slowly over 60 min, and the mixture was stirred for additional 60 min. The reaction was then quenched with saturated aqueous NH_4Cl, ether (250 mL) was added, and the organic phase was separated, washed with aqueous NH_4OH, water, and brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue chromatographed over silica gel (hexane/ethyl acetate, 25:1) to give **12a**[21] as a colorless oil (5.3 g, 66 %): NMR (270 MHz) 5.06–5.02 (m, 2 H), 3.91 (s, 3 H), 3.90 (s, 3 H), 3.78 (s, 6 H), 3.32 (d, $J = 4$ Hz, 2 H), 2.14 (s, 3 H), 2.05 (t, $J = 6$ Hz, 2 H), 2.01 (t, $J = 6$ Hz, 2 H), 1.76 (s, 3 H), 1.64 (s, 3 H), 1.57 (s, 3 H).

(2′*Z*)-1-(3,7-Dimethylocta-2,6-dienyl)-6-methyl-2,3,4,5-tetramethoxybenzene (12b). Coupling neryl bromide to **11** according to the procedure described above gave compound **12b**[21] (68% yield): NMR (270 MHz) 5.19 (t, $J = 7$ Hz, 1 H), 5.04 (t, $J = 6$ Hz, 1 H), 3.92 (s, 3 H), 3.91 (s, 3 H), 3.80 (s, 6 H), 3.32 (d, $J = 7$ Hz, 2 H), 2.27–2.05 (m, 4 H), 2.14 (s, 3 H), 1.69 (s, 3 H), 1.65 (s, 3 H), 1.57 (s, 3 H).

(2′*E*,6′*E*)-1-(3,7,11-Trimethyldodeca-2,6,10-trienyl)-6-methyl-2,3,4,5-tetramethoxybenzene (12c). Coupling farnesyl bromide to **11** according to the procedure described above gave 5.3 g of **12c**[21] (73% yield): NMR (270 MHz) 5.11–5.01 (m, 3 H), 3.90 (s, 6 H), 3.78 (s, 6 H), 3.31 (d, $J = 6.3$ Hz, 2 H), 2.14 (s, 3 H), 2.08–1.91 (m, 8 H), 1.77 (s, 3 H), 1.66 (s, 3 H), 1.61 (s, 3 H), 1.57 (s, 3 H).

(2′*E*)-1-(3,7,11,15-Tetramethylhexadec-2-enyl)-6-methyl-2,3,4,5-tetramethoxybenzene (12d). Coupling phytyl bromide to **11** according to the procedure described above gave **12d**[21] (52% yield): NMR (270 MHz) 5.02 (t, $J = 6$ Hz, 1 H), 3.91 (s, 3 H), 3.90 (s, 3 H), 3.78 (s, 6 H), 3.32 (d, $J = 6$ Hz, 2 H), 2.14 (s, 3 H), 1.94 (t, $J = 7.6$ Hz, 2 H), 1.75 (s, 3 H), 1.59–1.43 (m, 2 H), 1.41–0.96 (m, 17 H), 0.86 (br d, $J = 7$ Hz, 6 H), 0.83 (br d, $J = 7$ Hz, 3 H), 0.82 (br d, $J = 6$ Hz, 3 H).

Ubiquinone 2 (13a). Oxidation of **12a** with CAN according to the procedure described above for preparation of ubiquinone 0 (**9**) gave ubiquinone 2 (**13a**)[18] in 87% yield (2.21 g): NMR (270 MHz) 5.03 (t, $J = 8$ Hz, 1 H), 4.93 (t, $J = 7$ Hz, 1 H) 4.00 (s, 3 H), 3.99 (s, 3 H), 3.19 (d, $J = 8$ Hz, 2 H), 2.07–1.93 (m, 4 H), 2.01 (s, 3 H), 1.74 (s, 3 H), 1.65 (s, 3 H), 1.57 (s, 3 H). Anal. Calcd or $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 70.25; H, 8.26.

(2′*Z*)-2-(3,7-Dimethylocta-2,6-dienyl)-3-methyl-5,6-dimethoxy-1,4-benzoquinone (13b). Oxidation of **12b** according to the procedure described above gave **13b**[18] in 73% yield: NMR (270 MHz) 5.15 (t, $J = 6.6$ Hz, 1 H), 4.93 (t, $J = 6.9$ Hz, 1 H), 3.99 (s, 3 H), 3.98 (s, 3 H), 3.19 (d, $J = 6.9$ Hz, 2 H), 2.21–2.04 (m, 4 H), 2.02 (s, 3 H), 1.70 (s, 3 H), 1.68 (s, 3 H), 1.63 (s, 3 H). Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 70.50; H, 8.23.

