

WITTIG-HORNER REACTION CATALYZED BY ACTIVATED BARIUM HYDROXIDE  
IN THE PRESENCE OF ULTRASOUND

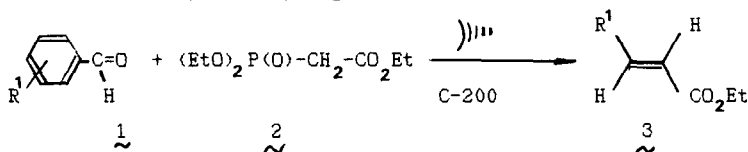
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**Summary.**—The sonochemical Wittig-Horner reaction, catalyzed by an activated barium hydroxide catalyst in interfacial solid-liquid conditions leads to E-acrylates with very good yields. The sonochemical process takes place at room temperature and with lower catalyst weight and reaction time than the thermal process.

**Resumé.**—La réaction de Wittig-Horner en phase hétérogène solide-liquide sous sonication est catalysée par l'hydroxyde de baryum activé. On obtient les E-acrylates avec de bons rendements. Le processus sonochimique a lieu à température ambiante et avec une quantité du catalyseur et un temps de réaction inférieurs à ceux nécessaires dans le processus thermique.

The activated barium hydroxide catalyst, C-200, has been used as catalyst in several thermochemical organic reactions e.g. Michael addition<sup>1</sup>, Claisen-Schmidt<sup>2</sup> and aldol condensations<sup>3</sup>, Wittig-Horner reaction<sup>4</sup> with very good yields. Recently this catalyst has been used under sonochemical conditions. Under ultrasounds, C-200 can catalyze reactions that are not catalyzed by C-200 in thermal conditions such as Cannizzaro reaction<sup>5</sup>. In order to have a general scope of the catalytic activity of C-200 in sonochemical conditions, a general study is carried out. In the present paper we show the first results obtained in the synthesis of E-acrylates by regio and stereoselective Wittig-Horner reaction.



The preparation of the catalyst has been described previously<sup>1,3</sup>.

The sonochemical Wittig-Horner reaction was carried out by mixing 2.5mmol of aldehyde, 1, 2.5mmol of 2, 3mL of solvent; 0.05mL of water and the convenient amount of C-200. Then, the mixture was sonicated in an ultrasound bath P. Selecta, model 513 for 10min. The mixture was left to stand for 24h at 09-49°C to produce the sedimentation of the solid.

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The mixture was analyzed by HPLC using a Perkin-Elmer Series 2 chromatograph with UV-visible detector ( $\lambda=254\text{nm}$ ) and anthracene as the internal standard. MeOH/H<sub>2</sub>O=80/20(v/v) was used as the eluent. Flux=0.8mL/min. 5 $\mu$  C<sub>18</sub> column

The aldehydes and anthracene were from Merck p.a., triethyl phosphonoacetate, **2**, was from Aldrich. The pure solvents: THF; EtOH; NN-DMF and 1,4-dioxane were from Ferosa p.a.

Table 1

Synthesis of E-acrylates by Wittig-Horner reaction catalyzed by C-200 under sonochemical conditions 25mmol of **1** and **2**; 3mL of solvent; 0.05mL of water

