the washed (water) ether extracts afforded an oily residue, which was subjected to semipreparative TLC (eluant petroleum ether/ether 9:1). Extraction of the slower moving band afforded *trans*-diol **16** (0.015 g).

Reaction of Epoxide 4a with CCl_3COOH in Anhydrous Benzene. A solution of epoxide **4a** (0.10 g) in anhydrous benzene was treated with CCl_3COOH, and then the crude reaction mixture was hydrolyzed as described for the corresponding reaction on **4b**. The crude solid reaction product was recrystallized from hexane to give pure *cis*-diol **15** (0.020 g).

Reaction of Epoxide 4b with $BF_3 \cdot Et_2O$. A solution of epoxide **4b** (0.10 g, 0.50 mmol) in anhydrous benzene (10 mL) was treated at 0 °C with $BF_3 \cdot Et_2O$ (0.07 mL, 0.55 mmol) and then stirred 1 min at room temperature. Evaporation of the washed (saturated aqueous $NaHCO_3$ and water) organic solution afforded a solid residue (0.090 g) mostly consisting of ketone **18** (^1H NMR), which was subjected to semipreparative TLC (eluant petroleum ether/ether 85:15). Extraction of the most intense band afforded pure **(4aα,10aα)-*cis*-1,2,3,9,10,10a-hexahydro-4(4a*H*)-phenanthrenone (18)** (0.030 g) as a solid, mp 47–48 °C: IR 5.88 μm (C=O); ^1H NMR δ 7.40–6.83 (m, 4 H, aromatic protons), 3.76 (d, 1 H, $J = 5.2$ Hz, H_{4a}), 3.06–2.73 (m, 2 H, benzylic CH_2). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.04. Found: C, 84.05; H, 8.20.

Reaction of Epoxide 4a with $BF_3 \cdot Et_2O$. A solution of epoxide **4a** (0.040 g, 0.2 mmol) was treated with $BF_3 \cdot Et_2O$ as previously described for **4b** to give an oily residue mostly consisting of ketone **19** (^1H NMR, and GLC), which was subjected to semipreparative TLC (eluant petroleum ether/ether, 8:2). Extraction of the most intense band afforded pure **(4aβ,10aα)-*trans*-1,2,3,9,10,10a-hexahydro-4(4a*H*)-phenanthrenone (19)** (0.020 g) as a solid, mp 88–90 °C: IR 5.84 μm (C=O); ^1H NMR δ 7.40–7.00 (m, 4 H, aromatic protons), 3.66 (unresolved multiplet, 1 H, $W_{1/2} = 16.0$ Hz, H_{4a}), 2.90–2.50 (m, 2 H, benzylic CH_2). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.04. Found: C, 83.75; H, 7.90.

Reaction of Epoxides 4a and 4b in 1:1 Dioxane/H_2O in the Presence of Acid. A solution of the epoxide (0.020 g) in thermostatted (25 °C) 1:1 0.2 N aqueous H_2SO_4/dioxane (20 mL) was stirred for 1 min, then quenched with solid $NaHCO_3$ and saturated aqueous $NaHCO_3$, and extracted with ether. Evaporation of the washed (water) and dried ether extracts yielded mixtures consisting of diols **16** and **14**, of alcohol **13** and ketone **18** from **4b**, and of diols **17** and **15**, of alcohol **13** and ketone **19** from **4a** (see Table I).

Reaction of Epoxides 4a and 4b with Trichloroacetic Acid in Anhydrous Benzene. A solution of the epoxide (0.030 g, 0.15 mmol) in anhydrous benzene (3 mL) was treated at 25 °C with a 1 M solution of CCl_3COOH in the same solvent (0.165 mL) and left for 1 min at the same temperature. The reaction mixture was then washed (saturated aqueous $NaHCO_3$ and water), dried, and evaporated to give an oily residue consisting of monotrichloroacetates of the corresponding diols (**16** and **14** from **4b** and **17** and **15** from **4a**) together with consistent amounts of rearrangement products (alcohol **13** and ketone **18** from **4b** and alcohol **13** and ketone **19** from **4a**, GLC). The crude mixture was dissolved in anhydrous ether (10 mL) and then treated at room temperature with $LiAlH_4$ (0.050 g) under stirring. After 30 min, the excess hydride was destroyed with water and 10% aqueous NaOH, and the organic solution was filtered and evaporated to give a residue that was directly analyzed by GLC. Because of the reduction of the ketone present in the crude reaction product from each epoxide, the percentages of the ketone relative to the diols and to alcohol **13** were determined by measuring (GLC) the peaks of diols and alcohol **13** relative to the only two other peaks present. These latter were attributed to the reduced ketones by comparison with an analytical sample of the ketones reduced under the same conditions. The monotrichloroacetates of diols **14**–**17**, alcohol **13**, and ketones **18** and **19** were completely stable under the reaction conditions used.