(2′*E*,6′*E*)-2-(3,7,11-Trimethyldodeca-2,6,10-trienyl)-3-methyl-5,6-dimethoxy-1,4-benzoquinone (Ubiquinone 3) (13c). Oxidation of **12c** according to the procedure described above gave **13c**[18] in 48% yield: NMR (270 MHz) 5.07 (t, $J = 6.0$ Hz, 1 H), 5.05 (t, $J = 6.0$ Hz, 1 H), 4.93 (t, $J = 6.9$ Hz, 1 H), 3.99 (s, 3 H), 3.98 (s, 3 H), 3.18 (d, $J = 6.0$ Hz, 2 H), 2.08–1.91 (m, 8 H), 2.01 (s, 3 H), 1.74 (s, 3 H), 1.67 (s, 3 H), 1.59 (s, 3 H), 1.57 (s, 3 H). Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.58; H, 8.86. Found: C, 73.59; H, 8.94.

(2′*E*)-2-(3,7,11,15-Tetramethylhexadec-2-enyl)-3-methyl-5,6-dimethoxy-1,4-benzoquinone (13d). Oxidation of **12d** according to the procedure described above gave **13d**[19] in 55% yield: NMR (270 MHz) 4.92 (t, $J = 7$ Hz, 1 H), 3.99 (s, 3 H), 3.98 (s, 3 H), 3.18 (d, $J = 7$ Hz, 2 H), 2.01 (s, 3 H), 1.92 (t, $J = 7.2$ Hz, 2 H), 1.72 (s, 3 H), 1.56–1.42 (m, 2 H), 1.45–0.92 (m, 17 H), 0.87–0.81 (m, 12 H). Anal. Calcd for $C_{29}H_{48}O_4$: C, 75.61; H, 10.50. Found: C, 75.09; H, 10.63.

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Registry No. **1**, 303-98-0; **7**, 2432-14-6; **8**, 6443-69-2; **9**, 605-94-7; **10**, 36776-51-9; **11**, 35896-58-3; **12a**, 83036-57-1; **12b**, 95778-32-8; **12c**, 95778-33-9; **12d**, 109364-39-8; **13a**, 606-06-4; **13b**, 38658-30-9; **13c**, 1173-76-8; **13d**, 51077-59-9; geranyl bromide, 6138-90-5; neryl bromide, 25996-10-5; fornesyl bromide, 6874-67-5; phytyl bromide, 76524-59-9.

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Ba(OH)$_2$ as Catalyst in Organic Reactions. 17. Interfacial Solid–Liquid Wittig–Horner Reaction under Sonochemical Conditions

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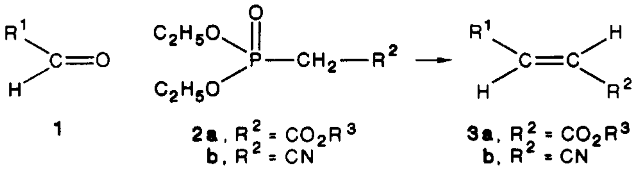
The sonochemical Wittig–Horner reaction, catalyzed by an activated barium hydroxide catalyst, is carried out in interfacial solid–liquid conditions. The sonochemical process takes place at room temperature and with a lower catalyst weight and reaction time than the thermal process. In these conditions, similar yields to those of the thermal process are obtained. The influence on the yield of the sonication time, catalyst weight, and the solvent is analyzed. Small amounts of water must be added in order for the reaction to take place. The nature of the active site of the catalyst acting in the process is analyzed. An ETC mechanism is proposed for the sonochemical process.

The Wittig–Horner reaction is a versatile method for the synthesis of functionalized olefins such as acrylates **3a** or acrylonitriles **3b** from aldehydes **1** under mild conditions with good yields (Scheme I).

