CF ₃ | C ₂ H ₅ | 93 |
| | | C ₄ H ₉ | 95 |

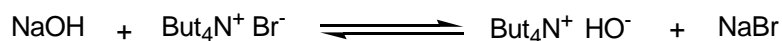
Effect of the phase-transfer catalyst



As observed, the addition of a phase transfer catalyst such as tetraalkylammonium salts or crown ethers is highly beneficial for the reactivity in organic solvents. This is no more the case in aqueous media. The catalyst leads to an exaltation of the basicity of carbonate ions *via* ionic exchange equilibria of K⁺ or Na⁺ with (R₄)N⁺ or *via* complexation of the metal cations (K⁺ or Na⁺) by crown ethers :



In reactions involving sodium hydroxide as the base, the ionic exchange equilibrium leads to the formation of a tetraalkylammonium hydroxide.



With $\text{Bu}_4\text{N}^+ \text{ Br}^-$, the active base would be $\text{Bu}_4\text{N}^+ \text{ OH}^-$ so that the cation could no more be associated with the carbonyl. The OH^- ions abstract the acidic hydrogen of the phosphonium salt, decreasing the rate of secondary reactions (Cannizzaro and aldol condensations). The phenomenon is clearly observed with aromatic aldehydes. Conversely, the aldol reaction could progress in concert with the Wittig reaction owing to the possibility of abstraction of an α -proton of the carbonyl group in the case of aliphatic aldehydes.

Table 8. Effect of the PT catalyst in the condensation of propyltriphenylphosphonium bromide and various aldehydes with potassium carbonate as the base

| Solvent | Time | Additive | R | Yield / % | |
|--------------------------|--------------------------|----------------------------------|----------------------------------|----------------------------------|----|
| Water | 24 h | - | C ₆ H ₅ | 78 | |
| | | | Cl-C ₆ H ₄ | 64 | |
| | | | n-C ₈ H ₁₇ | 32 | |
| | | HTMAB | C ₆ H ₅ | 50 | |
| | | | Cl-C ₆ H ₄ | 46 | |
| | | | n-C ₈ H ₁₇ | 20 | |
| | | TBAB | C ₆ H ₅ | 52 | |
| | | | Cl-C ₆ H ₄ | 45 | |
| | | | n-C ₈ H ₁₇ | 20 | |
| | Dicyclohexano-18-crown-6 | C ₆ H ₅ | 54 | | |
| | | Cl-C ₆ H ₄ | 48 | | |
| | | n-C ₈ H ₁₇ | 19 | | |
| | Dioxane | 3 h | - | C ₆ H ₅ | 72 |
| | | | | Cl-C ₆ H ₄ | 62 |
| | | | | n-C ₈ H ₁₇ | 44 |
| TBAB | | | C ₆ H ₅ | 88 | |
| | | | Cl-C ₆ H ₄ | 77 | |
| | | | n-C ₈ H ₁₇ | 64 | |
| Dicyclohexano-18-crown-6 | | | C ₆ H ₅ | 93 | |
| | | | Cl-C ₆ H ₄ | 81 | |
| | | | n-C ₈ H ₁₇ | 62 | |
| Methanol | | 3 h | - | C ₆ H ₅ | 84 |
| | | | | Cl-C ₆ H ₄ | 79 |
| | | | | n-C ₈ H ₁₇ | 52 |
| | | | TBAB | C ₆ H ₅ | 87 |
| | | | | Cl-C ₆ H ₄ | 85 |
| | | | | n-C ₈ H ₁₇ | 73 |
| | Dicyclohexano-18-crown-6 | | C ₆ H ₅ | 88 | |
| | | | Cl-C ₆ H ₄ | 83 | |
| | | | n-C ₈ H ₁₇ | 75 | |
| | Dichloro-methane | 3 h | - | C ₆ H ₅ | 20 |
| | | | | Cl-C ₆ H ₄ | 17 |
| | | | | n-C ₈ H ₁₇ | 10 |
| | | | Dicyclohexano-18-crown-6 | C ₆ H ₅ | 39 |
| | | | | Cl-C ₆ H ₄ | 31 |
| | | | | n-C ₈ H ₁₇ | 30 |

HTMAB, Hexadecyltrimethylammonium bromide; TBAB, Tetrabutylammonium bromide.