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The Wittig–Horner Reaction in Weakly Hydrated Solid/Liquid Media: Structure and Reactivity of Carbanionic Species Formed from Ethyl (Diethylphosphono)acetate by Adsorption on Solid Inorganic Bases

Z. Mouloungui, M. Delmas,* and A. Gaset

Laboratoire de Chimie des Agroressources, Institut National Polytechnique de Toulouse, Ecole Nationale Supérieure de Chimie, 118 Route de Narbonne, 31077 Toulouse Cedex, France

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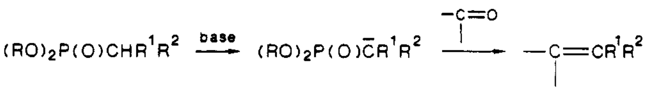
The rate and yield of the Wittig–Horner reaction of furfural with ethyl (diethylphosphono)acetate (**1**) in dioxane in the presence of solid $Ba(OH)_2 \cdot H_2O$, $K_2CO_3 \cdot 1.5H_2O$, or $Cs_2CO_3 \cdot 3H_2O$ depended on the quantity of water added to the reaction medium. Different configurations of phosphorus anionic species formed and adsorbed at the surface of each base account for the difference in reactivity of phosphonate with inorganic solids. The formation of phosphonate carbanion and the decomposition of the oxaphosphetane intermediate into diethylphosphoric acid depend on the action of water molecules added to the aprotic organic medium, indicating novel acid–base interactions at the solid/liquid interface. The rate of reaction of several substituted benzaldehydes with **1** in dioxane in the presence of $K_2CO_3 \cdot 1.5H_2O$, and the yield of ethyl cinnamates, increases with increasing electrophilic character of the aldehyde.

Introduction

A useful modification of the Wittig reaction, known as the Wittig–Horner (or Horner–Wadsworth–Emmons) reaction[1] involves the base-catalyzed condensation of a phosphonate ylide with a carbonyl compound. The use of a weak base in a heterogeneous solid/liquid system[2] has led to improve yields and selectivity in these reactions. Thus Foucaud and Texier-Boullet[3] used solid KOH/THF to transform aromatic aldehydes and ketones into α,β-unsaturated esters and nitriles and obtained better yields than those obtained in reactions carried out under liquid/liquid transfer conditions.[4] These authors also found



$$(RO)_2P(O)CHR^1R^2 \xrightarrow{\text{base}} (RO)_2P(O)\bar{C}R^1R^2 \xrightarrow{-\overset{|}{C}=O} -\underset{|}{C}=CR^1R^2$$

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Table I. Effect of Water on the Wittig–Horner Reaction in the Presence of Activated $Ba(OH)_2$[a]

water, mol	yield,[b] %	water, mol	yield,[b] %
0	20	0.056	98
0.011	65	0.110	97
0.016	75	0.280	80
0.028	98		

[a] Furfural (0.02 mol), **1** (0.02 mol), $ba(OH)_2{\cdot}H_2O$ (0.013 mol), dioxane (20 mL), 70 °C, 25 min. [b] Yield of 3-(2-furyl)-2-propenoate determined by GC with $C_{16}H_{34}$ as internal standard.

improved selectivity by combining KF, $2H_2O$/DMF/tetrabutylammonium bromide (TBAB) and controlling hydration of the reaction medium.[5] These reactions were limited to aromatic substrates, with the drawback of needing a phase-transfer agent in the latter.[5] Foucaud[3,5] and Villieras[6] reported that the synthesis of ethyl cinnamates in a biphasic solid/liquid anhydrous organic medium in the presence of K_2CO_3 or $KHCO_3$ was only possible at the solvent reflux temperature.

We have shown that the addition of small amounts of water to an anionic-activated Wittig reaction in a heterogenous solid/liquid medium has the same effect as crown ethers and other phase-transfer agents.[7]

We here report on a study of the conversion of furfural and benzaldehydes into α,β-unsaturated esters by reaction with ethyl (diethylphosphono)acetate (**1**) in the presence of solid $Ba(OH)_2{\cdot}H_2O$, $K_2CO_3{\cdot}1.5H_2O$, and $Cs_2CO_3{\cdot}3H_2O$.[8] We were particularly interested in the structure of the phosphorus carbanionic species formed in this Wittig–Horner reaction, and in the effect of water on the formation of these carbanions. First results of this work were reported in a preliminary communication.[9]

Results and Discussion

Influence of Reaction Medium Hydration. Furfural was condensed with **1** in the presence of activated $Ba(OH)_2$, $K_2CO_3{\cdot}1.5H_2O$, or $Cs_2CO_3{\cdot}3H_2O$ in dioxane containing various amounts of water at 70 °C (Tables I and II). The condensation proceeded rapidly and stereoselectively to form ethyl 3-(2-furyl)-2-propenoate (*E*:*Z* 98:2). The reactions in the presence of $Ba(OH)_2{\cdot}H_2O$ and $K_2CO_3{\cdot}1.5H_2O$ were quite sensitive to the degree of hydration of the medium;[7,10] maximum conversions were achieved with 2 equiv of water per mole of $Ba(OH)_2{\cdot}H_2O$ and with 1 equiv of water per mole of $K_2CO_3{\cdot}1.5H_2O$. On the other hand, $Cs_2CO_3{\cdot}3H_2O$ was almost as effective without water as with it. These two solid bases have reticular energy values[11] higher than that of Cs_2CO_3, which explains the higher reactivity of Cs_2CO_3 in the anhydrous medium.

Under our conditions, the reaction proceeded by anionic activation and involved three principal steps.