Scheme I



Therefore, many works have been done to improve the yield of the process.[1] Recently, the Wittig–Horner reaction has been carried out by using polymer-supported phosphonates[2] and two-phase liquid–liquid[3] or solid–liquid

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Table I. Influence of the Experimental Conditions in the Wittig-Horner Reaction[e]

entry	sonicatn time, min	catal wt, g	solvent	dielec const	yield, % molar
1	*f*	2.5[a]	1,4-dioxane	2.2	89
2	10	0.0	THF[b]	9.0	0
3	5	0.15	THF[b]	9.0	92
4	8	0.15	THF[b]	9.0	90
5	10	0.15	THF[b]	9.0	85
6	15	0.15	THF[b]	9.0	85
7	30	0.15	THF[b]	9.0	90
8	10	0.02	THF[b]	9.0	62
9	10	0.05	THF[b]	9.0	80
10	10	0.10	THF[b]	9.0	81
11	10	0.20	THF[b]	9.0	91
12	10	0.20	THF[c]	7.9	46
13	10	0.20	EtOH (99.9%)	24.3	32
14	10	0.20	EtOH (96%)	26.5	70
15	10	0.20	DMF (99%)	36.7	9
16	10	0.20	1,4-dioxane[d]	2.3	27

[a] Moles of 4-ClC_6H_4CHO = moles of **2a** = 0.025; $T = 70$ °C;[10] $t = 30$ min. [b] THF with water (0.05 mL of water/3 mL of solvent). [c] THF anhydrous (100%). [d] 1,4-Dioxane with water (0.05 mL of water/3 mL of solvent). [e] **2a** and 4-ClC_6H_4CHO, 2.5×10^{-3} mol; catalyst C-200; 0.05 mL of water; 3 mL of solvent.

phase-transfer conditions with or without phase-transfer catalyst.[4]

However, in spite of the good yields obtained, the reaction time is great or moderate, and anhydrous solvents are necessary in some cases. This disadvantage could be avoided by using the sonochemical conditions that improve the yields and diminish the reaction time in many organic reactions.[5]

We have previously described the use of activated barium hydroxide catalysts in several interfacial solid–liquid processes such as Michael additions,[6] the Claisen–Schmidt reaction,[7] aldol condensation,[8] etc. Recently we have studied the catalytic activity of these new basic solid catalysts in the Wittig–Horner reaction[9] and the mechanism of the process in thermal conditions.[10]

In this paper we describe the results obtained with these catalysts in the interfacial solid–liquid Wittig–Horner reaction in sonochemical conditions. The process is carried out at room temperature and the reaction time is shortened with respect to the thermochemical Wittig–Horner process.

Results and Discussion

Influence of the Experimental Variables. The influence of several experimental variables on the sonochemical reaction yield is shown in Table I. This study was carried out with 4-$ClC_6H_4CH{=}O$ due to its stability vs. the oxidation and because the reaction product, 4-$ClC_6H_4CH{=}CHCO_2Et$, is well-known.[10] The (*E*)-acrylate was obtained in all cases as shown by ^1H NMR spectra.

Table II. Wittig-Horner Reaction Yields in 3a with Different Aldehydes[a]

entry	R	yield, % molar
1	H	57
2	4-Cl	85
3	4-CH_3	61
4	4-CH_3O	32
5	4-NO_2	74
6	3-NO_2	*b*

[a] RC_6H_4CHO (0.025 mol); **2a** (0.025 mol); 3 mL of THF; 0.05 mL of water; catalyst weight (C-200 = 0.15 g; sonication time, 10 min. [b] Mixture unresolved.

From the results in Table I we can observe that ultrasound diminishes the reaction time and the necessary amount of barium hydroxide catalyst, C-200, to obtain the same yields (entries 3–7 vs. entry 1). On the other hand, the sonochemical process takes place at room temperature vs. the thermochemical Wittig–Horner reactions that are carried out at 70 °C (entry 1). Due to this, the Wittig–Horner process is accelerated by ultrasounds, like other organic process.[5] Nevertheless, large sonication time does not seem to be important, because similar yields are obtained after 5 or 30 min of sonication time (entries 3–7). This fact could be explained by a very high activation of the reaction produced by ultrasound or by a single electron-transfer catalysis process (ETC) initiated by ultrasound. Evidence for this kind of process has been shown by Olah et al. in the thermal Wittig process with hindered ketones and phosphonium ylides,[11] by ourselves in the Cannizzaro reaction, catalyzed by C-200 under sonochemical conditions,[12] and by Chanon in a recent review.[13]

The amount of solid catalyst slightly influences the yield. No reaction is observed without C-200 (entry 2). Greater amounts than 50 mg do not increase the yield, because increasing the amount of catalyst from 50 mg to 200 mg increases the yield only by 10% (entries 9–11).

