

Ba(OH)₂ as Catalyst in Organic Reactions. 20. Structure-Catalytic Activity Relationship in the Wittig Reaction

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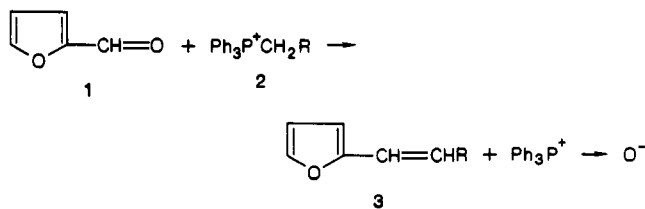
Three barium hydroxide catalysts with different surface-area values and amounts of basic and reducing sites are used as catalysts in the Wittig reactions. These catalysts have different microcrystalline structures and therefore different geometrical properties in the active sites, that govern the adsorption of the reagents on the solid surface. Several phosphonium salts (Ph₃P⁺CH₂R; R = H, CH₂CH₂CH₃, CO₂Et, and COPh) with different pK_a, geometrical, and electronic characteristics have been used. The structure-catalytic activity relationship is analyzed. The most active catalyst, C-200, is less active in the Wittig reaction than in the Wittig-Horner reaction. This fact is explained by geometrical reasons. The process takes place in the homogeneous phase with phosphonium salts of a strong acid character (R = CO₂Et, COPh) that lead to stable ylides. The weak acids (R = H, CH₃CH₂CH₂) lead to reaction products in the heterogeneous solid-liquid conditions. The cell lattice of the solid governs the process that is carried out in the heterogeneous phase. The process with the strongest acid (R = COPh, pK_a = 6.0) is not governed by the cell lattice because this acid can react to any kind of basic site in the solid. The reaction with R = CO₂Et (pK_a = 8.8) is carried out in the homogeneous phase because the ylide is stable. However, the formation of the ylide is controlled by the cell lattice because basic sites with pK_a > 8.8 and adequate geometry are necessary to produce the ylide on the solid surface.

Introduction

The catalytic activity of solids used as catalysts in organic reactions that are carried out in heterogeneous gas-solid conditions has been related to several chemical and/or structural properties of the solid catalyst such as (i) the surface area and number of active sites,¹⁻³ (ii) the surface area and pore size,^{4,5} (iii) the metallic particle size in the metallic supported catalysts used in hydrogenation,⁶⁻⁸ and (iv) the microcrystalline structure of the solid.⁹ Nevertheless, these aspects have not been well studied in the case of heterogeneous solid-liquid conditions, which are being used more and more by synthetic organic chemists, e.g., phase-transfer solid-liquid conditions. Several dispersed papers have been reported, e.g., CaO as polymerization catalyst,¹⁰ Al₂O₃¹¹ and CaCO₃¹² in aldol condensation, KOH, Ba(OH)₂·8H₂O, and K₂CO₃ in epoxide synthesis,¹³ etc.

We have previously described several barium hydroxide catalysts with different microcrystalline structures. These catalysts have been used in several organic reactions such as aldol and Claisen-Schmidt condensations,¹⁴ Michael addition,¹⁵ Wittig-Horner reaction,¹⁶ etc., with very good results. Nevertheless, these catalysts have not been useful in other organic reactions such as aliphatic nucleophilic substitution or epoxide synthesis with sulfonium salts. In order to explain these experimental results and due to the fact that the microcrystalline structure and the nature and number of these basic catalyst active sites are well-known,^{14a,17,18} we have analyzed the influence of the physical and chemical properties of these catalysts on the mechanisms of several organic reactions that occur in interfacial solid-liquid conditions, e.g., synthesis of epoxides,¹³ Michael addition,^{15b} aldol condensation,^{14a} Wittig-Horner reaction,^{19,20} etc. From this systematic study, we have deduced that when the precursor of the carbanion is a weak acid (pK_a > 9.0), the reaction takes place in the

Scheme I^a



^a 2a, 3a: R = H. 2b, 3b: R = CH₂CH₂CH₃. 2c, 3c: R = CO₂Et. 2d, 3d: R = COPh.

solid-liquid interface. In this case the process is governed by the microcrystalline structure of the solid. Nevertheless,

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Table I. Chemical and Textural Properties of the Activated Barium Hydroxide Catalysts

	C-0	C-200	C-300
surface area (m ² /g)	1.4 ± 0.1	1.9 ± 0.1	1.4 ± 0.1
no. of active sites (mequiv/g of catalyst)			
basic sites vs			
TBMPE (pK _a > 11.7)	(2.6 ± 0.3) × 10 ⁻¹ ^a	(6.3 ± 0.2) × 10 ⁻³	(2.2 ± 0.1) × 10 ⁻³
BA (pK _a > 4.2)	- ^b	(9 ± 1) × 10 ⁻²	(6.0 ± 0.6) × 10 ⁻²
reducing sites vs DNB (EA = 2.21 eV)	(5.5 ± 0.6) × 10 ⁻²	(3.5 ± 0.3) × 10 ⁻²	(0.7 ± 0.07) × 10 ⁻³
oxidizing sites vs PNTZ (IP = 7.13 eV)	- ^c	- ^c	- ^c
acid sites vs Py (pK _a < 5.3)	- ^c	- ^c	- ^c

^aThe solid slowly dissolved by the TBMPE. ^bNo adsorption equilibrium is reached. The solid is slowly dissolved by the cyclohexanic solution of BA. ^cNo adsorption was observed.