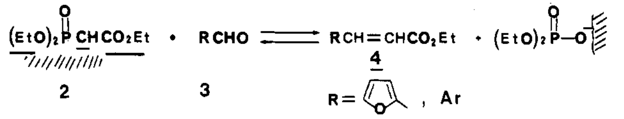
Table II. Effect of Water on the Wittig–Horner Reaction in the Presence of $K_2CO_3{\cdot}1.5H_2O$ and $Cs_2CO_3{\cdot}3H_2O$[a]

water, mol	$K_2CO_3{\cdot}1.5H_2O$ yield,[b,c] %	$Cs_2CO_3{\cdot}3H_2O$ yield,[b,c] %
0	43	96
0.011	60	98
0.016	80	98
0.030[e]	98	98
0.045	98	98
0.056	98	95
0.105	98	90
0.120	91	88
0.135	85	80

[a] Furfural (0.02 mol), **1** (0.025 mol), alkali carbonate (0.03 mol), dioxane (20 mL), 70 °C. [b] Yield of 3-(2-furyl)-2-propenoate determined by GC with $C_{16}H_{34}$ as internal standard. [c] Reaction time 2 h. [d] Reaction time 45 min. [e] With this quantity of water, maximum conversion was reached in 90 min with $K_2CO_3{\cdot}1.5H_2O$ and 30 min with $Cs_2CO_3{\cdot}3H_2O$.

(1) Adsorption of phosphonate on basic sites with the formation and transformation of carbanionic species.

(2) Reaction between carbanion and carbonyl substrate at a surface or interface followed by the formation of final products, of which at least one is adsorbed.



(3) Desorption of reaction products.

The quantity of water necessary for a rapid and quantitative reaction depends on the nature of the base cation.[10a,12,13] Apparently water decreases the reticular energy of the crystalline structure of the solid base at the interface level. However, excess water converts the solid base to a pasty state, reflecting the formation of less reactive higher hydrates and resulting in conditions similar to those of a liquid/liquid phase-transfer reaction without catalyst.[14]

The low reactivity observed in the absence of water could also be due to degradation of the solid structure of the base. We established by ^1H NMR that a proportion of the water from initial crystallization of the base[8] was extracted by anhydrous dioxane. The consequence would be a contraction of the crystalline structure and a reduced capability of the carbonate or hydroxide anions for removing a proton from **1**.

It appears that the interaction between H_2O and the solid bases in this medium corresponds to the solid/liquid equilibrium known in binary systems for $H_2O/Ba(OH)_2$[15]

$$Ba(OH)_2{\cdot}8H_2O \rightleftharpoons Ba(OH)_2{\cdot}3H_2O \rightleftharpoons Ba(OH)_2{\cdot}H_2O \rightleftharpoons \beta Ba(OH)_2$$

and H_2O/K_2CO_3,[16]

$$K_2CO_3{\cdot}5H_2O \rightleftharpoons K_2CO_3{\cdot}1.5H_2O \rightleftharpoons K_2CO_3{\cdot}0.5H_2O \rightleftharpoons K_2CO_3$$

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Table III. Properties[a] and Reactivities[b] of Solid Bases in the Wittig–Horner Reaction

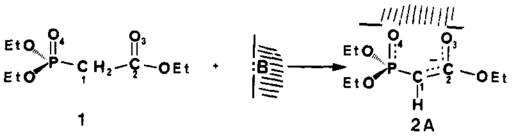
base	strong basic sites, mequiv/g	reducing sites, mequiv/g	specific surface, m^2/g	base, mol	reaction time, min	yield %
$Ba(OH)_2{\cdot}H_2O$	6.3 ± 0.2	35 ± 4	1.9 ± 0.1	0.030	25	98
				0.013	25	98
				0.0063	60	64
$K_2CO_3{\cdot}1.5H_2O$	80 ± 8	95 ± 10	2.1 ± 0.2	0.060	90	98
				0.030	90	98
				0.020	150	90
$Cs_2CO_3{\cdot}3H_2O$	0.20 ± 10	60 ± 10	*c*	0.030	30	98
				0.020	45	98

[a] Basic and reducing sites were determined by a literature method.[18c] [b] Reaction conditions for $Ba(OH)_2{\cdot}H_2O$:furfural (0.02 mol), 1 (0.02 mol), dioxane (20 mL), H_2O (0.5 mL, 0.028 mol), 70 °C. For $K_2CO_3{\cdot}1.5H_2O$ and $Cs_2CO_3{\cdot}3H_2O$:furfural (0.02 mol), 1 (0.025 mol), dioxane (20 mL), H_2O (0.54 mL, 0.03 mol), 70 °C. [c] Not determined because of hygroscopicity of $Cs_2CO_3{\cdot}3H_2O$.

which depends on the quantity of water added at the beginning of the reaction. Titration of water in the reaction medium at the end of the reaction by the Karl Fischer method indicated that half of the added water remained on the solid. We have shown[7] that dehydration of the solid base surface by the aprotic solvent, which generally decreased the reaction yield, had to be compensated by adding water to the medium. The carefully quantified additional water allows the crystalline structure of the solid to regain a form suitable for anionic activation at the interface.