The high value of the dielectric constant of the solvent does not seem to affect the yield because a higher yield is obtained with aqueous THF (entry 11) than with EtOH (96%) (entry 14). The low yield obtained with DMF (99%) must be related to the hydrolytic activity of basic catalyst C-200 vs. amides and esters.[21] Similar results were observed in the Cannizzaro reaction, catalyzed by C-200 under sonochemical conditions.[12]

The presence of water in the solution dramatically increases the yield (entry 12 vs. 11 and 13 vs. 14). This fact was observed in the thermochemical conditions too[9] and with other catalysts like commercial K_2CO_3.[4a,14] There is a controversy with respect to activating role of water in the process. Some say that water destroys the 1,2-oxaphosphetane intermediate by a process similar to that of crown ether,[15,16] but others say the activating role of water is related to the crystalline structure of solids[17] which is stabilized by the water in the medium. We have confirmed this explanation in a previous paper,[10] where we showed that the active structure of C-200 catalyst in the thermo-

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Table III. Selective Poisoning Experiments in the Wittig–Horner Reaction Catalyzed by Several Basic Solid Catalysts[a]

entry	catal	surf area, m^2/g	active sites, μequiv/g of catal	adsorbd poison μequiv/g of catal	yield, % molar
		Reducing Sites (vs. DNB)			
1	C-200	1.9 ± 0.1	35 ± 4		91
2	C-200	1.9 ± 0.1	35 ± 4	40 ± 8	82
3	C-0	1.4 ± 0.1	55 ± 5		80
4	C-0	1.4 ± 0.1	55 ± 5	63 ± 6	80
5	K_2CO_3	2.1 ± 0.2	95 ± 10		80
6	K_2CO_3	2.1 ± 0.2	95 ± 10	105 ± 10	80
		Strong Basic Sites (vs. TBMPHE)			
7	C-200	1.9 ± 0.1	6.3 ± 0.2		91
8	C-200	1.9 ± 0.1	6.3 ± 0.2	8.8 ± 4	0
9	C-0	1.4 ± 0.1	260 ± 30		80
10	C-0	1.4 ± 0.1	260 ± 30	280 ± 40	8
11	K_2CO_3	2.1 ± 0.2	80 ± 8		80
12	K_2CO_3	2.1 ± 0.2	80 ± 8	80 ± 8	8

[a] $4\text{-}ClC_6H_4CHO$ (0.025 mol); **2a** (0.025 mol); catalyst weight = 0.2 g; 3 mL of THF; 0.05 mL of water; sonication time, 10 min.

chemical Wittig–Horner reaction ($Ba(OH)_2{\cdot}H_2O$) was stabilized by small amounts of water in the medium.

The nature of aromatic ring substituents is important (Table II). The presence of the strong electron-donating group (entry 4) diminishes the electrophility of C=O, and the yield also diminishes. Electron-withdrawing groups favor the process (entries 2 and 5). Nevertheless these effects are less important than in the thermochemical process catalyzed by C-200,[9] e.g., R = H 95%/25 min, R = OMe 77%/60 min (T = 70 °C).

In order to learn more about the nature of the catalyst active sites that participate in the sonochemical process and the influence of the solid catalyst structure on the yield, selective poisoning experiments were carried out. The results are shown in Table III.

Three different solid catalysts were tested: activated barium hydroxide C-200 and two commercial catalysts, C-0 ($Ba(OH)_2{\cdot}8H_2O$) and K_2CO_3 ($K_2CO_3{\cdot}1.5H_2O$). The surface areas are similar in all cases. All the solids have only reducing sites vs. 1,3-dinitrobenzene (DNB) and strong basic sites vs. 4-methyl-2,6-di-*tert*-butylphenol (TBMPHE)[18] (see Table III).

The number of reducing sites is one the order of (K_2CO_3 > C-0 > C-200, and the strong basic sites are on the order of C-0 ≫ K_2CO_3 > C-200.