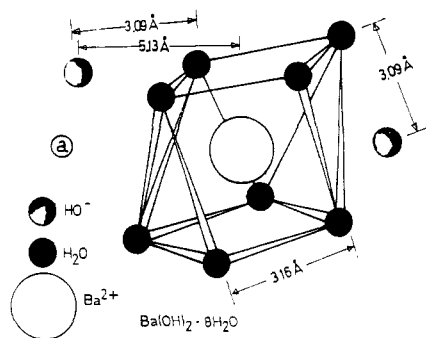


Figure 1. Coordination sphere of Ba(II) in Ba(OH)₂·8H₂O crystalline structure.

when the precursor of the carbanion is moderately acidic (pK_a < 9.0), the reaction seems to take place by means of barium salt complexes²⁰ in a homogeneous medium. In this way the present paper has analyzed the Wittig reaction between furfural, 1, and several phosphonium salts 2 (Scheme I) using three basic catalysts C-0, C-200, and C-300. These catalysts have different microcrystalline structures and numbers of active sites. The phosphonium salts used in this paper have different pK_a values in order to analyze the influence of this variable on the reaction pathway.

The yield obtained in 3 is compared to those obtained by Gaset et al. using NaOH, KOH, and K₂CO₃·1.5H₂O²¹ under similar experimental conditions.

Results and Discussion

Catalyst. The chemical and textural properties of the basic catalysts are shown in Table I. Through thermogravimetric analysis (TGA),¹⁸ we have deduced the empirical formula for solids:

C-0	Ba(OH) ₂ ·8H ₂ O
C-200	Ba(OH) ₂ ·0.2H ₂ O
C-300	Ba(OH) ₂ ·0.06H ₂ O

From X-ray powder diffraction diagrams we have deduced that C-0 is pure microcrystalline Ba(OH)₂·8H₂O.²² This solid crystallizes in the monoclinic system.²³ The barium ions are coordinated by eight water oxygens in the form of a slightly distorted Archimedean antiprism. The OH⁻ ions are outside the prism (Figure 1). The average OH⁻...H₂O distance is 3.09 Å, and those of Ba-OH⁻ and Ba-H₂O are 4.76 and 2.7 Å, respectively. C-200 is αBa-

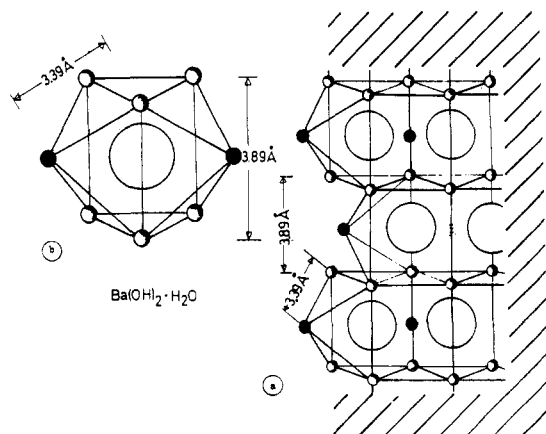


Figure 2. Microcrystalline structure: (a) Ba(OH)₂·H₂O crystalline structure and (b) coordination sphere of Ba(II) in Ba(OH)₂·H₂O cell lattice.

(OH)₂ in the bulk and Ba(OH)₂·H₂O on the solid surface (2% in weight).¹⁸ The cell lattice of Ba(OH)₂·H₂O is orthorhombic.^{24,25} In this structure, each Ba(II) is coordinated to six OH⁻ and two water molecules (Figure 2) with an average OH⁻...H₂O distance of 3.39 Å. C-300 is βBa(OH)₂ with a very small amount of Ba(OH)₂·H₂O in the solid surface.¹⁸ The Ba(OH)₂ crystallizes in the orthorhombic system.²⁶

From the data of Table I we can deduce that the low surface-area values of the three solids (Table I) are due to the microcrystalline structure of the catalysts. These values are similar in all cases. On the other hand, we can deduce that the catalysts have only basic and reducing sites because no adsorption has been observed with phenothiazine (PNTZ) and pyridine (Py) as selective poisons in oxidizing and acid sites, respectively (Table I).

The total basicity of the solids can be determined by selective poisoning of basic sites by benzoic acid (BA).^{14a} The relative number of basic sites is indicated by

$$C-200 > C-300$$

C-0 is dissolved by the cyclohexanic solution of BA, and the total basicity cannot be determined by this method. The strong basic sites without steric hindrance can be titrated by 2,6-di-*tert*-butyl-4-methylphenol (TBMPE), a weak and hindered acid that can only titrate the strong basic sites (pK_a > 11.7) on the solid surface. The relative number of strong basic sites is indicated by

$$C-0 \gg C-200 > C-300$$

These sites are responsible for the catalytic activity in these solids in organic reactions that take place in heterogeneous solid-liquid conditions such as Michael addition^{15b} or the Wittig-Horner reaction.¹⁹

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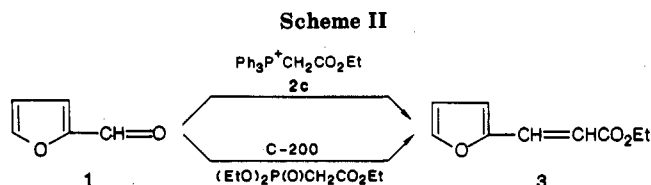
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Table II. Influence of the Experimental Conditions on the Synthesis of 3c by Wittig Reaction^a

entry	temp, °C	reactn time, min	cat. wt (C-200), g	yield in 3c, mol %
1	70	5	0.5	64
2	70	10	0.5	75
3	70	15	0.5	80
4	70	20	0.5	85
5	70	25	0.5	88
6	70	40	0.5	96
7	70	60	0.5	95
8	18	60	0.5	60
9	40	60	0.5	69
10	70	15	0.3	68
11	70	15	0.1	48

^a 2c, 2.56×10^{-3} mol; 5 mL of 1,4-dioxane; 0.1 mL of H₂O.