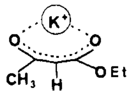
Properties and Reactivity of Solid Bases. Since the surface properties of the solid base influence the reaction mechanism,[17] we determined the nature and number of active sites and their specific surface areas (Table III). Although $K_2CO_3{\cdot}1.5H_2O$ had more strong basic sites than $Ba(OH)_2{\cdot}H_2O$ or $Cs_2CO_3{\cdot}3H_2O$, reactivity followed a totally different order. Since their specific surfaces[18a] were almost identical, this property apparently does not affect reactivity. However, stoichiometry of the base compared to 1 was not a factor in the reaction. We therefore wished to determine the structure of the carbanionic species which were formed at the interface whatever was the quantity of base in contact with 1.

Structure of Carbanionic Species Formed after Adsorption of 1 on Solid Bases. The structures of the phosphorus anionic species were established from IR spectra of solid phases recovered after adsorption of 1 on the solid base.[9] The possible existence of ionic species in solution was explored by ^{31}P NMR of the organic phase. The principal IR vibration bands of 1 and anionic species **2A**, **2B**, and **2C–D** adsorbed on activated $Ba(OH)_2$, $K_2CO_3{\cdot}1.5H_2O$, and $Cs_2CO_3{\cdot}3H_2O$ are shown in Table IV. The IR spectra of 1 before and after adsorption showed that passing from phosphonate to the intermediate **2A** was characterized by the disappearance of elongation frequencies ν ($C_2{=}O_3$) at 1740 cm^{-1} and ν ($P \rightarrow O_4$) at 1210–1275 cm^{-1} of 1 and the appearance of absorption bands at 1675, 1570, and then 1384 and 1194 cm^{-1} in **2A**.

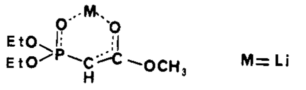


1 2A

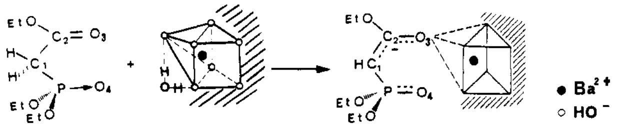
By comparison with frequencies of the enolate anion of chelated ethyl acetoacetate,[19] the bands at 1675 and 1570 cm^{-1} were attributed respectively to vibration frequencies ν ($C_2{=}{-}{=}O_3$) and ν ($C_1{=}{-}{=}C_2$), which are characteristic of a conjugated system. By analogy with vibration spectra



of the anionic species of methyl (diethylphosphono)acetate,[20] the bands at 1384 and 1194 cm^{-1} were attributed respectively to frequencies ν ($C_1{=}{-}{=}C_2$) and ν ($P{=}{-}{=}O_4$) with a partial double bond. These observations are similar to those reported by Kirilov and Petrov[21] on the chelate formed by ethyl (diethylphosphono)acetate in the solid state with Li or Ca cations.



The bonds $C_2{=}O_3$ and $P{=}O_4$ of 1 are elongated in the intermediate adsorbed species **2A**, indicating that both oxygen atoms O_3 and O_4 approach Ba^{2+} in the microcrystalline structure[22] of activated $Ba(OH)_2$ and lead to the formation of a chelate in a configuration of type *Z*.[9]



1 2A

A strong carbanionic character could also be noted in the anionic species adsorbed on activated $Ba(OH)_2$ since a band with an unusual double bond $C_1{=}C_2$ was observed.

Table IV. IR Peaks (cm^{-1})[a] of 1 and Anionic Species Adsorbed on Solid Bases

bond	1	2A[b]	2B[b]	2C–D[c]
ν ($C_2{=}O_3$)	1740 (s)	–	–	1740 (m)
ν ($C_2{=}{-}{=}O_3$)	–	1675 (s)	1730 (s)	1653 (m)
ν ($C_1{=}{-}{=}C_2$)	–	1570 (w)	–	1420 (s)
ν ($C_1{=}{-}{=}C_2$)	–	1384 (m)	–	1375 (w)
ν ($P{=}O_4$)	1275 (s) 1210 (s)	–	–	–
ν ($P{=}{-}{=}O_4$)	–	1194 (s)	–	1270 (m) 1167 (w)
ν ($C_2{-}O$)	1120 (m)	–	–	1120 (w)
ν ($P{-}OEt$)	1060 (m) 1030 (s)	– 1054 (w)	1060 (m) 1020 (m)	1055 (m) 1030 (m)

[a] The precision was ±2 cm^{-1}. [b] Adsorption was carried out in dioxane-d_8 containing a little D_2O. [c] The spectra from adsorption in dioxane-d_8 and DMSO-d_6 were similar.