Nevertheless, C-200 is more active than the other catalysts (entries 1, 3, and 5, Table III). This can only be related to the microcrystalline cell lattice in the solids, which plays an important role in the reactions catalyzed by microcrystalline solids.[8,10] The microcrystalline structure of C-200 is $Ba(OH)_2{\cdot}H_2O$[8] with Ba–OH and $OH\text{–}H_2O$ average distances of 2.6 and 3.5 Å, respectively (Figure 1). The C-0 structure ($Ba(OH)_2{\cdot}8H_2O$) has been previously described.[19] In this case, the Ba–OH and $OH\text{–}H_2O$ distances are 2.77 and 3.6 Å, respectively. The cell lattice of K_2CO_3 is monoclinic with β = 95.92° and a_0 = 10.29 Å, b_0 = 13.82 Å, and c_0 = 7.12 Å with the averages distances[20] of $CO_3^{2-}\text{–}K^+$ = 6.67 Å, $K^+\text{–}H_2O$ = 6.75 Å, and $CO_3^{2-}\text{–}H_2O$ = 5.1 Å.

Therefore, the Wittig–Horner reaction under ultrasound is sensitive to the structure of the catalyst like the thermal process[9] and other organic reactions catalyzed by activated barium hydroxide catalysts, e.g., aldol condensation,[8] Michael addition,[18b] benzyl–benzylic acid rearrangement,[21] etc., or the Wittig–Horner reaction catalyzed by KF.[17] Nevertheless under sonochemical conditions, the influence of the structure of the solid is less important than in the thermal process,[9] e.g.,

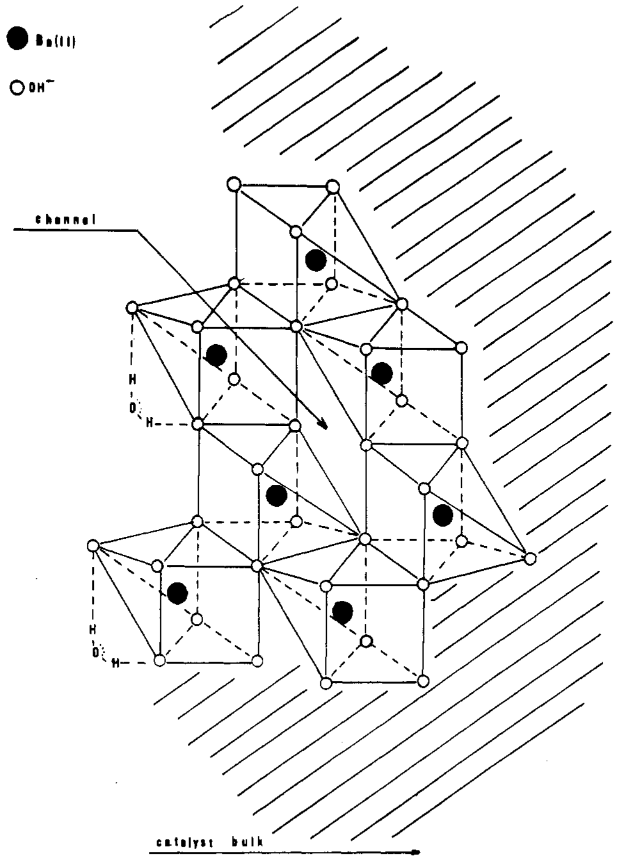

Figure 1. Microcrystalline structure of C-200 catalyst.

	time	ethyl 3-(2-furyl)acrylate yield[9]
NaOH	1 h	93%
K_2CO_3	1.5 h	96%
C-0	2.5 h	96%
C-200	20 min	100%

This fact can be explained if we assume that the Wittig–Horner reaction under ultrasound takes place by a

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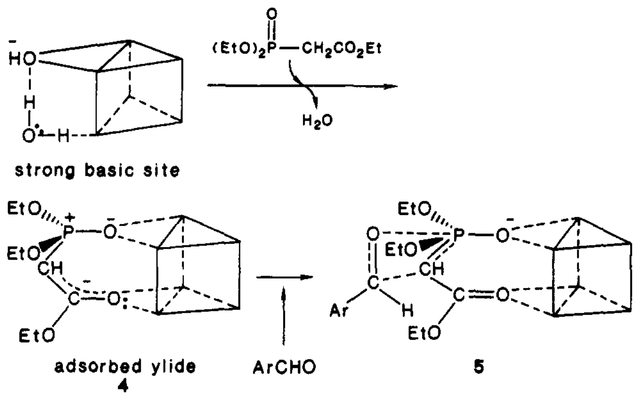
Scheme II. Structure of Postulated Wittig-Horner Intermediates in the Sonochemical Process (Catalyst C-200)



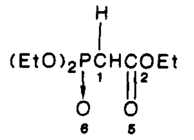
mechanism less related to the crystalline structure than the thermal process. Those reactions are characterized in heterogeneous catalysis by monoadsorbed intermediates and could be explained by SET or ETC mechanisms. The formation of monoadsorbed species under ultrasound vs. multiadsorbed ones in the thermal Wittig–Horner reaction[10] can be explained by the ultrasonic phenomena that sequentially produce ΔT and ΔP in certains points of the solid surface that can break up some weaks bonds between the adsorbed species and the solid surface, e.g., Π^2 C=O → $5d^0$ Ba(II) (see next section).