Table 9. Effect of the PT catalyst in the condensation of propyltriphenylphosphonium bromide and various aldehydes with various bases

| Solvent/Base | Additive | R | Yield / % |
|---|------------------------------|----------------------------------|-----------|
| Dioxane/NaOH [3 h] | - | C ₆ H ₅ | 40 |
| | | Cl-C ₆ H ₄ | 35 |
| | | n-C ₈ H ₁₇ | 26 |
| | TBAB | C ₆ H ₅ | 84 |
| | | Cl-C ₆ H ₄ | 73 |
| | | n-C ₈ H ₁₇ | 59 |
| | Dicyclohexano- 18-crown-6 | C ₆ H ₅ | 44 |
| | | Cl-C ₆ H ₄ | 37 |
| | | n-C ₈ H ₁₇ | 27 |
| Methanol/NaOH [3 h] | - | C ₆ H ₅ | 32 |
| | | Cl-C ₆ H ₄ | 24 |
| | | n-C ₈ H ₁₇ | 18 |
| | TBAB | C ₆ H ₅ | 82 |
| | | Cl-C ₆ H ₄ | 69 |
| | | n-C ₈ H ₁₇ | 34 |
| | Dicyclohexano- 18-crown-6 | C ₆ H ₅ | 52 |
| | | Cl-C ₆ H ₄ | 44 |
| | | n-C ₈ H ₁₇ | 34 |
| Methanol/Na ₂ CO ₃ [3 h] | - | C ₆ H ₅ | 15 |
| | | Cl-C ₆ H ₄ | 10 |
| | | n-C ₈ H ₁₇ | 8 |
| | TBAB | C ₆ H ₅ | 71 |
| | | Cl-C ₆ H ₄ | 62 |
| | | n-C ₈ H ₁₇ | 56 |

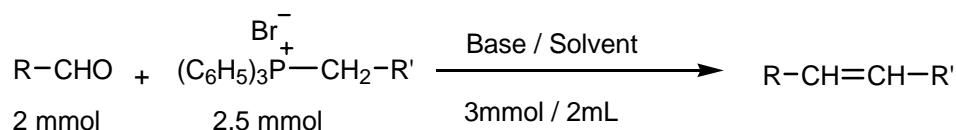
Activation on alumina

Table 10 reports the results. Sodium hydroxide adsorbed on alumina activates the Wittig reaction at the same level as it does in dioxane. The addition of a phase-transfer catalyst decreases the yield, with apparent prevalence of Cannizzaro and aldol reactions. The ammonium cation of the PT catalyst and its complexation with the carbonyl group increases the electrophilicity of the carbon and favors the nucleophilic attack of the hydroxide ion, yielding the Cannizzaro product,

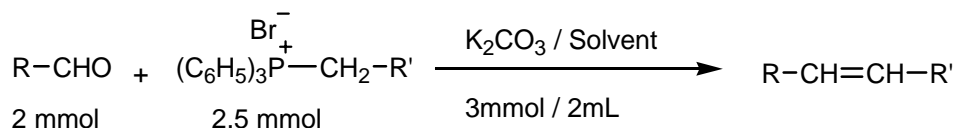
or the aldol product in the case of enolizable aldehydes. In addition, the ylide formed after abstraction of the acidic hydrogen of the phosphine salt is adsorbed and seemingly fixed on the alumina surface.

Table 10. Effect of the medium on the Wittig reaction

| Medium [time] | R | R' | Yield / % |
|--|----------------------------------|-------------------------------|-----------|
| NaOH/Dioxane (*) [3 h] | C ₆ H ₅ | C ₂ H ₅ | 40 |
| | | C ₄ H ₉ | 42 |
| | Cl-C ₆ H ₄ | C ₂ H ₅ | 35 |
| | | C ₄ H ₉ | 35 |
| | n-C ₈ H ₁₇ | C ₂ H ₅ | 18 |
| | | C ₄ H ₉ | 18 |
| NaOH/Methanol [3 h] | C ₆ H ₅ | C ₂ H ₅ | 32 |
| | | C ₄ H ₉ | 33 |
| | Cl-C ₆ H ₄ | C ₂ H ₅ | 24 |
| | | C ₄ H ₉ | 24 |
| | n-C ₈ H ₁₇ | C ₂ H ₅ | 18 |
| | | C ₄ H ₉ | 18 |
| Al ₂ O ₃ [60 h] | C ₆ H ₅ | C ₂ H ₅ | 0 |
| | | C ₄ H ₉ | 0 |
| | Cl-C ₆ H ₄ | C ₂ H ₅ | 0 |
| | | C ₄ H ₉ | 0 |
| | n-C ₈ H ₁₇ | C ₂ H ₅ | 0 |
| | | C ₄ H ₉ | 0 |
| NaOH/ Al ₂ O ₃ [12 h] | C ₆ H ₅ | C ₂ H ₅ | 50 |
| | | C ₄ H ₉ | 51 |
| | Cl-C ₆ H ₄ | C ₂ H ₅ | 45 |
| | | C ₄ H ₉ | 46 |
| | n-C ₈ H ₁₇ | C ₂ H ₅ | 34 |
| | | C ₄ H ₉ | 35 |
| NaOH/ Al ₂ O ₃ + Aliquat-336 [12 h] | C ₆ H ₅ | C ₂ H ₅ | 26 |
| | | C ₄ H ₉ | 25 |
| | Cl-C ₆ H ₄ | C ₂ H ₅ | 17 |
| | | C ₄ H ₉ | 15 |
| | n-C ₈ H ₁₇ | C ₂ H ₅ | 14 |
| | | C ₄ H ₉ | 14 |
| NaOH/ Al ₂ O ₃ + HTMAB [12 h] | C ₆ H ₅ | C ₂ H ₅ | 24 |
| | | C ₄ H ₉ | 24 |
| | Cl-C ₆ H ₄ | C ₂ H ₅ | 18 |
| | | C ₄ H ₉ | 17 |
| | n-C ₈ H ₁₇ | C ₂ H ₅ | 14 |
| | | C ₄ H ₉ | 13 |