The reducing sites are titrated by 1,3-dinitrobenzene (DNB), and the relative number of these sites is indicated by



Optimization of the Reaction Conditions. The optimization of the reaction conditions was carried out in all cases with similar qualitative results. The optimal experimental conditions for the synthesis of the acrylate, 3c, are shown in Table II.

From these results we can deduce that the optimal conditions are 40 min, 70 °C, and 0.5 g of catalyst (entry 6). Other solvents with a higher dielectric constant than 1,4-dioxane were used: THF ($\epsilon = 7.4$) and EtOH, 96% ($\epsilon = 24.3$). These solvents lead to a high percentage of secondary reactions such as oxidation by air of furfural leading to furoic acid and the Cannizzaro reaction. These results agree with those reported by Gaset et al.^{21e} with NaOH as the basic catalyst in similar experimental conditions. Therefore 1,4-dioxane was chosen as the solvent. The stereochemistry of the alkene was mainly *Z* (90–95%) in all cases according to the ¹H NMR data. These results agree with those reported by Gaset et al.²¹ using other basic solids such as alkaline hydroxides or carbonates in solid-liquid heterogeneous-phase conditions. Similar stereochemistry is observed in the homogeneous phase using salt-free conditions and nonpolar solvents such as 1,4-dioxane. Therefore the microcrystalline structure of the solid and the nature of solid barium hydroxide do not seem to determine the alkene stereochemistry that is controlled by the stability of phosphonium salt. (*E*)-Alkenes (95%) are obtained with C-200, C-300, and C-0 by the Wittig-Horner reaction.^{16a,19}

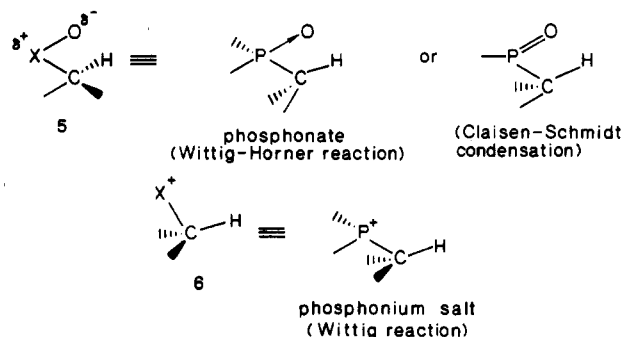
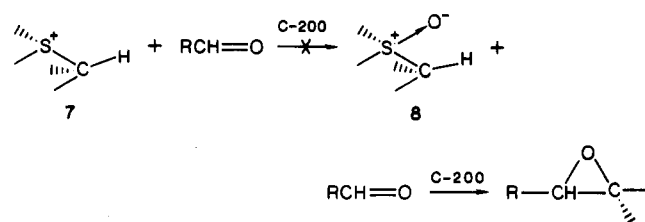
Influence of the Structure of the Ylide Precursor on the Yield. If we compare optimal experimental conditions (entry 6, Table II) with the one reported by Sinisterra et al.^{16a} for the synthesis of 3c by means of the Wittig-Horner (W-H) reaction (25×10^{-3} mol of 1 and of triethyl phosphonoacetate; 0.5 g of C-200; $T = 70$ °C; 100% yield; $t = 25$ min), we can deduce that the nature of the ylide precursor is very important as the controlling factor on the yield (Scheme II).

In the same way, we have obtained chalcones 4 by means of the Wittig reaction, and the yields are compared to those obtained by means of Claisen-Schmidt condensation with

Table III. Yield in the Synthesis of Chalcones 4 by Wittig Reaction versus the Claisen-Schmidt Reactions^a

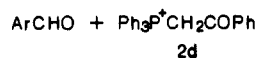
ArCH=O	chalcone	yield (mol %)/reactn time (min)	
		Wittig	Claisen-Schmidt
4-ClC ₆ H ₄ CHO	4a	49/90	94–8/60 ^{b,15a}
4-NO ₂ C ₆ H ₄ CHO	4b	80/90	94–7/60 ^{b,15a}
3-NO ₂ C ₆ H ₄ CHO	4c	52/60	– ^c
4-CH ₃ C ₆ H ₄ CHO	4d	20/60	– ^c
4-CH ₃ OC ₆ H ₄ CHO	4e	36/120	92–5/60 ^{b,15a}

^a ArCHO, 2.5×10^{-3} mol; molar ratio ArCHO/2d = 1; 2.4 g of C-200; $T = 70$ °C; 30 mL of 1,4-dioxane; 0.5 mL of water.
^b Obtained by Claisen-Schmidt. Reaction at reflux of EtOH. ^c No product obtained by Claisen-Schmidt with C-200.

Scheme III**Scheme IV**

the same catalyst, C-200.^{15a} The results obtained are shown in Table III.