On the other hand, from the results in Table III we can deduce that the active sites that take part in the sonochemical process are strong basic sites without steric hindrance titrated by the bulky weak acid molecule of TBMPHE ($pK_a > 11.7$) as occurs in the thermal process.[10] This can be explained by the low acidity in the active hydrogen in the phosphonoacetate ($pK_a = 12.2$)[22] which needs strong basic sites to be removed. Due to the steric hindrance of the transition state **5** (Scheme II) the reaction can only take place in active sites with small steric hindrance such as the sites titrated by TBMPHE.

On the other hand the catalytic behavior of the C-200 is very evident because of the following: 0.20 g of C-200 equivalent to 1.26×10^{-6} equiv of strong basic sites [titrated by TBMPHE; (0.2 g of catalyst)(6.3×10^{-6} equiv/g of catalyst (see Table III and ref 18)] can transform 5×10^{-3} mol of 4-ClC_6H_4CHO in 10 min. Therefore the turnover number is 4×10^2 mol of aldehyde transformed by active site per minute.

This fact eliminates the classic mechanism catalyzed by bases where the OH^- is not regenerated.

Nature of Adsorbed Species. In order to learn more about the mechanism of the sonochemical Wittig–Horner process, the nature of the adsorbed species produced from **1** and **2a** during the sonication was studied by IR spectra. In Table IV we show the main bands of **2a** and of the adsorbed species produced in the thermal[10] and sonochemical conditions on the C-200 catalytic surface.



$$\mathrm{(EtO)_2}\underset{\underset{6}{O}}{P}\overset{H}{\underset{1}{C}}\mathrm{H}\underset{\underset{5}{O}}{\overset{}{\underset{2}{C}}}\mathrm{OEt}$$

2a

Table IV. Main IR Bands (cm^{-1}) *of 2a and of the Adsorbed* Species on C-200

bond	2a	adsorbd species IR bands	
		therm conditns[10]	sonochem conditns
$C_2{=}O_5$	1740		
$C_2\underline{- - - -}O_6$[24]		1676	1675
$C_1\underline{- - - -}C_2$[24]		1570	1570
$C_1\underline{- - - -}C_2$[24]		1384	*a*
$P{\rightarrow}O_6$	1275		
	1210		
$P\underline{- - -}O_6$[24]		1194	1059

[a] No observable band. Under the strong 1500–1350-cm^{-1} carbonate band.[23]

From the data in Table IV we can deduce that the adsorbed species produced on the solid surface from **2a** are similar in both cases. There is no C=O band, but adsorptions from relaxed $C{\cdots}O_5$ and $C_1{\cdots}C_2$ bonds are observed (1676 cm^{-1}).[10,24] The *only difference can be related* to the $P{\cdots}O_6$ bond. The intermediate produced in sonochemical conditions seems to have a more relaxed $P{\cdots}O_6$ bond (1059 cm^{-1}) than the thermal one (1194 cm^{-1}).[10] Therefore, we could postulate a ylide like **4** (Scheme II) adsorbed on the strong basic sites of C-200 related to the surfacial OH of the $Ba(OH)_2\ H_2O$ lattice.

Contrary to what occurs in thermal process,[10] the aldehyde is not adsorbed on the catalytic surface in sonochemical conditions. The explanation for this fact is that the weak $\pi^2{}_{C=O} \rightarrow 5d^\circ$ Ba(II) bond produced during the thermal adsorption[10] would be broken up by the ultrasound. This fact changes the mechanism of the process. The thermal Wittig–Horner reaction takes place between the adsorbed ylide and the adsorbed aldehyde.[10] So, the transition state will be more rigid and multiadsorbed than the one under sonochemical conditions.