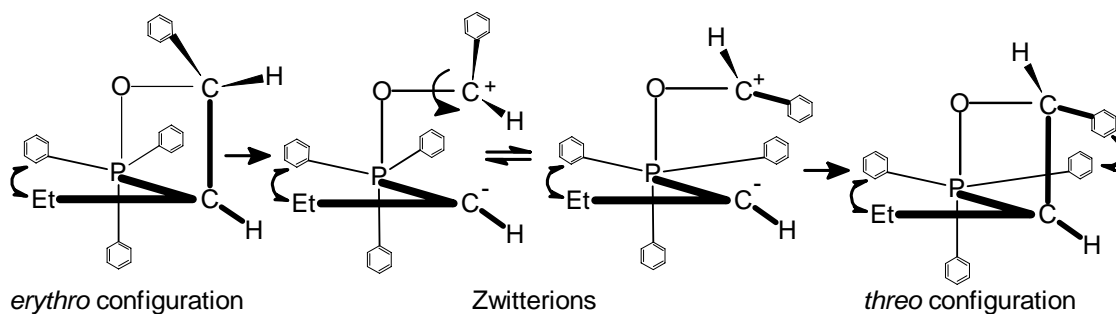
* Water, 2 mmol, is added.

Effect on the isomer distribution



The solvent is a major parameter for the stereochemical outcome in the Wittig reaction. The (*E*)-olefin percentage increases in a polar medium. In a protic solvent like methanol the dominant (*E*) isomer suggests preferential formation of the *threo* betaine^{21,32} as a consequence of the solvation of ionic species, more precisely, the reactivity of the ylide towards the aldehyde. It is magnified by the hydrogen bonds between the ylide and the molecules of solvent. The preferential formation of the *threo* betaine, which is stabilized by hydrogen bonds, contrary to the oxaphosphetane leads to the formation of the (*E*)-olefin. In an apolar medium, coordination of the O atom of the aldehyde and the P atom of the ylide is promoted. This means formation of an O-P bond *prior* to the C-C bond (Scheme 3). The structure of the intermediate acknowledges the location of an aldehyde group (phenyl) in a least sterically congested position so that the alkyl group (ethyl) of the ylide interacts with a phenyl group of the phosphine. The formation of oxaphosphetane requires rotation around the C-O bond, promoting the *erythro* configuration of the oxaphosphetane and, consequently, the (*Z*) olefin. It seems that the oxaphosphetane-forming step is believed to resemble a concerted [2+2] cycloaddition between the ylide and the carbonyl compound,³³ then it can open to zwitterions which are free to rotate to the thermodynamically more stable *threo* isomers before decomposing to products.³²

In contrast, the *threo* configuration is disfavored as a consequence of high steric hindrance imposed by the interactions between the aldehyde group and a phenyl group of the phosphine as well as between the alkyl group of the aldehyde and the phenyl group of the phosphine (Scheme 3). Table 11 indicates that selecting dichloromethane as the solvent in the presence of water, or phase-transfer agents such as crown-ethers, leads to olefins with a (*Z*): (*E*) ratio close to unity. It is worthwhile underlining the synthesis of (*Z*) olefins by using an apolar aprotic weakly hydrated medium via a solid-liquid transfer process.



