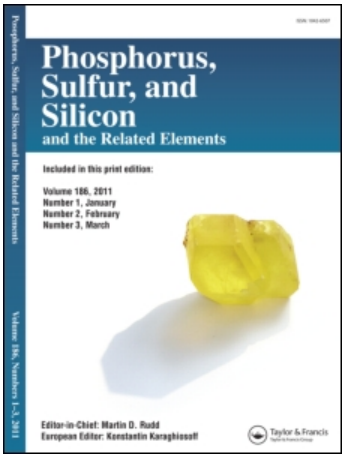

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Studies on the Wittig Reaction (IV) A Stereoselective Synthesis of the Insect Sex Pheromone of Laspeyresia pomonella, E,E,-8,10-Dodecadien-1-ol

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Studies on the Wittig Reaction (IV)
A Stereoselective Synthesis of the Insect Sex Pheromone of Laspeyresia pomonella, E,E,-8,10-Dodecadien-1-ol

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The Wittig reaction was widely used in the synthesis of natural products particularly in the area of insect pheromone synthesis. But unfortunately when a moderated triphenylphosphonium ylid is used, the resultant compound is a impractical E,Z mixture. For instance, the title compound was once synthesized by the Wittig reaction between butenylidene triphenylphosphorane and 8-oxo-octanoate, followed by hydrolysis and reduction. The product was a mixture containing 75% 8E,10E isomer and 25% 8Z,10E isomer. Recently we have reported that a simple change in phosphorus substituents from $Ph_3P{=}CHR$ to $Ph_2(R'CH_2)P{=}CHR$ (R'=alkenyl or H) dramatically increases the proportion of E olefin formed from moderated ylides (R=alkenyl) and aliphatic aldehydes. According to this fact, here we report a stereoselective synthesis of E,E,-8,10-dodecadien-1-ol from butenylidene methyl diphenylphosphorane and 8-oxo-octanoate in the absence of lithium salt (SchemeI). After hydrolysis and reduction, the title compound containing 94.7% 8E,10E isomer was obtained. This approach affords a convenient synthesis for insect pheromones bearing a E,E, conjugated diene moiety. This experimental fact once again illustrates the stereochemistry of allylic diphenylphosphonium ylid is quite different from the corresponding triphenylphosphonium one.

$$Ph_2(CH_3)\overset{\oplus}{P}CH_2CH{=}CHCH_3\,I^{\ominus} \xrightarrow[N_2,\ -20^{\circ}C]{t\text{-}BuOK\text{-}THF} Ph_2(CH_3)P{=}CHCH{=}CHCH_3$$

$$\xrightarrow{OHC(CH_2)_6COOMe} CH_3CH{=}CHCH{=}CH(CH_2)_6COOMe \xrightarrow[\text{②}\ KOH\text{-}EtOH,\ \text{③}\ LiAlH_4\text{-}Et_2O]{} CH_3CH{=}CHCH{=}CH(CH_2)_6CH_2OH$$

(Scheme I)

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