When 4-$ClC_6H_4CH{=}O$ is added on the adsorbed ylide and the IR spectrum of the adsorbed species is recorded, no C=O or P → O bonds are registered as in the case of the thermal process.[10] Therefore an adsorbed species, **5**, similar to previously 1,2-oxaphosphetane described,[10] is postulated (Scheme II).

When HCl (1 M) solution is added to this species and the organic products are analyzed by ^1H NMR, (*E*)-acrylate is detected. Therefore, we can say that the sonochemical Wittig–Horner reaction is an interfacial solid–liquid reaction.

Additional evidence was supplied by the use of a polymer-supported reagent, Ⓟ–CH=O, from a Merrifield resin. When Ⓟ–CH=O and a mixture of **2a** and C-200 in THF with water were submitted to sonochemical conditions for 1 h, no Ⓟ–CH=$CHCO_2Et$ was detected. Therefore, the ylide never leaves the solid surface to react with the aldehyde.

From the results shown in this paper we could postulate an ETC mechanism that would be consistent with these experimental evidences (Scheme III).

The process would be initiated by a single electron-transfer process (SET) between the strong basic sites of the catalyst (OH^-) and **2a**, (1) giving a radical anion that will be monoadsorbed. (2) The radical anion will react with $OH^\bullet$ radical from the water, regenerating it and giving the adsorbed ylide **4**, detected by IR. This step can explain the role of water which is necessary at a trace level in order for the process to be carried out (Table I), because the OH

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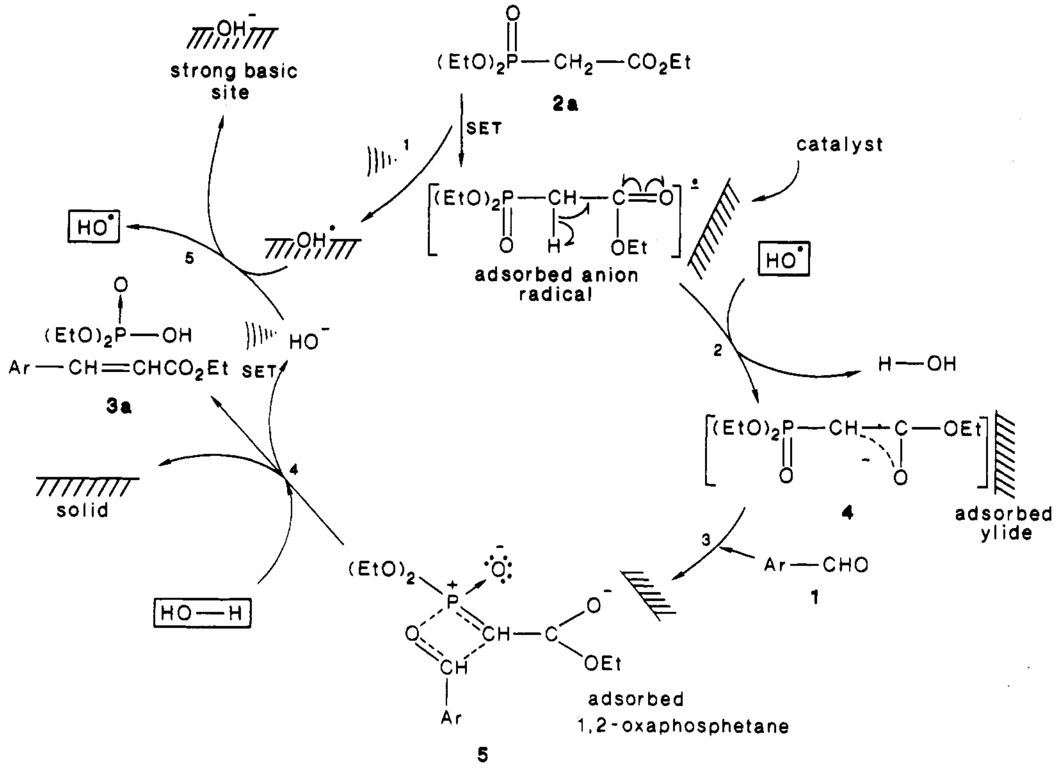
[22] Seno, M.; Tsuchiya, Sh.; Kise, H.; Asahara, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2001.

[23] The sonication in the air of the solution with C-200 dramatically increases the carbonation of the solid catalyst by the CO_2 from the air.

[24] Bottin-Strazalko, T.; Corset, J.; Fromet, F.; Pouet, M. J.; Seyden-Penne, J.; Simonnin, M. P. *J. Org. Chem.* **1980**, *45*, 1270.