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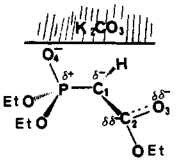
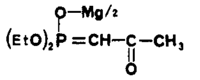
Adsorption of **1** on $K_2CO_3{\cdot}1.5H_2O$ leads to an anionic species with a band ν (C_2=–=O_3) at 1730 cm^{-1}; the vibration frequency of a $P{=}O_4$ bond was not observed. It seems that oxygen O_4 forms a real ionic bond with the potassium cationic site. Since the band at 1730 cm^{-1} corresponds essentially to the vibration frequency ν (C_2=–=O_3), we could deduce the following structure for the carbanion formed on $K_2CO_3{\cdot}1.5H_2O$. Anionic species **2B**



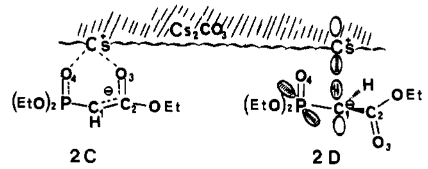
is analogous to structures determined by Kirilov and Petrov[23] for the magnesium derivative of diethyl phosphonoacetone in $CHCl_3$.



$$(EtO)_2\overset{\overset{O-Mg/2}{|}}{P}=CH-\underset{\underset{O}{\|}}{C}-CH_3$$

The phosphorylidene anionic species **2B** has a low carbanionic character compared with chelate **2A** formed on activated $Ba(OH)_2$. This difference in charge distribution explains why activated $Ba(OH)_2$ is more reactive than $K_2CO_3{\cdot}1.5H_2O$ (Tables I–III).

The vibration frequencies of **1** on adsorbed $Cs_2CO_3{\cdot}3H_2O$ are similar to those of **2A** and **2B**. Bands at 1653, 1447–1379, and 1166 cm^{-1}, respectively, corresponding to vibration frequencies of ν (C_2=–=O_3), ν (C_1=–=C_2) and ν (P=–=O_4), are characteristic of chelate **2C**. Absorptions at 1740 and 1270 cm^{-1}, corresponding to vibration frequencies ν ($C_2{=}O_3$) and ν ($P{=}O_4$), imply a C-metal form **2D** coexisting with chelate **2C** on the $Cs_2CO_3{\cdot}3H_2O$ surface.



2C 2D

The presence of **2D** with **2C** differentiates $Cs_2CO_3{\cdot}3H_2O$ from the other two solid bases and explains its increased reactivity. We have reported that $Cs_2CO_3{\cdot}3H_2O$ is highly reactive in the transformation of phenolic and pyrrolic aldehydes with acidic hydrogen atoms into α,β-unsaturated esters because of the formation of a highly nucleophilic phosphonate carbanion similar to the C-metal derivative **2D**.[24]

Moreover, in preparing the magnesium derivative of diethyl phosphonoacetone, Kirilov and Petrov[23] observed only the chelated form in the solid state, but they also found an equilibrium between the chelate and a C-metal species in solution in CCl_4, with a carbanionic intermediate whose negative charge was located on the a carbon of the phosphonate. Accordingly, we searched for ionic species in solution by ^{31}P NMR.

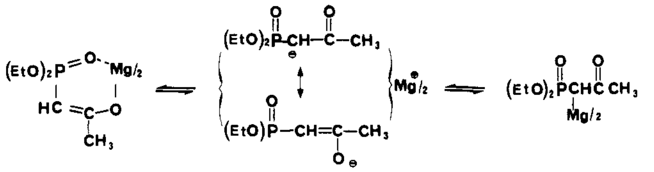
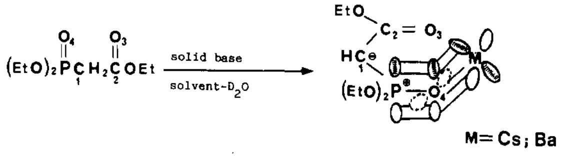
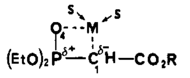


Table V. Chemical Shifts (ppm) in ^{31}P NMR Data of **1** and Anionic Species in Solution

base solvent	δ ^{31}P (1)	δ ^{31}P (2)	$\Delta\delta$ ^{31}P	2/1
$Ba(OH)_2{\cdot}H_2O$/dioxane-d_8	23.72	31.57	7.85	98/2
$Ba(OH)_2{\cdot}H_2O$/toluene-d_8	19.40	27.17	7.77	60/40
$Cs_2CO_3{\cdot}3H_2O$/dioxane-d_8	22.16	31.42	9.26	90/10
$Cs_2CO_3{\cdot}3H_2O$/toluene-d_8	18.75	28.00	9.25	13/87
$K_2CO_3{\cdot}1.5H_2O$/dioxane-d_8	24.21	–	–	0/100

^{31}P NMR Spectroscopy of Organic Liquid Phases. Only phosphonate was observed in the dioxane phase recovered after chemical adsorption of **1** on $K_2CO_3{\cdot}1.5H_2O$ (Table V). On the other hand, in the presence of activated $Ba(OH)_2$ or $Cs_2CO_3{\cdot}3H_2O$ in either dioxane-d_8 or toluene-d_8, there were a phosphorus species with a chemical shift different from that of **1** and with weak resonance. This indicated the development of a positive charge around the phosphorus atom[25] and a decrease in the double bond pπ-dπ of $P{=}O_4$ of the phosphonate and an increase in $\pi^2{}_{P=O}$-$5d^\circ{}_{xz}$ (Ba^{2+},Cs^+) with a partial single bond in the anionic species. The lengthening of $P{=}O_4$ was previously shown by IR. The variations of chemical shifts $\Delta\delta^{31}P$ were similar and quite low compared to those of analogous chelated anions ($\Delta\delta^{31}P$ = 17–20).[20,26] According to Bottin-Strzalko and Seyden-Penne,[26] these anionic species could represent the C-metal derivative, whose existence in traces had no significant role in the formation of the α,β-unsaturated ester in solution.[9]