Wittig reaction



Claisen-Schmidt condensation



If we compare the yields obtained for the same chalcone by both methods, we can say that the Wittig reaction leads to lower yields at greater reaction times than Claisen-Schmidt condensation. From the results in Tables II and III we can deduce that C-200 acts as a basic catalyst to remove the proton to produce the carbanion, better with a structure such as 5 rather than with 6 (Scheme III).

This fact has been observed too in the case of epoxide synthesis with sulfonium salt 7 and sulfoxonium salt 8 (Scheme IV).

Sulfonium salt 7, with a structure analogous to 6, does not lead to a reaction, but sulfoxonium salt 8, similar to 6, gives epoxide.²⁰ This fact has been explained by means of geometrical and electronic reasons, controlled by the microcrystalline structure of C-200 which favors the formation of the adsorbed ylide in the case of 8 (detected by IR spectroscopy²⁰) and discourages the formation of the adsorbed ylide in the case of 7.^{20,27} Therefore a similar

Table IV. Influence of the Phosphonium Salt Structure of $\text{Ph}_3\text{P}^+\text{CH}_2\text{R}$ on the Yield^a

R	phosphonium salt	product	yield in 3, mol %
H	2a	3a	55
$\text{CH}_2\text{CH}_2\text{CH}_3$	2b	3b	46
CO_2Et	2c	3c	80
COPh	2d	3d	90

^a 1, 2.56×10^{-3} mol; 2, 2.56×10^{-3} mol of 2; $t = 15$ min; $T = 70$ °C; 0.5 g of C-200; 0.1 mL of H_2O ; 5 mL of 1,4-dioxane.

Table V. Influence of the Basic Catalyst Structure on the Yield

catalyst	yield in 3b, ^a mol %	yield in 3c, ^a mol %	yield in chalcone 4a, ^b mol %
C-200	49	80	49
C-300	47	43	46
C-0	25	66	44

^a 1 and 2c, 2.56×10^{-3} mol; $t = 15$ min; $T = 70$ °C; 0.5 g of basic catalyst; 5 mL of 1,4-dioxane; 0.1 mL of water. ^b 4- $\text{ClC}_6\text{H}_4\text{CHO}$ and 2d, 2.5×10^{-3} mol; 2.4 g of basic catalyst; 30 mL of 1,4-dioxane; 0.5 mL of water.

reason could be postulated by the Wittig and Wittig-Horner reactions in order to explain why the Wittig-Horner reaction works better than the Wittig reaction.

On the other hand, we have observed that the nature of the substituent R of active methylene in the phosphonium salt influences the yield of the process (Table IV). Z type substituent (2c and 2d), which increases the acidity of the hydrogen atoms in CH_2 , favors the process versus R = H or alkyl (2a and 2b) (Table IV). This fact can be related to the increase of $\text{p}K_a$ in CH_2 which favors the reaction of weaker basic sites ($\text{p}K_a < 11.7$) in the solid to the more acidic methylene. Contrary to what was reported by Gaset et al.,^{21e} the increasing length of the chain bonded to phosphorus (2a, R = H, to 2b, R = $\text{CH}_2\text{CH}_2\text{CH}_3$) diminishes the yield in 3 slightly (Table IV). This result agrees with that obtained in the homogeneous phase²⁸ and those reported by Dehnlow et al.²⁹ with $\text{KOBu}^t/\text{C}_6\text{H}_6$. This fact can be explained by the increase of steric hindrance in the phosphonium salt which discourages the adsorption of salt on the cell lattice of C-200, because the $\text{p}K_a$ of CH_2 is very similar, as are the number of active basic sites that can react to weak acids ($\text{Ph}_3\text{P}^+\text{CH}_2\text{R}$).

The yield obtained in 2b with C-200 (46%) is poor if we compare it to those reported by Gaset et al.^{21c,21e} with NaOH (70%) or K_2CO_3 (96%) under heterogeneous solid-liquid conditions. Nevertheless, we must say that our result is obtained at 15 min and 70 °C while those of Gaset et al.^{21c,22e} are obtained at 120 min and 95 °C. Unfortunately, if we increase the reaction temperature and the time, secondary reactions are obtained with C-200. Therefore the synthetic procedure cannot be improved with C-200 versus NaOH or K_2CO_3 .

Influence of the Microcrystalline Structure in Basic Catalysts. The Wittig reaction is sensitive to the structure of the basic catalyst when a moderate acid such as $\text{Ph}_3\text{P}^+\text{CH}_2\text{CO}_2\text{Et}$, 2c ($\text{p}K_a > 8.8^{30}$) is used as the ylide precursor (Table V). We can observe that C-200 is the most active barium hydroxide catalyst, then C-0, and then C-300. This relative catalytic activity cannot be explained by the surface-area values (similar in all cases) or by the number of basic sites titrable by TBMPHE or BA (see

Table I). The only structural difference that could explain this behavior is the microcrystalline structure in each solid that determines the geometric factors of the solid basic sites that react to 2c. The more adequate these factors are for the geometry of 2c, the greater the production of the ylide and, therefore, the yield. Due to the fact that 2c dissolves C-200, we are led to think that the rate-controlling step is the formation of the ylide on the solid surface. When very strong acids such as $\text{Ph}_3\text{P}^+\text{CH}_2\text{COPh}$, 2d ($\text{p}K_a = 6.0^{30}$) are used, the reaction is not sensitive to the microcrystalline structure of the solid because similar yields are obtained in all cases. This fact can only be explained by assuming that the formation of the ylide by the reaction of 2d with the solid surface is not the rate-controlling step.