Scheme 3

Table 11. Effect of the medium on the *E/Z* ratio

| Medium | R' | R | <i>E/Z</i> ^{a,b} |
|---|-------------------------------|----------------------------------|---------------------------|
| Acetonitrile/2mmol water/80°C 2 h | | C ₆ H ₅ | 43/57 |
| | C ₂ H ₅ | Cl-C ₆ H ₄ | 46/54 |
| | | n-C ₈ H ₁₇ | 41/59 |
| | | C ₆ H ₅ | 45/55 |
| | C ₄ H ₉ | Cl-C ₆ H ₄ | 45/55 |
| | | n-C ₈ H ₁₇ | 42/58 |
| Dioxane/2mmol water/95°C 3 h | | C ₆ H ₅ | 19/81 |
| | C ₂ H ₅ | Cl-C ₆ H ₄ | 26/74 |
| | | n-C ₈ H ₁₇ | 26/74 |
| | | C ₆ H ₅ | 16/84 |
| | C ₄ H ₉ | Cl-C ₆ H ₄ | 26/74 |
| | | n-C ₈ H ₁₇ | 25/75 |
| Methanol/65°C 3 h | | C ₆ H ₅ | 76/24 |
| | C ₂ H ₅ | Cl-C ₆ H ₄ | 80/20 |
| | | n-C ₈ H ₁₇ | 82/18 |
| | | C ₆ H ₅ | 80/20 |
| | C ₄ H ₉ | Cl-C ₆ H ₄ | 80/20 |
| | | n-C ₈ H ₁₇ | 85/15 |
| CH ₂ Cl ₂ /40°C/ 0.1 mmol dicyclohexano-18-crown-6 3 h | | C ₆ H ₅ | 52/48 |
| | C ₂ H ₅ | Cl-C ₆ H ₄ | 50/50 |
| | | n-C ₈ H ₁₇ | 51/49 |
| | | C ₆ H ₅ | 54/46 |
| | C ₄ H ₉ | Cl-C ₆ H ₄ | 52/48 |
| | | n-C ₈ H ₁₇ | 55/45 |
| CH ₂ Cl ₂ /2mmol water/40°C 3 h | | C ₆ H ₅ | 50/50 |
| | C ₂ H ₅ | Cl-C ₆ H ₄ | 49/51 |
| | | n-C ₈ H ₁₇ | 52/48 |
| | | C ₆ H ₅ | 52/48 |
| | C ₄ H ₉ | Cl-C ₆ H ₄ | 52/48 |
| | | n-C ₈ H ₁₇ | 53/47 |
| Hexane/65°C 3 h | | C ₆ H ₅ | 18/82 |
| | C ₂ H ₅ | Cl-C ₆ H ₄ | 20/80 |
| | | n-C ₈ H ₁₇ | 19/81 |
| | | C ₆ H ₅ | 21/79 |
| | C ₄ H ₉ | Cl-C ₆ H ₄ | 19/81 |
| | | n-C ₈ H ₁₇ | 23/77 |

| | | | |
|---------------------|-------------------------------|----------------------------------|-------|
| Water/100°C 24 h | | C ₆ H ₅ | 88/12 |
| | C ₂ H ₅ | Cl-C ₆ H ₄ | 89/11 |
| | | n-C ₈ H ₁₇ | 87/13 |
| | | C ₆ H ₅ | 90/10 |
| | C ₄ H ₉ | Cl-C ₆ H ₄ | 88/12 |
| | | n-C ₈ H ₁₇ | 90/10 |

^a Determined by ¹H-NMR of the product. ^b In the ¹H-NMR the system $\overset{\text{A}}{\text{CH}}=\overset{\text{B}}{\text{CH}}-\overset{\text{X}}{\text{CH}_2}$ gives the following characteristic values: for the *E*-isomer $J_{H_A H_B} = 15.6 (\pm 0.3)$ Hz, $J_{H_B H_X} = 6.9 (\pm 0.3)$ Hz, for the *Z*-isomer $J_{H_A H_B} = 11.4 (\pm 0.3)$ Hz, $J_{H_B H_X} = 6.9 (\pm 0.3)$ Hz. In the ¹³C-NMR, the values of the chemical displacements of α -carbons of double links are higher, by 5 to 6 ppm in the case of the *E*-isomer, to those observed with a *Z* configuration of the alkenes.

In conclusion, the use of alkaline carbonates in slightly hydrated solid-liquid aprotic media allowed the synthesis of alkenes from polyfunctional aldehydes or activated ketones with high yield in a *Z* preferential stereochemistry. However, the *E*- isomer is promoted in protic media. Wittig reactions were also performed in sodium hydroxide adsorbed on alumina.

Addition of phase transfer catalyst accelerates the Wittig reaction rate in organic media. On the contrary, in aqueous media it appears that phase-transfer agents play a harmful role.

Experimental Section

General Procedures. ¹H-NMR (300 MHz) and ¹³C-NMR (75MHz) spectra were recorded on a Bruker AC300 spectrometer in CDCl₃ solvent, with tetramethylsilane as internal reference. Melting points were taken on a Reichert-Heizbank apparatus.

Synthesis of the phosphonium salts

Propyltriphenylphosphonium bromide. In a 250 mL two-necked flask equipped with a cooling system and magnetic stirrer, 68.1g (260 mmol) of triphenylphosphine are introduced into 60 mL toluene. Then, 43.05g (31.8ml, 350 mmol) of bromopropane are poured into the solution. The mixture is stirred during 24 h at 95°C. After cooling, additional stirring is maintained for 6h at room temperature. The mixture is filtered off, and the crystals are collected and washed with 80 mL hot toluene. The resulting product is dried at 100°C during 48h. Yield: 66g (66%). mp = 233-237°C.