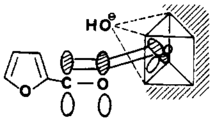




M=K R=Me S: THF $\Delta\delta^{31}P$=+9,30 ppm[26]

M=Cs R=Et S: Dioxane $\Delta\delta^{31}P$=+9,25 ppm (this work)

Adsorption of Furfural in the Presence of Solid Bases and Reaction Mechanism in the Presence of $Ba(OH)_2{\cdot}H_2O$. After adsorption of furfural on all three solid bases, the C=O band at 1675 cm^{-1} disappeared. After adsorption on $Ba(OH)_2{\cdot}H_2O$, there appeared a conjugated band ν (C=–=O) at 1550–1590 cm^{-1} which was explained by an interaction $\pi^2 \rightarrow d^\circ$ between the carbonyl group of furfural and orbital 5d of Ba^{2+}. On the other hand, with alkaline carbonates the presence of a band for carboxylate ion at 1730–1733 cm^{-1} indicated a possible evolution toward the Cannizzaro reaction. In any case, this secondary reaction was observed at the end of the Wittig–Horner reaction.



It could be concluded that the carbonyl compound was adsorbed on activated $Ba(OH)_2$ like chelate **2A**, which would lead to a reaction with a transition state where reactants and products would be adsorbed on the solid surface (Figure 1). The formation of an intermediate adsorbed oxaphosphetane[10b,27] is indicated by the IR

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[26] Bottin-Strzalko, T.; Seyden-Penne, J. *J. Chem. Soc., Chem. Commun.* **1976**, 905.

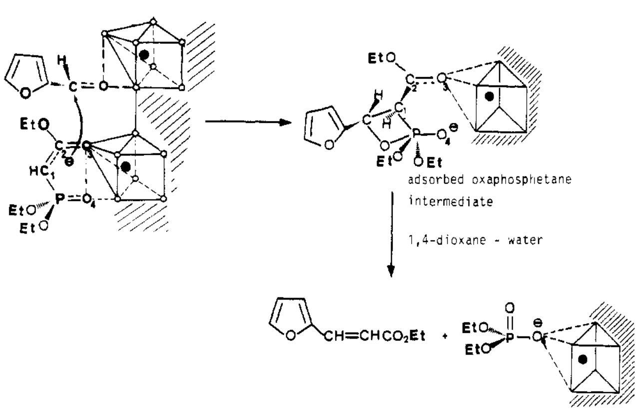

Figure 1. A multiadsorbed process for the Wittig–Horner reaction in the presence of activated barium hydroxide.

Table VI. Condensation of 1 with ArCHO in the Presence of $K_2CO_3 \bullet 1.5H_2O$[a]

Ar	reaction time	yield,[b] %
$4\text{-}CH_3OC_6H_4$	6 h	59
$4\text{-}ClC_6H_4$	6 h	80
C_6H_5	2 h	90
$3\text{-}O_2NC_6H_4$	30 min	94
$4\text{-}O_2NC_6H_4$	15 min	90
$2\text{-}O_2NC_6H_4$	30 min	88

[a] ArCHO (0.02 mol), 1 (0.025 mol), $K_2CO_3 \cdot 1.5H_2O$ (0.03 mol), dioxane (20 mL), H_2O (0.54 mL, 0.03 mol), 70 °C. [b] Yield of isolated products determined by flash chromatography (silica gel, hexane/ether, 8:2). All the ethyl cinnamates had the *E* configuration, determined by ^1H NMR spectroscopy ($CDCl_3$ + TMS).

spectrum of the solid obtained by addition of furfural to the previously formed carbanionic species. This spectrum did not show the characteristic frequency of the ester or aldehyde carbonyl, but rather a band at 1630 cm^{-1}, which was attributed to the loose frequency ν ($C_2{=}O_3$). Moreover, neither bands ν ($P{=}O_4$) nor bands ν ($C_1{=}C_2$) were observed, but only the vibration frequencies ν (P—O—C), ν (P—C_1), and ν (P—O) at 1100, 970, and 873 cm^{-1}, respectively. Addition of dioxane with an additional quantity of water on this solid support of the oxaphosphetane intermediate led to formation of the furylacrylate, as shown by ^1H NMR of the liquid phase. An IR spectrum of the solid residue showed vibration frequencies at 1230 and 1100 cm^{-1} attributed to vibration modes ν (P=O) and ν (P—OEt). These bands indicated the presence of diethyl phosphate, which remained adsorbed on the solid.[27]

The mechanism of the Wittig–Horner reaction in the presence of activated $Ba(OH)_2$ involves an oxaphosphetane intermediate[29,30] in agreement with a multiadsorbed process. Water added to the medium initiated rapid decomposition of the oxaphosphetane into the reaction products.[10,27,28] However, adsorption of phosphorus carbanionic species at the surface of the solid alkaline carbonates was obvious, the aldehyde remaining in solution. Under these conditions, evolution into a state of monoadsorbed transition[18] would depend on the electrophilic character of the carbonyl carbon of the aldehyde.