The very weak acid $\text{Ph}_3\text{P}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, which gives a very unstable ylide, leads to similar yields with the dehydrated solids C-200 and C-300.

The $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (C-0) gives low yields. This could be explained by the fact that very, very strong basic sites ($\text{p}K_a > 11$) are necessary to produce the ylide (which is also strongly basic). This ylide reacts, due to reasons of proximity, better to the water molecule near the basic sites in the C-0 structure than to the aldehyde that must be adsorbed on the solid surface (see reaction intermediate section). Strong basic sites ($\text{p}K_a > 11.7$) are present in all catalysts (Table I), and the water crystallization is greater in C-0 than in C-200 and C-300.

water in the solid
C-0 >> C-200 > C-300
number of strong basic sites

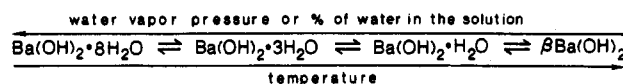
Influence of the Volume of Water Added to the Medium. It has been reported by Gaset et al.^{13,21e} that this experimental methodology needs the presence of water in the medium (near moles of water by moles of solid base) to obtain good results. As in the cases of $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$, NaOH, and KOH reported by Gaset et al.,^{13,21} the C-200 catalyst needs the presence of water in the medium to obtain good yields in the Wittig-Horner reaction.^{16a} Similar results are obtained in the case of the Wittig reaction (Table VI).

We can observe that the maximum yield is obtained at a similar ratio, milliliters of solvent/milliliters of H_2O .

2b,c	5 mL of solvent/0.1 mL of $\text{H}_2\text{O} = 50$
2d	30 mL of solvent/0.5 mL of $\text{H}_2\text{O} = 60$

The yields obtained with high or low ratios are lower than those obtained in these conditions.

It is well-known that there are several hydrated barium hydroxides^{31,32} in equilibria with different microcrystalline structures.^{14a,22,23,24}



These equilibria can be shifted by the temperature and water concentration in the medium. As we have shown,^{14a,18} C-200 is a bulk of $\alpha\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ on the surface. Therefore it is easy to assume that the presence or absence of water can shift the equilibrium in one way or another, changing the microcrystalline structure of the basic solid catalyst. When anhydrous 1,4-dioxane is stirred with C-200 for 15 min and the mixture is filtered, we can observe the presence of water by the ^1H NMR of the liquid

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Table VI. Influence of the Volume of Water Added to the Medium^a

aldehyde	phosphonium salt	water, mL	time, min	yield in 3b, mol %	yield in 3c, mol %	yield in 4a, mol %
1	2b	0.0 ^b	15	—	—	—
1	2b	0.1 ^b	15	49	—	—
1	2b	0.3 ^b	15	47	—	—
1	2b	0.5 ^b	15	35	—	—
1	2c	0.0 ^b	15	—	59	—
1	2c	0.1 ^b	15	—	85	—
1	2c	0.3 ^b	15	—	83	—
1	2c	0.5 ^b	15	—	66	—
4-ClC ₆ H ₄ CHO	2d	0.0 ^c	135	—	—	0
4-ClC ₆ H ₄ CHO	2d	0.5 ^c	135	—	—	84
4-ClC ₆ H ₄ CHO	2d	1.0 ^c	135	—	—	75
4-ClC ₆ H ₄ CHO	2d	1.5 ^c	135	—	—	46

^a Aldehyde and phosphonium salt, 2.56×10^{-3} mol; $T = 70$ °C; 0.5 g of C-200. ^b In 5 mL of 1,4-dioxane. ^c In 30 mL of 1,4-dioxane.

Table VII. Spectroscopic Data from 2c and 2d and the Ylides 5 and 6

compd	¹ H (CH or CH)		³¹ P: δ , ppm	¹³ C (CH ₂ or CH)		IR C=O bond, cm ⁻¹
	δ , ppm	J_{P-C-H} , Hz		δ , ppm	J_{H-C} , Hz	
Ph ₃ P ⁺ CH ₂ CO ₂ Et (2c)	5.25	15.8	-20.5	32.6	57	1725
5	2.85	—	-17.9	28.0	129	1620
Ph ₃ P ⁺ CH ₂ CO ₂ Et (2d)	6.40	13.6	-20.6	55.8	52	1662
6	4.40	24.8	-16.3	49.0	108	1527

(broad peak at 4.9 ppm). This phenomenon can only be explained if we assume that C-200 has been dehydrated to β Ba(OH)₂ by the solvent. This fact is confirmed by an X-ray powder diffraction diagram that shows the presence of β Ba(OH)₂ as the only product in the solid.³³ When ratios of milliliters of solvent/milliliters of water = 45–60 are used, the solid is a mixture of β Ba(OH)₂³³ and Ba(OH)₂·H₂O.^{24,25} Thus, the active structure is present. Nevertheless, when the percentage of water in the medium increases, Ba(OH)₂·3H₂O or Ba(OH)₂·8H₂O^{22,23} is characterized by an X-ray powder diagram analysis as the microcrystalline structure of the solids. Therefore we can say that the role of water is, in the case of C-200, to stabilize the most active structure, Ba(OH)₂·H₂O, on the solid surface. The dehydration of the solid has also been observed in the case of K₂CO₃·1.5H₂O, used as the catalyst in the Wittig–Horner reaction to obtain 3c.³⁷ This solid is dehydrated to K₂CO₃ in the presence of 1,4-dioxane, and the yield obtained is lower in this case than in the presence of water; 43% (0.0 mL of H₂O), 80% (0.3 mL of H₂O), and 98% (0.54 mL of H₂O). Therefore, we aim to foster collaboration between organic and inorganic chemists to carry out a more detailed study of the microcrystalline structure of hydrates used as basic catalysts in order to explain the different reactivity of catalysts used in solid–liquid conditions.