Scheme III. Postulated ETC Mechanism for the Wittig–Horner Reaction on C-200, under Sonochemical Conditions



radical is regenerated in step 5.

Step 3 would be the same as in thermal conditions. **5** would be broken up by a chemical step giving **3a** and $(EtO)_2P(O)OH$ which has been detected as a reaction product.[9,10] The basic site could be regenerated from OH^- by a second SET process giving $OH^\bullet$ that would be reused in step 2. Therefore, the catalytic role of water would be explained in this case. On the other hand the regeneration of the basic site may explain the high yield obtained with small amount of solid.

The scheme proposed agrees with the lack of influence of the dielectric constant in the solvent on the yield (Table I). Only a solvent miscible with water is necessary to carry out the process. When two anhydrous solvents are compared (THF and EtOH, entries 12 and 13), similar yields are obtained. Probably due to the high hygroscopic character of THF as compared to EtOH, THF is quickly hydrated by air under ultrasonic conditions, resulting in a better yield with THF (dry) than with EtOH (dry).

The ETC mechanism is also consistent with the detection of adsorbed species **4** and **5** by IR spectroscopy and with high catalytic activity of the strong basic catalyst sites (Table III), which have a high turnover number.

On the other hand, it is in accordance with the fact that the ylide **4** is not trapped by the Ⓟ–CH=O resin. It shows that this Wittig–Horner process under sonochemical conditions is an interfacial solid–liquid process.

Experimental Section

Preparation of C-200. This catalyst was obtained from commercial barium hydroxide, C-0 ($Ba(OH)_2{\cdot}8H_2O$), by calcination at 200 °C for 3 h according to a previous paper.[21]

The C-0 was a commercial barium hydroxide (Probus S.A.) ($Ba(OH)_2{\cdot}8H_2O$), and the commercial K_2CO_3 ($K_2CO_3{\cdot}1.5H_2O$) was obtained from Fluka S.A.

The titration of active sites was carried out by the spectrophotometric method described previously.[18] 4-Methyl-2,6-di-*tert*-butylphenol (TBMPHE), $pK_a = 11.7$, was used as the titrating agent for the strong basic sites. 1,3-Dinitrobenzene (DNB) EA = 2.21 eV was used as the titrating agent for reducing sites.

Sonochemical Wittig–Horner Reaction. The Wittig–Horner reaction was carried out by mixing 2.5×10^{-3} mol of the aldehyde, 2.5×10^{-3} mol of **2a**, 3 mL of solvent, and a convenient amount of catalyst. Then, the mixture was sonicated in an ultrasound bath (P-Selecta S.A. Model 513) for 10 min. Then, the mixture was allowed to stand for 24 h in a refrigerator at 4 °C to produce the sedimentation of the solid. Similar results are obtained if the sample is centrifuged after sonication.

The mixture was analyzed by HPLC using a Perkin-Elmer Series 2 chromatograph with UV–vis detector (λ = 254nm) and anthracene as the internal standard. $MeOH/H_2O$ [30/20 (v/v)] was used as the eluent: flux = 0.8 mL/min; 5-μm C_{18} column.

The aldehydes used were from Merck p.a. The triethyl phosphonoacetate (**2a**) was from Aldrich. The pure solvents, THF, EtOH, DMF, and 1,4-dioxane, were from Ferosa p.a.

IR Spectra of Adsorbed Species. The IR spectra of the adsorbed species produced from **1** and **2a** were carried out by mixing the organic compound and the catalyst with the aqueous solvent. Then, the mixture was sonicated for 2 min, filtered, and washed with anhydrous solvent to eliminate the physisorbed organic products.

The IR spectra were recorded on a Perkin-Elmer 599B spectrometer with a Data Station 3600. The PECDS program was used for the manipulation of the spectra.

Reaction with Polymeric-Supported Reagent, Ⓟ–CH=O. The polymeric-supported reagent Ⓟ–CH=O was obtained from a Merrifield resin (Ega-Chemie) by a process described previously.[25]

The Ⓟ–CH=O was mixed with C-200 and **2a** and sonicated for 1 h. Then, HCl (1 M) was added to destroy the basic catalyst. The polymer was washed with water and the IR spectrum recorded as above.

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(25) Frecket, J. M.; Pelle, G. *J. Chem. Soc., Chem. Commun.* **1975**, 225.