Condensation of 1 with Substituted Benzaldehydes in the Presence of $K_2CO_3 \cdot 1.5H_2O$. The results of condensation of 1 with some substituted benzaldehydes are presented in Table VI. Since the anionic species from the interaction of 1 with $K_2CO_3 \cdot 1.5H_2O$ are only weakly nucleophilic and since the aromatic aldehydes remained in solution,[31] the reaction between the carbanion adsorbed on the surface of the base and the carbonyl derivatives was sensitive to the electrophilic nature of the aromatic nucleus. The reaction was interfacial, monoadsorbed.

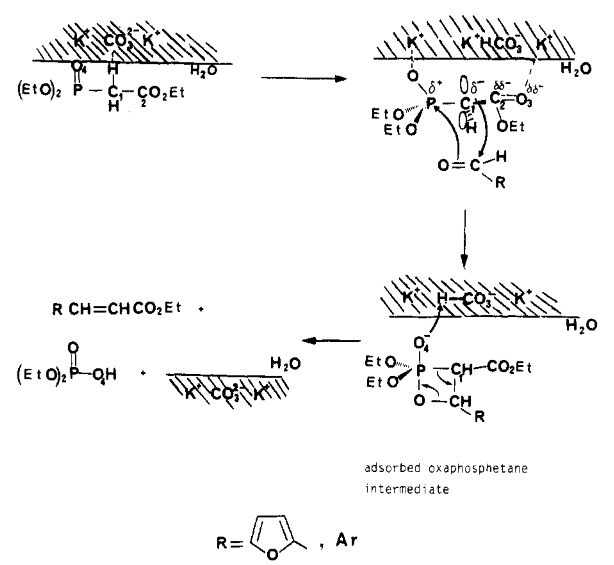

Figure 2. A monoadsorbed process for the Wittig–Horner reaction in the presence of potassium carbonate.

After carrying out a Wittig–Horner reaction over $K_2CO_3 \cdot 1.5H_2O$, the base could be reused after cleaning dioxane and ether. The use of this K_2CO_3 in a new reaction medium in the absence of addition water led to a 40% yield, whereas adding a quantity of water identical with that used in the first test gave a 70% yield. A third use of this K_2CO_3 gave a 40% yield but led to its destruction as a viscous solution.

These results could indicate that $KHCO_3$, formed by the action $K_2CO_3 \cdot 1.5H_2O$ on the phosphonate, was responsible for the successive reactions. However, this hypothesis is wrong because a similar test carried out with $KHCO_3$ only led to a 15% yield.

Another main point in the reaction mechanism is the nature of the phosphorus subproduct of the Wittig–Horner reaction. In the presence of $Ba(OH)_2 \cdot H_2O$, the reaction leads to $(EtO)_2P(O)O^-$ which remains adsorbed at the solid surface. In the case of $K_2CO_3 \cdot 1.5H_2O$, we showed (i) the presence after filtration in the liquid reaction medium, of phosphorus acid $(EtO)_2P(O)OH$ characterized by ^{31}P NMR, and ^1H NMR, and mass spectrometry,[32] and (ii) that cleaning the solid phase with 1,4-dioxane indicated the presence of a significant quantity of this acid (δ ^{31}P = −1.18 ppm).

These results indicated that potassium carbonate was the only basic species responsible for the condensation reaction and that potassium hydrogenocarbonate formed

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[30] (a) Larsen, R. O.; Aksnes, G. *Phosphorus Sulfur* **1983**, *15*, 219 (b) *Ibid.* **1983**, *15*, 229.

[31] Chemical adsorption of isolated aldehydes in the presenced of potassium carbonate showed no benzaldehyde band (C=O) at 1685–1700 cm^{-1} but the presence of a band for carboxylate ion at 1700–1733 cm^{-1} which is characteristic of benzoate. The absence of Cannizzaro reaction products at the end of the Wittig reaction was explained by the location of benzaldehydes in the solution. See: Tanabe, K.; Saito, K. *J. Catal.* **1974**, *35*, 247.

[32] Physical characteristics of diethylphosphoric acid $(C_2H_5O)_2P(O)OH$. ^1H NMR (dioxane-d_8 + TMS) δ (ppm): 8.52 (s, 1 H, POH), 3.85 (dq, 4 H, J = 14 Hz and 7 Hz, $POCH_2CH_3$), 1.17 (t, 6 H, J = 7 Hz, $POCH_2CH_3$). MS: m/e 155 (M + H), 99 (base peak) $HOP(OH)_3$. $\delta^{31}P$: (dioxane-d_8) = −1.18 ppm. See: Bielawski, J.; Casida, J. E. *J. Agric. Food Chem.* **1988**, *36*, 610.

was systematically regenerated in potassium carbonate by interaction between the oxaphosphetane anion and the solid phase (Figure 2).

It was clear that the capacity of this anion on the regeneration of potassium carbonate could be used in other reactions which would not involve a solid base in stoichiometry.[28]

We observed a quantitative transformation of furfural with a quantity of $K_2CO_3 \cdot 1.5H_2O$ significantly lower than the stoichiometry required for phosphonate (Table III). Potassium carbonate would first act by classical acid-base interaction followed by regeneration of its active basic sites by the intermediate oxaphosphetane anion at the interface. Such an interfacial process could only be explained by the intervention of water molecules, which dilate superficial meshes of the solid and therefore promote these interactions between species weakly monoadsorbed on the solid and molecules in the dioxane organic phase.