Pentyltriphenylphosphonium bromide. The protocol is identical to the preceding. Yield, 79%; mp = 165-167.5°C.

Preparation of NaOH/Al₂O₃. NaOH (1g, 25 mmol) is dissolved in a minimal volume of water (2 mL). Alumina (4g) is added. After magnetic stirring the solid is dried at 120°C for 12h.

Synthesis of olefins

In a 25 mL two-necked flask equipped with a cooling system and magnetic stirrer, the phosphonium salt (2.5mmol), the base (3mmol), the solvent (2mL), the aldehyde (2mmol) are successively placed. The mixture is stirred at the desired temperature. After filtration the solvent is removed *in vacuo*. The residue is washed with ether to remove most of the triphenylphosphine oxide. The alkene is isolated by column chromatography with hexane as eluent.

In reactions carried out in aqueous media, the process is the same except that after reaction and the usual work-up the residue is dried over anhydrous magnesium sulfate.

(E)- 1-Phenyl-1-butene (1). ¹H-NMR (300 MHz, CDCl₃) δ 0.96 (3H, t, *J* = 7.5 Hz), 2.14-2.26 (2H, m), 6.22 (1H, dt, *J* = 15.6, 6.9 Hz), 6.38 (1H, d, *J* = 15.6 Hz), 7.15-7.35 (3H, m), 7.45 (2H, d, *J* = 8.1 Hz). ¹³C-NMR (75MHz, CDCl₃) δ 13.77, 27.01, 126.46, 128.14, 128.50, 130.76, 131.73, 133.15.

(Z)- 1-Phenyl-1-butene (1). ¹H-NMR (300 MHz, CDCl₃) δ 0.98 (3H, t, *J* = 7.5 Hz), 2.25-2.34 (2H, m), 5.66 (1H, dt, *J* = 11.7, 6.9 Hz), 6.37 (1H, d, *J* = 11.7 Hz), 7.14-7.36 (3H, m), 7.44 (2H, d, *J* = 8.1 Hz). ¹³C-NMR (75 MHz, CDCl₃) δ 13.97, 22.59, 126.80, 128.25, 128.61, 130.88, 131.70, 133.25.

(E)- 1-Phenyl-1-hexene (2). ¹H-NMR (300 MHz, CDCl₃) δ 0.94 (3H, t, *J* = 7.5 Hz), 1.32-1.59 (4H, m), 2.14-2.26 (2H, m), 6.23 (1H, dt, *J* = 15.6, 7.2 Hz), 6.39 (1H, d, *J* = 15.6 Hz), 7.14-7.35 (3H, m), 7.44 (2H, d, *J* = 8.1 Hz). ¹³C-NMR (75 MHz, CDCl₃) δ 13.91, 23.48, 31.97, 32.74, 127.66, 128.66, 130.75, 130.88, 131.74, 135.12.

(Z)- 1-Phenyl-1-hexene (2). ¹H-NMR (300 MHz, CDCl₃) δ 0.96 (3H, t, *J* = 7.5 Hz), 1.32-1.60 (4H, m), 2.15-2.28 (2H, m), 5.69 (1H, dt, *J* = 6.9, 11.7 Hz), 6.37 (1H, d, *J* = 11.7 Hz), 7.14-7.38 (3H, m), 7.41 (2H, d, *J* = 8.1 Hz). ¹³C-NMR (75 MHz, CDCl₃) δ 14.10, 23.50, 26.67, 32.75, 127.64, 128.66, 130.76, 130.90, 131.75, 135.18.

(E)- 1-(4-Chlorophenyl)-1-butene (3). ¹H-NMR (300 MHz, CDCl₃) δ 1.13 (3H, t, *J* = 7.5 Hz), 2.26 (2H, qd, *J* = 7.5, 6.6 Hz), 6.24-6.39 (2H, m), 7.23 (2H, d, *J* = 8.1 Hz), 7.33 (2H, d, *J* = 8.1 Hz). ¹³C-NMR (75 MHz, CDCl₃) δ 13.64, 26.17, 127.20, 127.72, 128.66, 133.39, 135.46, 136.60.

(Z)- 1-(4-Chlorophenyl)-1-butene (3). ¹H-NMR (300 MHz, CDCl₃) δ 1.13 (3H, t, *J* = 7.5 Hz), 2.35 (2H, qd, *J* = 7.5, 7.2 Hz), 5.70 (1H, dt, *J* = 11.7, 7.2 Hz), 6.34 (1H, d, *J* = 11.7 Hz), 7.22 (2H, d, *J* = 8.1 Hz), 7.32 (2H, d, *J* = 8.1 Hz). ¹³C-NMR (75MHz, CDCl₃) δ 14.42, 22.03, 127.17, 127.18, 128.63, 133.29, 135.38, 136.20.

