Supporting Information

Oxidative Heck-Type Reaction Involving Cleavage of a Carbon–Phosphorus Bond of Arylphosphonic Acids (JA026758V)

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General Methods Melting points were obtained on a Yanako MP-50929 melting point apparatus and are uncorrected. ^1H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in CDCl_3 as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. ^{19}F and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer. IR spectra were determined on a JASCO IR-810 spectrometer. Mass spectra were determined on a JEOL JMS-700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merk Silica gel 60F₂₅₄. Column chromatography was done with silica gel (Wakogel 200 mesh). The analyses were carried out at the Elemental Analysis Center of Kyoto University. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Experimental

Preparation of Aryl- and Alkenylphosphonic Acids

Diethyl arylphosphonates¹ and diethyl (*E*)- β -styrylphosphonate² were prepared according to the reported procedures. Under argon atmosphere, phosphonic ester (10 mmol) was treated with bromotrimethylsilane (30 mmol) in MeCN (10 mL) for 3 h at room temperature.³ Most of the solvent was evaporated under reduced pressure. Et₂O (10 mL) and water (0.5 mL) was added, and the mixture was vigorously stirred for 0.5 h at room temperature. Solvent was removed under reduced pressure. Washing the resultant white solid with pentane and drying under reduced pressure provided the corresponding phosphonic acid in good yields.

Reaction of Arylphosphonic Acids with Alkenes under Palladium Catalysis

Arylphosphonic acid (0.3 mmol), Pd(OAc)₂ (3.4 mg, 0.015 mmol), and Me₃NO·2H₂O (100.0 mg, 0.9 mmol) were placed in a flask, and argon was flushed. Dioxane (3 mL), alkene (0.36 mmol), and tetrabutylammonium fluoride (0.6 mL, 1.0 M solution in THF, 0.6 mmol) were sequentially added, and the mixture was then stirred at 100 °C for 24 h. The mixture was diluted with ethyl acetate (10 mL), filtered with a short column of Na₂SO₄ and silica gel, and concentrated in vacuo. Purification of the residue by silica gel column chromatography afforded the desired product.

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¹ (a) Tavs, P. *Chem. Ber.* **1970**, *103*, 2428. (b) Hirao, T.; Masunaga, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 909.

² Kiddle, J. J.; Babler, J. H. *J. Org. Chem.* **1993**, *58*, 3572.

³ (a) McKenna, C. E.; Schmidhauser, J. J. *Chem. Soc., Chem. Commun.* **1979**, 739. (b) Salomon,

NMR Experiment

In a vial, phenylphosphonic acid was mixed together well with varying amounts of TBAF in 1,4-dioxane at room temperature. The homogeneous solution was transferred into an NMR tube under air at room temperature. A glass capillary containing C_6D_6 was then inserted into the NMR tube for locking.

Figure 1. ^{31}P and ^{19}F NMR spectra of phenylphosphonic acid in dioxane at 25 °C with varying amounts of TBAF.