Nature of Reaction Intermediates. In order to supply data to explain the catalytic activity of C-200, the structure of ylides adsorbed on C-200 (the most active catalyst) was determined. We have previously reported that aldehydes are adsorbed on the catalytic surface by the $\pi_{C=O} \rightarrow 5d^{\circ}$ (Ba(II)) bond under thermal conditions.³⁴ When C-200 is mixed with an excess of Ph₃P⁺CH₂COPh, 2d, under reaction conditions ($pK_a = 6.0$ ³⁰), or with Ph₃P⁺CH₂CO₂Et, 2c ($pK_a = 8.8$ ³⁰), the solid dissolves. These data are in accordance with previous data reported by Sinisterra et al., e.g., C-200 is dissolved by acetylacetone ($pK_a = 9.0$ ³⁵)

or by α -ketophosphonate ($pK_a \approx 6.0$ ³⁶) giving barium complex salts. On the other hand, Ph₃P⁺CH₃, 2a, and Ph₃P⁺CH₂CH₂CH₂CH₃, 2b, very weak acids ($pK_a = 10$ –11), do not dissolve C-200. Unfortunately the presence of P=C–H bands from the ylide adsorbed on the solid cannot be detected by adsorbed species IR because the absorption is within the HO⁻ and Ba–O broad absorptions of the catalyst. Therefore a detailed study on the nature of these adsorbed ylides cannot be carried out.

Therefore, the Wittig reaction with 2c and 2d seems to take place in the homogeneous phase. The first step would be the reaction of the strong acid 2c and 2d to the OH⁻ on the solid surface.

The strong acid 2d ($pK_a = 6.0$) reacts quickly and unselectively to the OH⁻ on the solid surface, giving a stable ylide that goes to the medium. 2c is a weaker acid than 2d and needs an active site with adequate geometry and pK_a to give the ylide. Therefore the Wittig reaction, in this case, is sensitive to the solid structure. Nevertheless, the ylide is stable enough to go to the solution. Finally, 2a and 2b, very weak acids, need very strong acid sites in the solid surface to carry to the ylide, which is unstable as the conjugated base of a weak acid. Therefore in this case the reaction can only take place in the solid surface if there is an adsorbed aldehyde near the strong basic sites where the ylides formed. Thus, the yields are lower with 2a and 2b than with 2c and 2d (see Table IV), because a very ordered structure of the adsorbed reagent is necessary to carry out the reaction. These affirmations agree with the ones previously reported for the Wittig–Horner reactions that take place in the heterogeneous phase with the weak acid (EtO)₂P(O)CH₂CO₂Et ($pK_a = 12.2$ ^{37,19}) and in the homogeneous phase with strong acids such as ketophosphonates.³⁶

In order to verify these assumptions in the Wittig reaction, IR, ¹H NMR, ¹³C NMR, and ³¹P NMR spectra of the solutions obtained after dissolution (total or partial) of C-200 by 2c and 2d was recorded. The main significant results obtained are shown in Table VII.

From the IR data (Table VII) we can deduce that the new species 9 and 10 exhibit C=O stretching bands at lower frequencies than the parent phosphonium salts. These absorptions must be related to very conjugated C=O bands. They are similar to the description for the ylides from 2c and 2d obtained in the classical way by Seno

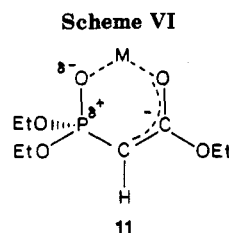
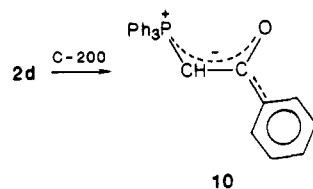
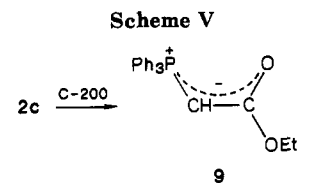
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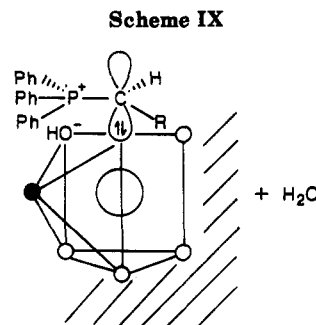
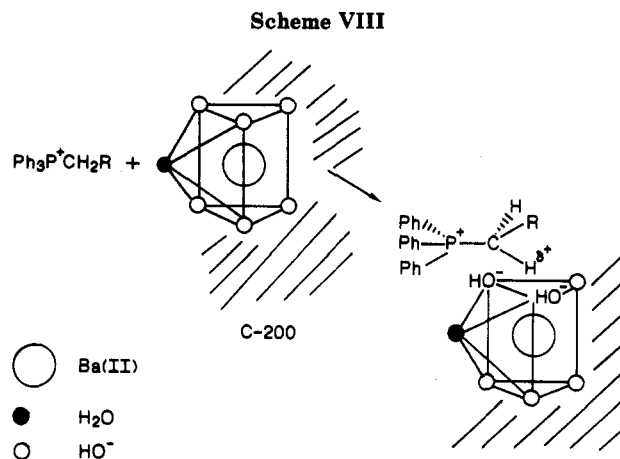
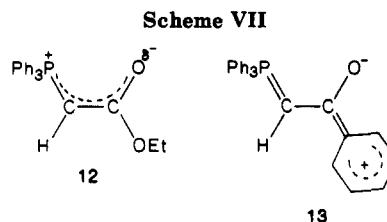
et al.,³⁰ 1620 and 1527 cm^{-1} , respectively. Therefore **9** and **10** could be postulated as the ylides produced in the homogeneous phase by the reaction of **2c** and **2d** with C-200 (Scheme V).