(E)- 1-(4-Chlorophenyl)-1-hexene (4). ¹H-NMR (300 MHz, CDCl₃) δ 0.91 (3H, t, *J* = 7.2 Hz), 1.29-1.57 (4H, m), 2.22 (2H, dt, *J* = 7.2, 6.6 Hz), 6.22 (1H, dt, *J* = 15.9, 6.6 Hz), 6.36 (1H, d, *J* = 15.9 Hz), 7.21 (2H, d, *J* = 8.4 Hz), 7.30 (2H, d, *J* = 8.4 Hz). ¹³C-NMR (75MHz, CDCl₃) δ 14.05, 22.48, 32.12, 32.79, 127.58, 128.57, 130.08, 132.00, 133.99, 136.47.

(Z)- 1-(4-Chlorophenyl)-1-hexene (4). ¹H-NMR (300 MHz, CDCl₃) δ 0.95 (3H, t, *J* = 7.2 Hz), 1.29-1.57 (4H, m), 2.31 (2H, dt, *J* = 7.2, 6.6 Hz), 5.69 (1H, dt, *J* = 11.7, 7.2 Hz), 6.36 (1H, d, *J* = 11.7 Hz), 7.21 (2H, d, *J* = 8.4 Hz), 7.30 (2H, d, *J* = 8.4 Hz). ¹³C-NMR (75 MHz, CDCl₃) δ 14.24, 22.37, 28.39, 31.49, 127.15, 127.58, 128.31, 132.00, 133.99, 136.27.

(E)- 1-(4-Methylphenyl)-1-butene (5). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.12 (3H, t, $J = 7.5$ Hz), 2.25 (2H, qd, $J = 7.5, 6.6$ Hz), 2.32 (3H, s), 6.25-6.39 (2H, m), 7.08 (2H, d, $J = 8.1$ Hz), 7.19 (2H, d, $J = 8.1$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.00, 21.20, 26.12, 126.80, 127.72, 129.23, 130.09, 132.22, 136.22.

(Z)- 1-(4-Methylphenyl)-1-butene (5). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.12 (3H, t, $J = 7.5$ Hz), 2.34 (qd, 2H, $J = 7.5, 7.2$ Hz), 2.32 (3H, s), 5.72 (2H, dt, $J = 11.4, 7.2$ Hz), 6.36 (1H, d, $J = 11.4$ Hz), 7.09 (2H, d, $J = 8.1$ Hz), 7.18 (2H, d, $J = 8.1$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) 14.41, 21.18, 21.85, 126.81, 127.62, 129.23, 130.11, 132.21, 136.61.

(E)- 1-(4-Methylphenyl)-1-hexene (6). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.98 (3H, t, $J = 7.5$ Hz), 1.30-1.57 (4H, m), 2.23 (2H, dt, $J = 7.5, 6.9$ Hz), 2.38 (3H, s), 6.19 (1H, dt, $J = 15.9, 6.9$ Hz), 6.41 (1H, d, $J = 15.9$ Hz), 7.04 (2H, d, $J = 8.1$ Hz), 7.21 (2H, d, $J = 8.1$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.18, 21.09, 23.20, 32.21, 32.68, 126.32, 127.21, 132.09, 133.15, 130.10, 137.27.

(Z)- 1-(4-Methylphenyl)-1-hexene (6). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.99 (3H, t, $J = 7.5$ Hz), 1.30-1.57 (4H, m), 2.29 (2H, dt, $J = 7.5, 6.9$ Hz), 2.38 (3H, s), 5.69 (1H, dt, $J = 11.1, 6.9$ Hz), 6.40 (1H, d, $J = 11.1$ Hz), 7.04 (2H, d, $J = 8.1$ Hz), 7.21 (2H, d, $J = 8.1$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.13, 21.09, 23.20, 27.19, 32.23, 126.32, 127.21, 132.10, 133.14, 130.10, 137.27.

(E)- 1-(4-Methoxyphenyl)-1-butene (7). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.14 (3H, t, $J = 7.5$ Hz), 2.24 (2H, qd, $J = 7.5, 6.6$ Hz), 3.80 (3H, s), 6.22-6.38 (2H, m), 7.02 (2H, d, $J = 8.1$ Hz), 7.23 (2H, d, $J = 8.1$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 13.54, 26.27, 58.12, 117.42, 127.74, 128.23, 128.81, 133.41, 159.36.

(Z)- 1-(4-Methoxyphenyl)-1-butene (7). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.13 (3H, t, $J = 7.5$ Hz), 2.34 (2H, qd, $J = 7.5, 7.2$ Hz), 3.81 (3H, s), 5.68 (1H, dt, $J = 11.4$ Hz, 7.2 Hz), 6.33 (1H, d, $J = 11.4$ Hz), 7.00 (2H, d, $J = 8.1$ Hz), 7.22 (2H, d, $J = 8.1$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 13.64, 21.98, 58.02, 116.72, 127.70, 128.03, 128.62, 133.41, 158.62.

