Stereoselective Synthesis of (*E*)- and (*Z*)-Allylphosphonium Salts by Palladium-Catalyzed Addition of Phosphine to Allene

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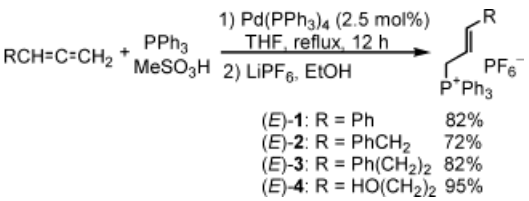
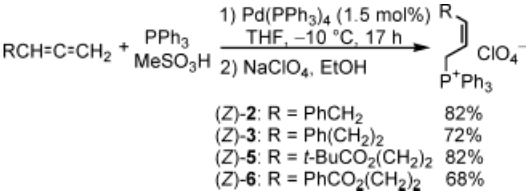
The (*E*)-allylphosphonium salt, used in the Wittig reaction, is generally synthesized by the substitution of an allyl halide with triphenylphosphine.[1] Use of allyl alcohol, allyl acetate, or nitropropene in the presence of palladium catalyst is also reported.[2] If the salt can be prepared by the addition of phosphine to an unsaturated compound, the scope of the methodology would be considerably broadened. Previously, we reported the transition metal-catalyzed addition reaction of phosphine with methanesulfonic acid to alkyne.[3] Described here is the addition reaction to allene, which is catalyzed by palladium. A notable aspect of this method is that it can control the stereochemistry of the phosphonium salt and that (*Z*)-allylphosphonium salts have been obtained for the first time.

1-Phenyl-1,2-propadiene is treated with an equimolar amount of triphenylphosphine and methanesulfonic acid in the presence of $Pd(PPh_3)_4$ (2.5 mol%) in refluxing THF for 12 h. The counteranion is exchanged with $LiPF_6$, and recrystallization gives (*E*)-(3-phenyl-2-propenyl)triphenylphosphonium hexafluorophosphate (*E*)-**1** in 82% yield. The phosphine attacks at the terminal carbon atom of the allene regioselectively. The (*E*)-stereochemistry of the double bond is determined by the H-H coupling constant, $^3J_{H-H}$ = 16.0 Hz. Methanesulfonic acid and the palladium catalyst are essential for the addition reaction, and no reaction occurs in their absence. Various terminal allenes react with triphenylphosphine to give the corresponding (*E*)-adducts in high yields with high regio- and stereoselectivities (Scheme 1). While small amounts of (*Z*)-isomers are detected in the synthesis of the (4-phenyl-2-butenyl)triphenylphosphonium salt **2** and the (5-phenyl-2-pentenyl)triphenylphosphonium salt **3**, isomerically pure (*E*)-**2** and (*E*)-**3** are obtained by recrystallization of the PF_6 salts.



Scheme 1.

When the reaction is conducted at –10 °C, the observed stereoselectivity of the reaction is opposite to that of the reaction under refluxing conditions (Scheme 2). Treatment of an equimolar mixture of 4-phenyl-1,2-propadiene, triphenylphosphine, and methanesulfonic acid with $Pd(PPh_3)_4$ (1.5 mol%) in THF at –10 °C for 17 h yields (*Z*)-**2** predominantly with a small amount of the (*E*)-**2** in a ratio of 13 : 1. The isomerically pure (*Z*)-**2** is obtained by recrystallization of the perchlorate salt in 82% yield. The (*Z*)-stereochemistry of the double bond is determined by NOE spectroscopy. The stereoselective synthesis of (*Z*)-allylphosphonium salts was not known previously. Isolated (*Z*)-**2** isomerizes to (*E*)-**2** when treated with methanesulfonic acid and $Pd(PPh_3)_4$ in THF under reflux.



Scheme 2.

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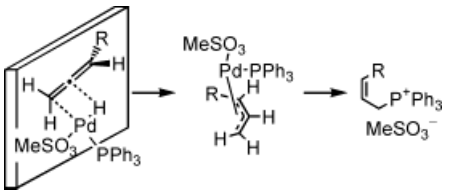
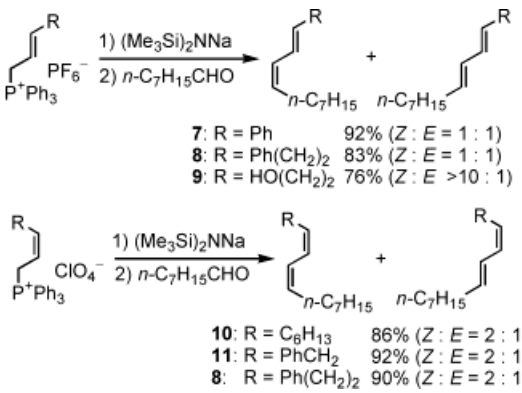
The mechanism of this reaction probably involves hydropalladation (Scheme 3). In order to minimize the steric repulsions, the palladium-hydride complex approaches the C=CH_2 moiety of the allene in the *anti*-Markovnikov mode from the side opposite to the substituent. This addition gives a π-allylpalladium complex with the (*Z*)-configuration,[4] which is converted to the (*Z*)-product by carbon-phosphine bond formation with regeneration of the Pd(0) catalyst.



Scheme 3.

Some uses of the allylphosphonium salts in the Wittig synthesis are shown in Scheme 4. This may be of interest since reactions of (*Z*)-allylidenephosphorane have not been studied before. The Wittig reaction of (*E*)-allylphosphonium salts is notorious for not being stereoselective.[5] Accordingly, the reaction of (*E*)-allylphosphonium salts with sodium hexamethyldisilazide in THF followed by treatment with octanal gives *ca.* 1 : 1 mixtures of (*E*,*E*)-isomers and (*E*,*Z*)-isomers. As an exception, (*E*)-**4** shows high (*E*,*Z*)-selectivity. Reaction of the (*Z*)-allylphosphonium salt again gives a comparable mixture of the (*Z*,*E*)-isomer and (*Z*,*Z*)-isomers. The stereochemistry of the double bond is determined by ^{1}H-NMR coupling constant. The Wittig reactions of (*E*)- and (*Z*)-allylphosphonium salts exhibit a similar behavior, at least under the present reaction conditions: while the stereochemistry of allylphosphonium salt is retained, a mixture of isomers is obtained with regard to the newly formed double bond.



Scheme 4.

Experimental Section

Typical Procedure

Under an argon atmosphere, a mixture of $Pd(PPh_3)_4$ (18 mg, 1.5 mol%), triphenylphosphine (1 mmol, 262 mg), 4-phenyl-1,2-propadiene (1 mmol, 130 mg), and methanesulfonic acid (96 mg, 1 mmol) in THF (2 mL) was stirred at –10 °C for 17 h. After being stirred with a small amount of decolorizing charcoal for 30 min, the insoluble materials were removed by filtration. The solution was concentrated under reduced pressure, and the residue was washed with ether. After dissolving the crude product in ethanol (2 mL), sodium perchlorate (2 mmol, 244 mg) was added, and the mixture was stirred at room temperature for 1 h. The precipitated solid was collected by filtration. To the solid was added $CHCl_3$, and insoluble lithium methanesulfonate was removed by filtration. The solution was concentrated, and the residue was recrystallized from acetone and ether (2 : 1) yielding (*Z*)-**2** (403 mg, 82%) as a colorless solid with m. p. 180.0–181.0 °C.

Acknowledgments

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