Conclusion

This study points out the importance of a perfect knowledge of structures of solid bases and reactive intermediate species formed at the surface or at the interface in reactions proceeding by anionic activation. In these conditions, the Wittig–Horner reaction is controlled by the structure of phosphorus carbanionic species whose nature depends on the structure of solid bases. This novel approach makes it possible to optimize reactions of this type and determine their mechanisms.

Experimental Section

^1H NMR spectra were recorded on a Varian T-60 spectrometer with TMS as internal standard. ^{31}P NMR spectra were recorded on a Brucker WH90 spectrometer with 85% H_3PO_4 as external standard. Mass spectrometry was carried out on a Girdel Chromatograph coupled with a Nermag R 10-10 spectrometer by chemical ionization (CH_4).

1,4-Dioxane (Prolabo) was distilled over $CaCl_2$ and kept on 4-Å molecular sieves. 1,4-Dioxane-d_8, toluene-d_8, and DMSO-d_6 (1-mL ampules) were used directly (CEA, France). The carbonyl substrates and ethyl (diethylphosphono)acetate were commercial products (Fluka). Furfural and benzaldehyde were distilled under reduced pressure in the presence of K_2CO_3 before use. Activated $Ba(OH)_2$ or $Ba(OH)_2 \cdot H_2O$ was prepared by heating[18] $Ba(OH)_2 \cdot 8H_2O$ (Prolabo) at 200 °C for 3 h. The product was ground and kept in a dessicator in the presence of NaOH. $K_2CO_3 \cdot 1.5H_2O$ and $Cs_2CO_3 \cdot 3H_2O$ (Fluka) were used directly.

The nature and number of active sites of the solid bases were determined with 2,6-di-*tert*-butyl-4-methylphenol, and 1,3-dinitrobenzene was used to titrate reducing sites. The bases did not show acidic or oxidizing sites after titration with pyridine and phenothiazine.[18c]

General Method for Synthesis of Ethyl Acrylates. Reactions were carried out in a 100-mL round-bottomed flask equipped with a reflux condenser, mechanical stirrer, and thermometer. The solid base, 1, and aldehyde (see tables for molar quantities) were added sequentially to dioxane, and water was added. The mixture was stirred at 70 °C in a thermostated bath.

The composition of the reaction mixture was determined periodically with an Intersmat Chromatograph IGC 120 DFL (flame ionization) equipped with an OV 101 5% column on Chromosorb W/AW 80/100. The temperature range 140–280 °C was programmed to increase 20 °C/min with a nitrogen gas flow of 25 mL/min. Injector and detector temperatures were 250 and 280 °C, respectively. Yield of 3-(2-furyl)-2-propenoate was determined by GC with hexadecane as internal standard.

At the end of the reaction, the solid phase was separated by filtration; addition of Silica 60H (Merck) or Celite gel to the bottom of the fritted tube aided retention of small particles of the solid. The solvent was evaporated in a rotavapor, and the product was purified by distillation or flash chromatography (silica gel, hexane/ether, 8:2). Physical properties of ethyl cinnamates agreed with literature data. Ethyl 3-(2-furyl)-2-propenoate has been described.[10a]

IR Spectra of Adsorbed Phosphorus Carbanions. The adsorption of the phosphorus reagent was carried out under the same conditions as the reaction: 1 (2.3 mmol) was mixed with 2 mL of deuterated solvent, 0.04 mL of D_2O, and $Ba(OH)_2 \cdot H_2O$ (1.2 mmol) or alkaline carbonate (3 mmol) at 70 °C for 25–40 min, depending on the base. The solid was filtered and dried under vacuum. The IR spectrum of the solid was recorded on pellets comprising 12 mg of the solid in 170 mg of KBr in a Brucker IFS spectrometer with a single Fourier transformed beam (1000 accumulations). The liquid phase was analyzed by ^{31}P NMR. Adsorption of furfural and other carbonyl substrates on the solid base were determined the same way in the absence of the phosphorus reagent.

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Secondary Deuterium Kinetic Isotope Effects in the Cleavage of Thiamin and *N*-Methylthiaminium Ion: First Evidence To Identify the Rate-Limiting Step

Georg Uray,* Claude Celotto, and Anton Ibovnik

Institut für Organische Chemie, Karl-Franzens Universität, 8010 Graz, Austria

John A. Zoltewicz

Department of Chemistry, University of Florida, Gainesville, Florida 32611

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Thiamin and 1'-methylthiaminium ion deuterated at the 6'- and *N*-methylene positions were cleaved by sulfite ion in aqueous phosphate at 25 °C. Observed secondary kinetic isotope effects (standard deviation of the ratio) were inverse for the 6'-position, 0.95 (0.09) and 0.95 (0.03), respectively, and normal for the *N*-methylene group, 1.08 (0.09) and 1.10 (0.03), respectively. These results confirm the multistep mechanism first proposed by us (*J. Am. Chem. Soc.* **1977**, *99*, 3134). They prove for the first time that sulfite ion adds to the 6'-position and that fragmentation of the CH_2–thiazole bond in the resultant adduct contributes to the rate in the multistep mechanism.

Thiamin (**1a**) and its *N*-methyl derivative **1d** undergo nucleophilic substitution at the heterobenzylic methylene group in the presence of aqueous sulfite ion by an unusual, multistep mechanism.[1] One sulfite ion adds to an elec-