(E)- 1-(4-Methoxyphenyl)-1-hexene (8). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.92 (3H, t, $J = 7.2$ Hz), 1.28-1.56 (4H, m), 2.24 (2H, dt, $J = 7.2, 6.6$ Hz), 3.78 (3H, s), 6.20 (1H, dt, $J = 15.9, 6.6$ Hz), 6.39 (1H, d, $J = 15.9$ Hz), 7.00 (2H, d, $J = 8.1$ Hz), 7.19 (2H, d, $J = 8.1$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , 25°C): δ 14.10, 23.21, 32.06, 32.69, 56.02, 117.41, 127.52, 128.28, 128.32, 132.82, 161.19.

(Z)- 1-(4-Methoxyphenyl)-1-hexene (8). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.96 (3H, t, $J = 7.2$ Hz), 1.28-1.56 (4H, m), 2.31 (2H, dt, $J = 7.2, 6.6$ Hz), 3.78 (3H, s), 5.63 (1H, dt, $J = 11.4, 7.2$ Hz), 6.38 (1H, d, $J = 11.4$ Hz), 6.98 (2H, d, $J = 8.1$ Hz), 7.21 (2H, d, $J = 8.1$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.08, 23.18, 26.81, 32.06, 56.32, 117.11, 127.54, 128.18, 128.32, 132.80, 160.19.

(E)- 1-Furanyl-1-butene (9). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.05 (3H, t, $J = 7.2$ Hz), 2.31 (2H, dq, $J = 7.2, 6.9$ Hz), 6.13-6.44 (4H, m), 7.43 (1H, d, $J = 1.8$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 13.68, 29.02, 111.09, 117.40, 128.49, 132.20, 133.16, 141.20.

(Z)- 1-Furanyl-1-butene (9). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.11 (3H, t, $J = 7.2$ Hz), 2.26-2.39 (2H, m), 5.55 (dt, 1H, $J = 12, 7.2$ Hz), 6.20-6.38 (3H, m), 7.43 (1H, d, $J = 1.8$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 13.98, 22.47, 111.10, 117.40, 128.65, 132.07, 133.26, 142.10.

(E)- 1-Furanyl-1-hexene (10). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.95 (3H, t, $J = 7.2$ Hz), 1.32-1.55 (4H, m), 2.20-2.34 (2H, m), 6.17-6.39 (4H, m), 7.41 (1H, d, $J = 1.8$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.02, 23.48, 29.98, 31.34, 111.93, 115.41, 127.92, 132.17, 135.26, 144.47.

(Z)- 1-Furanyl-1-hexene (10). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.02 (3H, t, $J = 7.2$ Hz), 1.29-1.53 (4H, m), 2.18-2.34 (2H, m), 5.65 (1H, dt, $J = 7.2, 12$ Hz), 6.25-6.46 (3H, m), 7.43 (1H, d, $J = 1.8$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.22, 23.38, 24.02, 31.41, 111.96, 115.41, 127.91, 132.17, 135.28, 144.46.

(E)- 1-(5-Methylfuranyl)-1-butene (11). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.06 (3H, t, $J = 7.2$ Hz), 2.19-2.31 (5H, m), 6.12-6.43 (4H, m). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 13.86, 15.10, 26.02, 108.76, 113.09, 127.86, 132.82, 148.50, 149.25.

(Z)- 1-(5-Methylfuranyl)-1-butene (11). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.04 (3H, t, $J = 7.2$ Hz), 2.12-2.30 (5H, m), 5.66 (1H, dt, $J = 7.2, 12$ Hz), 5.96-6.42 (3H, m). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 13.54, 15.10, 20.10, 108.52, 113.02, 127.62, 132.24, 148.50, 149.20.

(E)- 1-(5-Methylfuranyl)-1-hexene (12). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.02 (3H, t, $J = 7.2$ Hz), 1.33-2.20 (9H, m), 5.98-6.42 (4H, m). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.15, 15.12, 22.97, 30.12, 32.10, 108.60, 113.00, 127.46, 134.60, 149.52, 150.62.

(Z)- 1-(5-Methylfuranyl)-1-hexene (12). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.12, 15.10, 23.15, 24.25, 31.96, 108.54, 113.14, 127.32, 135.20, 149.02, 150.50.

(E)- 2-Pentene (13). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.16 (3H, t, $J = 7.5$ Hz), 1.76 (3H, d, $J = 7.2$ Hz), 2.11 (2H, dq, $J = 7.5, 6.9$ Hz), 5.47-5.54 (2H, m). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.02, 17.60, 26.71, 133.30, 123.70.

(Z)- 2-Pentene (13). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.16 (3H, t, $J = 7.5$ Hz), 1.76 (3H, d, $J = 7.2$ Hz), 2.11 (2H, dq, $J = 7.5, 6.9$ Hz), 5.41-5.48 (2H, m). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 12.38, 14.00, 20.51, 123.20, 132.70.