These facts can indirectly be backed by the IR absorptions detected by the workers in the case of the adsorbed ylide from $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$ ($\text{C}=\text{O}$, 1740 cm^{-1} ; $\text{C}=\text{O}$ in the adsorbed ylide, 1670 cm^{-1})¹⁹ that leads to Wittig Horner under interfacial solid-liquid conditions. On the other hand, a 1650- cm^{-1} absorption has been reported by the workers³⁵ in the hydroxyaquo(acetylacetonato)barium(II) isolated and characterized as an intermediate in the Michael addition of acetylacetonate ($\text{p}K_a = 9.0$) to enones catalyzed by C-200.

The $\text{C}=\text{O}$ stretching in ylide **9** exhibits a lower frequency than that reported for the ylide from triethyl phosphonoacetate, **11**, by Sinisterra et al. with Ba(II) (1670 cm^{-1})¹⁹ and by Seyden-Penne et al. (1620–1578 cm^{-1})^{38,40} according to the solvent and the cation, Li(I) or K(I). This can be explained by assuming that the change of the $(\text{EtO})_2\text{P}(\text{O})$ group for Ph_3P^+ favors the delocalization of the negative charge of the ylide to the phosphorus atom versus the case of **11** where no $\text{P}=\text{C}$ bonds were observed (Scheme VI).

Therefore, the $\text{C}=\text{O}$ bond has a stronger single-bond character in **9** than in **11**. This bond character is similar to that postulated by Seyden-Penne et al.³⁸ The greater delocalization of the negative charge of the carbanion in **9** than in **11** will produce a lower carbanionic character in the methyne of **9** than in **11**. Therefore, lower reactivity with respect to the aldehydes is to be expected and so lower yields will be obtained, as has been observed.

NMR studies of the solutions were carried out in order to have additional evidence on the structure of **9** and **10**. Comparison of the salts with ylides showed that methylene signals in **2c** and **2d** (^{13}C NMR) appeared at lower magnetic field than the methyne of **9** and **10**. This could be related to the higher electron density of this carbon in the soluble species (**9** and **10**) than in phosphonium salts.



Therefore a carbanionic character must be assigned to this carbon although, as generally observed, the partially double bond character of the $\text{P}=\text{C}$ bond in the ylide compensates for the high-field shift. Besides, the high values of the coupling constants $J_{\text{P-C}}$ in the ylides are consistent with the presence of a $\pi_{\text{PO}} \rightarrow \text{d}$ interaction in the $\text{P}-\text{C}$ bond of ylides **5** and **6**.

On the other hand, the ^{31}P NMR signals of **9** and **10** appear at a higher magnetic field than that of phosphonium salts (Table VII). This fact must be attributed to a less positive charge on phosphorus atoms in the ylides than the phosphonium salts.

The fact that the ^{31}P NMR of **9** appear at a lower magnetic field than those of **10** suggests a more positive charge in the phosphorus of **9** than in that of **10**. These results agree with IR and ^1H NMR data, and, according to Seno et al.,³⁰ the resonance structures are **12** for **9** and **13** for **10** as the large contribution to the structure of ylides could be postulated (Scheme VII).

Therefore, **10** will be a weak nucleophile and will therefore give poor results with moderate electrophilic aldehydes such as described in Table III. This weak carbanionic character could explain why lower yields in chalcones are obtained by the Wittig reaction than by Claisen-Schmidt where the enolate ion has a strong carbanionic character (Table III).

The ^{13}C chemical shift and $^{13}\text{C}-^{31}\text{P}$ nuclear spin coupling constant have been used to analyze the configuration of phosphorus ylides.^{30,39,40} If we compare the $J_{\text{P-C}}$ of the ylide versus those in the phosphonium salt, we obtain values of

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72 (9-2c) and 56 (10-2d) Hz that show (according to Seyden-Penne et al.⁴⁰) a Z configuration (see 9 and 10), with an additional electrostatic stabilization between P(δ^+) and O(δ^+).

Reaction Pathway. From the data shown in the paper we could postulate a pathway such as this: first step, adsorption of phosphonium salt on C-200 surface (Scheme VIII); second step, formation of the ylide on the solid surface (Scheme IX). These two steps are governed by geometrical factors and the pK_a of the active site and of phosphonium salts. If the phosphonium salt is a strong acid, the proton has a strong acid character. It will be strongly attracted by the solid surface and will react quickly to all OH⁻ on the solid surface. Therefore, if R = CPh, 2d ($pK_a = 6.0$), the reaction is not controlled by the surface structure because it is easy to find basic sites with $pK_a > 6.0$ with the adequate geometry to carry out these steps. In the case of a weaker acid, 2c, R = CO₂Et ($pK_a = 8.0$), the process is controlled by the solid surface because only basic sites with $pK_a > 8.0$ and adequate geometry can react with 2c giving the ylide. Thus, the reaction is sensitive to the solid structure.

