



Synthesis in high vacuum and synthesis in the absence of solvent. Two new options for obtaining β -styryl phosphonic acid

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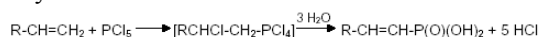
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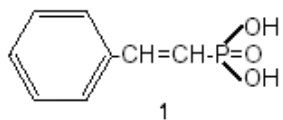
Introduction

Terminal olefins allow the addition of phosphorus pentachloride to give substances that can be considered as phosphonic acid chlorides. Hydrolysis transforms the addition products in phosphonic acids, usually with simultaneous dehydrochlorination.



The initial addition reaction takes place under mild conditions, in an inert solvent, and in 40 to 50% yields of α,β -unsaturated phosphonic acid.

Our interest in obtaining styryl phosphonic acid (**1**) lies in its properties as chelating (Rizkalla and Zaki, 1979; Dietze *et al.*, 1987), ion sequestrant (Balachandran *et al.*, 1987), surfactant (Schulz *et al.*, 1996), additive in paper industry (Elfers, 1995), corrosion inhibitor (Mikroyannidis, 1987) and forming polymers (Hurt *et al.*, 1990).



Search for alternative ways of preparing (**1**) led to establish the best reaction conditions for four different procedures: (a) microwave irradiation; (b) sonication; (c) solvent-free synthesis; (d) synthesis in high vacuum. Results were compared with those obtained by the conventional method.

One of the most significant advantages of microwave irradiation (since 1986 used in organic chemistry) (Loupy *et al.*, 1998) is the decrease in reaction times mainly due to an electromagnetic effect that causes heating by convection.

The action of ultrasound in chemical reactions, by contrast, is associated with the phenomenon of cavitation (Masson, 1990), promoting molecular activation by pressure and heat, in localized points of the reactants' mixture, in very short periods of time.

In the synthesis without solvent, good yields are achieved with lower costs; the technique is safer, less aggressive towards the environment, and may increase the reactivity of the reactants because of the absence of dilution (Loupy *et al.*, 1992).

One of the most appreciated synthesis particularities under conditions of high vacuum is that ensures the purity of the reactants in the reaction medium and ensures the quality of the products due to the absence of oxygen or external contaminants. The design and the construction of the reactor to be used for each type of experience, is part of the technique, but it contributes to make quantitative the process thus resulting in actual yields.

Methodology

The induction of organic reactions by microwaves consists in irradiating reactants, with a limited amount of high boiling point solvent, in open containers.

Sonication applied to chemical processes requires at least one of the components in liquid phase.

Without taking temperature into account, and considering fixed power in the microwave oven (2450 Hz/900 w) and fixed frequency in the sonicator (50-60 Hz), *time* was the reaction variable that was adjusted to achieve the best results.

Thus, in the *synthesis by microwaves*, it was observed that: (1) the shortest irradiation time was achieved with benzene as solvent and a water-receptor bath; (2) the intermittent



irradiation mode minimized the formation of by-products; (3) the reaction was incomplete for times less than 1 minute.

In *ultrasonic synthesis* was evident that: (1) the best result is obtained at 60 minutes of sonication, with external water bath at a constant temperature (45 °C); (2) there are no changes in yield for times larger than 1 hour.

For *synthesis in the absence of solvent*, the most suitable experimental conditions were found by changing the molar relationship between reagents and the reaction temperature, without modifying the prefixed times of the traditional technique. Thus, it was determined that: (1) stirring the mixture of reactants at room temperature leads to an incomplete reaction; (2)

the reaction time can be diminished if it is worked with a molar excess of styrene, with a temperature of 60 °C and stirring.

In *synthesis in high vacuum*, a single test was performed, under the same conditions as those of the conventional procedure (Table 1). The technique itself is an innovation because there are no references in the international literature on its use in the preparation of this type of compounds.

For comparison, the result of variables' optimization for each investigated method is shown in Table 1.

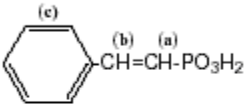
The spectroscopic characterization of β -styryl phosphonic acid (mp: 158-160 °C) is summarized in Table 2.

Table 1.

| Reaction conditions | Conventional method ^a | Non-conventional methods | | | |
|---------------------|------------------------------------|------------------------------------|------------------------------------|--------------|------------------------------------|
| | | Microwaves | Ultrasound | Solvent-free | High-vacuum |
| Solvent (ml) | C ₆ H ₆ (50) | C ₆ H ₆ (50) | C ₆ H ₆ (50) | - | C ₆ H ₆ (50) |
| Temperature (°C) | Room | Boiling | 45 | 60 | Room |
| Time (min) | 120 | 2 ^d | 30 | 60 | 120 |
| Yield (%) | 58 | 33 | 56 | 72 | 86 |

a- 1:2 Styrene/PCl₅ molar ratio; b- 3:1 Styrene/PCl₅ molar ratio; c- With receptor water bath; d- Intermittent irradiation mode.

Table 2. NMR signals (: ppm) and IR (: cm⁻¹) of β -styryl phosphonic acid.

| | ¹ H-RMN ¹ | ¹³ C-RMN ¹ | IR ² |
|---|---|----------------------------------|---|
|  | (a) 6.48 (1H), dd J^3_{HH} , J^2_{HP} | (a) 119.43 | 3000-2200 $\nu_{\text{OH(P-OH)}}$ |
| | (b) 7.20 (1H), dd J^3_{HH} , J^3_{HP} | (b) 143.39 | 1650-1550 $\nu_{\text{C=C}}$ |
| | (c) 7.30 – 7.60 (5H), m | (c) 121.87-135.79 (4 signals) | 1130 $\nu_{\text{P-O}}$ 1000 $\nu_{\text{P-O}}$ 710 and 650 $\gamma_{\text{-CH}}$ |

1. Solvent : DMSO-d₆; 2. KBr (1%); J^2_{HP} : 30 Hz; J^3_{HP} : 20Hz; J^3_{HH} : 14 Hz;
^a calculated =CH-PO₃H₂: 116.5; =CH-C₆H₅: 144.7.



Results and conclusions

In the reaction induced by microwaves, the lowest yield is obtained, with reproducibility of results, if the total irradiation time is of 2 minutes and intermittently. The advantage of this method is that it reduces reaction time, and the amount of solvent.

In the reaction induced by ultrasound, yield is comparable to that obtained in the conventional method. Whereas temperature is much higher, this disadvantage is compensated by the decrease in reaction time.

The achieved yield by solvent-free synthesis improves appreciably. Even when it is necessary to heat, the most obvious advantage is given by altering the molar relationship of reactants: the amount of PCl_5 is minimized, and the excess of styrene (which replaces the solvent) can be easily separated by extraction. The synthesis under high vacuum conditions is that of the highest yield, without heating requirements. The purity of the final product is optimal, thus recrystallization being unnecessary.

Of the four procedures, the latter two seem to be the most suitable for obtaining this type of α, β -unsaturated phosphonic acids. On the other hand, considering that the synthesis in high vacuum is propitious for anionic polymerizations, this technique opens the possibility to explore polymerization conditions for β -styryl phosphonic acid.

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