(E)- 2-Heptene (14). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.98 (3H, t, $J = 7.5$ Hz), 1.30-1.50 (4H, m), 1.79 (3H, s), 2.13 (2H, dt, $J = 7.5, 6.9$ Hz), 5.48-5.54 (2H, m). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.08, 17.70, 23.81, 33.20, 34.70, 126.20, 133.13.

(Z)- 2-Heptene (14). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 13.92, 13.60, 22.80, 29.42, 33.00, 125.00, 136.30.

(E)- 3-Hexene (15). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.14 (6H, t, $J = 7.5$ Hz), 2.13 (4H, dq, $J = 7.5, 6.9$ Hz), 5.48-5.55 (2H, m). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.00, 26.50, 131.30.

(Z)- 3-Hexene (15). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) 14.00, 21.20, 131.20.

(E)- 3-Octene (16). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.92 (3H, t, $J = 7.2$ Hz), 1.28-1.56 (4H, m), 2.10-2.31 (4H, m), 5.49-5.57 (2H, m). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.00, 14.15, 22.52, 26.40, 32.10, 32.80, 128.84, 133.44.

(Z)- 3-Octene (16). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.05, 14.15, 21.08, 27.10, 32.05, 128.84, 133.24.

(E)- 3-Heptene (17). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.94-1.10 (6H, m), 1.27-1.51 (2H, m), 2.09-2.32 (4H, m), 5.47-5.54 (2H, m). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 14.00, 14.20, 23.80, 27.05, 32.00, 33.30, 127.90, 132.74.

(Z)- 3-Heptene (17). ^{13}C -NMR (75 MHz, CDCl_3) δ 14.06, 14.15, 21.10, 23.12, 28.50, 128.52, 130.80.

(E)- 4-Nonene (18). ^1H -NMR (300 MHz, CDCl_3) δ 0.92-1.11 (6H, m), 1.22-1.49 (6H, m), 2.12-2.29 (4H, m), 5.51-5.59 (2H, m). ^{13}C -NMR (75 MHz, CDCl_3) δ 14.12, 14.18, 22.92, 23.15, 32.02, 33.30, 36.50, 128.90, 132.10.

(Z)- 4-Nonene (18). ^{13}C -NMR (75 MHz, CDCl_3) δ 14.08, 14.20, 23.04, 23.18, 27.02, 29.58, 33.22, 129.12, 132.15.

(E) 3-Undecene (19). ^1H -NMR (300 MHz, CDCl_3) δ 0.96-1.05 (6H, m), 1.29-1.59 (8H, m), 1.96-2.13 (4H, m), 5.47-5.54 (2H, m). ^{13}C -NMR (75 MHz, CDCl_3) δ 14.00, 14.20, 23.22, 26.80, 29.85, 30.25, 30.45, 32.62, 127.95, 133.35.

(Z)- 3-Undecene (19). ^{13}C -NMR (75 MHz, CDCl_3) δ 14.02, 14.20, 20.85, 23.20, 27.80, 29.82, 30.22, 30.50, 32.57, 128.00, 133.34.

(E)- 3-Tridecene (20). ^1H -NMR (300 MHz, CDCl_3) δ 0.94-1.12 (6H, m), 1.23-1.67 (12H, m), 1.93-2.14 (4H, m), 5.47-5.54 (2H, m). ^{13}C -NMR (75 MHz, CDCl_3) δ 14.01, 14.13, 23.18, 23.38, 30.10, 30.50, 30.54, 32.28, 32.45, 33.42, 33.92, 128.35, 132.62.

(Z)- 3-Tridecene (20). ^{13}C -NMR (75 MHz, CDCl_3) δ 14.00, 14.15, 23.20, 23.42, 26.17, 29.95, 30.09, 30.52, 30.62, 32.44, 33.23, 129.20, 132.12.

(E)- 3-Dodecene (21). ^{13}C -NMR (75 MHz, CDCl_3) δ 14.02, 14.16, 23.52, 26.20, 29.64, 30.20, 30.35, 30.42, 32.52, 33.38, 128.86, 132.54.

(Z)- 3-Dodecene (21). ^{13}C -NMR (75 MHz, CDCl_3) δ 14.04, 14.16, 20.18, 23.48, 28.60, 29.82, 30.20, 30.54, 30.60, 32.56, 129.00, 132.80.

(E)- 5-Tetradecene (22). ^1H -NMR (300 MHz, CDCl_3) δ 0.93-1.02 (6H, m), 1.22-1.67 (16H, m), 1.94-2.13 (4H, m), 5.46-5.58 (2H, m). ^{13}C -NMR (75 MHz, CDCl_3) δ 14.02, 14.16, 23.00, 23.42, 30.35, 30.48, 30.52, 32.58, 33.05, 33.41, 131.68, 131.85.

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