In both cases, the ylide is a neutral and stable species and can go to the solution giving 10 and 9. This fact produces a negative vacancy in the cell lattice of the solid that produces the demolition of the structure and the solubilization of the solid. Therefore with 2c and 2d, C-200 is destroyed and the reaction takes place in the homogeneous phase.

In the case of very weak acids, 2a and 2b, only very strong basic sites ($pK_a > 11.5$) can give the ylide, and so the process is controlled by the cell lattice. These very unstable conjugated bases cannot go to the medium without destruction by reaction with the water on the interface. So, they remain adsorbed on the solid, stabilized by the electrostatic bonds with the solid. There, they react with an adsorbed aldehyde giving the product in interfacial solid-liquid conditions but with low yields. Nevertheless, the ylides are very strong basic species and react quickly to the water from the cell lattice. Therefore C-0 leads to lower yields than the calcinated catalysts C-200 and C-300.

Experimental Section

Catalysts. The activated barium hydroxide catalysts C-200 and C-300 were obtained by dehydration of commercial Ba(OH)₂·8H₂O Probus S.A. (C-0). The preparation of these catalysts has been previously described.^{15a,41}

The surface area of the catalysts was determined by a sorptometric Carlo-Erba. The values obtained are shown in Table I.

The titration of active sites was carried out by a spectrophotometric method previously described.⁴² Benzoic acid (BA) ($pK_a = 4.2$) and 2,6-di-*tert*-butyl-4-methylphenol (TBMPE) ($pK_a = 1.7$) were used to titrate the total amount of basic sites. Pyridene (Py) ($pK_a = 5.3$) was used to titrate the acid sites, and 1,3-dinitrobenzene (DNB) (EA = 2.2 eV) and phenothiazine (PNTZ)

(IP = 7.13 eV) were used to titrate the reducing and oxidizing sites, respectively. The results are shown in Table II.

X-ray diffraction powder diagrams were recorded by a Philips PW1130 diffractometer using monochromated Co K α radiation ($\lambda = 1.79026 \text{ \AA}$). The experimental conditions were as follows: 35 kW; 25 mA; scanning $15^\circ < 2\theta < 45^\circ$; scanning rate $1^\circ 2\theta \text{ min}^{-1}$.

Wittig Reaction. Aldehyde (2.56 mmol), 2.56 mmol of phosphonium salt, C-200 (see Tables II and III), 5 mL of 1,4-dioxane, and 0.1 mL of water were mixed and heated at the reaction temperature (see Tables II and III) during the reaction time. Then the reaction mixture was filtered, and the composition of the filtrate was analyzed by HPLC or GLC.

Determination of the Reaction Yield. HPLC. The yield obtained in the synthesis of chalcones (Table III) was determined by HPLC, using a Perkin-Elmer Series 2 HPLC chromatograph, with a UV-visible detector ($\lambda = 254 \text{ nm}$) and 5 μm C18 column. MeOH/H₂O, 80/20 (v/v), was used as the eluant, and the flux was 1.0 mL/min.

GLC. In the other cases, three reaction yields were determined by GLC using a Hewlett-Packard 5710 A gas chromatograph. The column was a 2 m \times 1/8 in. 0.65% EGA on 80/100 Chromosorb WAW; carrier gas, nitrogen; flux = 20 mL/min; detector and injection temperatures equal to 200 °C; initial temperature = 100 °C; end temperature = 170 °C; heating rate = 8 °C/min.

Adsorption Experiments. The adsorption experiments on aldehyde and phosphonium salts were carried out by using 0.2 mL (liquid) or 0.2 g (solid) of the product in 10 mL of 1,4-dioxane with 0.05 mL of water. Then, 0.1 g of catalyst was added. The mixture was heated for 15 min at the reaction temperature. Then the mixture was filtered and the filtrate analyzed by IR, ³¹P NMR, ¹³C NMR, and ¹H NMR. The solid was analyzed by IR spectroscopy.

NMR Spectroscopy. ¹H NMR spectra were recorded on a Hitachi R-26/NMR spectrometer (90 MHz) with deuteriochloroform as the solvent and TMS as the internal standard.

¹³C NMR spectra were recorded on the same spectrometer in the Fourier transform mode, which was operated at 10 MHz. ¹³C-¹H coupling was eliminated by using broad-band ¹H-noise-modulated decoupling. The ylides and salts were run in saturated deuteriochloroform solution, and TMS was used as the internal standard.

³¹P NMR were in the same apparatus at 24.3 MHz using 85% H₃PO₄ as the external reference. The spectra were taken in deuteriochloroform.

IR Spectra of Adsorbed Species. The IR spectra of adsorbed species were recorded in a Perkin-Elmer 599B instrument with a Data Station 3600. The PECDs program was used for the accumulation and differentiation of spectra.

The experimental procedure was as follows: 0.2 g of catalyst was added to the solution of the compound to be adsorbed in 1,4-dioxane. The experimental conditions were those described in the experimental procedure. The mixture was stirred for 5 min to give rise to the adsorption process and to avoid the decomposition of the adsorbed species produced on the solid. The mixture was filtered and washed with 2 \times 5 mL of 1,4-dioxane to eliminate the physisorbed product, and the IR spectrum of the solid was recorded.

The IR spectra of the ylide in solution were recorded in the same way by using water-resistant windows.

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