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ORGANIC SYNTHESES WITH FUNCTIONALIZED POLYMERS:

II. WITTIG REACTION WITH POLYSTYRYL-*p*-DIPHENYLPHOSPHORANES.

F. Camps, J. Castells, J. Font and F. Vela

Instituto de Química. Centro de Investigación y Desarrollo. Patronato "Juan de la Cierva". Jorge Girona Salgado s/n. Barcelona-17. Spain.

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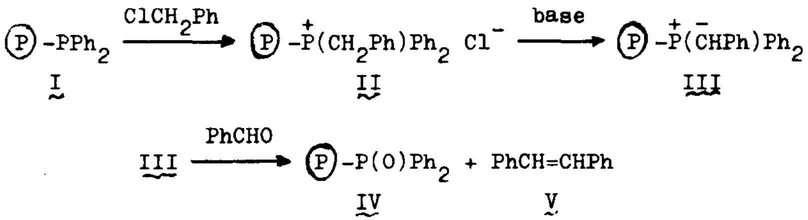
IN connection with a research program undertaken in this laboratory[1] to investigate the scope of the solid phase method in general organic synthesis, we describe herein the results obtained in the Wittig reaction with polymeric ylide III prepared from polystyryl-*p*-diphenylphosphine[2,3] (I) (Scheme 1).



$$\underset{\mathbf{I}}{\textcircled{P}\text{-}PPh_2} \xrightarrow{ClCH_2Ph} \underset{\mathbf{II}}{\textcircled{P}\text{-}\overset{+}{P}(CH_2Ph)Ph_2\ Cl^-} \xrightarrow{\text{base}} \underset{\mathbf{III}}{\textcircled{P}\text{-}\overset{+}{P}(\overset{-}{C}HPh)Ph_2}$$

$$\mathbf{III} \xrightarrow{PhCHO} \underset{\mathbf{IV}}{\textcircled{P}\text{-}P(O)Ph_2} + \underset{\mathbf{V}}{PhCH{=}CHPh}$$

Scheme 1

The substrate I here employed was a copolymer of 3:1 styrene:*p*-styryldiphenylphosphine[4], containing 2% divinylbenzene as cross-linking agent, prepared after the pearl technique using water as dispersant and azoisobutyronitrile as radical source. I, obtained in the form of white opaque beads was thoroughly washed with water, dioxane, ether and benzene, and dried over P_2O_5 under high vacuum. Its ir spectrum revealed the presence of aromatic *p*-substitution and its elementary analysis exhibited the expected percentage of phosphorus.

Treatment of I (60-140 mesh) with benzyl chloride without solvent afforded *p*-polystyryldiphenyl-benzyl-phosphonium chloride (II) in practically quantitative yield (P, Cl analysis).

A suspension of II in THF was reacted with a stoichiometric amount of base, then an equivalent amount of benzaldehyde was added, and the mixture was allowed to react overnight. The resulting polymeric phosphine oxide IV was removed by filtration and washed thoroughly with THF. The filtrate was evaporated at reduced pressure and the residue chromatographed on silica gel to give variable quantities of *cis*-,*trans*-stilbene (V), benzyl alcohol, benzoic acid and unreacted benzaldehyde. A 40% yield of V was obtained when potassium t-butoxide was used as base and 60% with sodium hydride.

No substantial yield improvement was observed when an excess of base or aldehyde was used. The removal of the excess of certain bases, like butyllithium , by filtration and repeated washings, previous to the addition of the aldehyde, was difficult, whereby in these cases an increase in the amount of side products, benzyl alcohol and benzoic acid, was observed. The presence of base can promote the formation of these products by a Cannizaro reaction that can compete with the Wittig reaction[5].

Further work is in progress to improve the results obtained and to make them comparable to those reported for the conventional Wittig procedure[6].

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