Entry	R <sup>1</sup>	sonication time (min)	catalyst weight (g)	solvent	dielectric constant $\epsilon$	yield in <b>3</b> (% molar)
1	Cl	0.0 (30min) <sup>a</sup>	2.5 <sup>a</sup>	1,4-dioxane <sup>a,b</sup>	2.2	89 <sup>a</sup>
2	Cl	10	0.0	THF	9.0	0
3	Cl	5	0.15	THF	9.0	92
4	Cl	8	0.15	THF	9.0	90
5	Cl	10	0.15	THF	9.0	85
6	Cl	15	0.15	THF	9.0	85
7	Cl	30	0.15	THF	9.0	90
8	Cl	10	0.02	THF	9.0	62
9	Cl	10	0.05	THF	9.0	80
10	Cl	10	0.10	THF	9.0	81
11	Cl	10	0.20	THF	9.0	91
12	Cl	10	0.20	THF <sup>c</sup>	7.9	46
13	Cl	10	0.20	EtOH (99.9%)	24.3	32
14	Cl	10	0.20	EtOH (96%)	26.5	70
15	Cl	10	0.20	DMF (99%)	36.7	9
16	Cl	10	0.20	1,4-dioxane <sup>b</sup>	2.2	27
17	H	10	0.15	THF	9.0	57
18	4-CH <sub>3</sub>	10	0.15	THF	9.0	61
19	4-OCH <sub>3</sub>	10	0.15	THF	9.0	32
20	4-NO <sub>2</sub>	10	0.15	THF	9.0	74

<sup>a</sup> 0.025=mole 4-Cl-C<sub>6</sub>H<sub>4</sub>-CHO=moles **2**; T=70°C

<sup>b</sup> 1,4-dioxane with 0.05mL of water/3mL solvent

<sup>c</sup> THF anhydrous

The results obtained are shown in Table 1. The E-acrylate was obtained in all cases as shown by PMR spectra, like in the thermal process. Therefore the ultrasound do not affect the stereoselectivity of the process catalyzed by C-200.

The ultrasounds diminish the reaction time and the necessary amount of barium hydroxide catalyst, C-200, to obtain similar yield (entries 3-7 versus entry 1). On the other hand, the sonochemical process takes place at room temperature versus the thermochemical Wittig-Horner reaction that are carried out at 70°C. So, the process is accelerated by ultrasounds like other organic processes.<sup>7</sup>

Nevertheless the necessary sonication time appears to be very short, because similar yields are obtained after 5 or 30 min. of sonication time. This fact could be explained by a very high activation of the reaction, produced by ultrasounds or by a simple electron transfer catalysis (ETC) initiated by ultrasounds. Evidence of the radical process has been shown by Olah et al. in the thermal Wittig reaction with hindered ketones and phosphonium ylids<sup>8</sup>, by ourselves in the Cannizzaro reaction catalyzed by C-200 under sonochemical conditions<sup>5,9</sup>, and by Chanon in a recent review<sup>10</sup>.

The amount of solid catalyst slightly influences the yield. No reaction is observed without C-200 (entry 2) under sonochemical conditions but on increasing the amount of catalyst from 50 mg to 200 mg the yield only increases by 10%. (entries 8-11)

The dielectric constant of 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) or DMF (99%) (entry 15)<sup>11</sup>. This fact was observed in the thermal process and in the Cannizzaro reaction catalyzed by C-200 in presence of ultrasounds<sup>5</sup>. It was related to a ETC mechanism.<sup>9</sup>

The presence of water in the solution, dramatically increases the yield (entry 12 versus 11 and 13 versus 14). This fact was observed in the thermochemical Wittig-Horner reactions catalyzed by C-200<sup>4</sup> or by other commercial catalysts like  $K_2CO_3$ <sup>12,13</sup>. There is a controversy with respect to the activating role of water. Some workers say that water destroys the 1,2-oxaphosphetane intermediate by a process similar to that of crown ethers<sup>14,15</sup> but others say that the activating role of water is related to the crystalline structure of solids which is stabilized by the water in the medium. We think that the later one will be valid because we have proved in a previous paper<sup>4</sup> that the water stabilizes the  $Ba(OH)_2 \cdot H_2O$  structure of C-200, responsible for the catalytic activity in the thermal Wittig-Horner process.

The nature of aromatic ring substituents is important. The presence of strong electron-donating group (entry 19), diminishes the electrophilicity of C=O and the yield also diminishes. Electron-withdrawing groups favour the process (entries 3 and 20). Nevertheless these effects are less important than in the thermochemical process catalyzed by C-200.<sup>4</sup>

Thus, ultrasound give a very good synthetic method to E-acrylates under interfacial solid-liquid conditions in the presence of C-200.

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