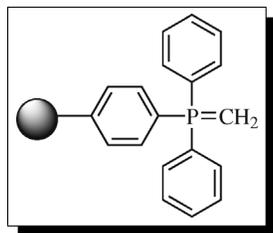


Methylenetriphenylphosphorane, Polystyrene-supported



[3487-44-3]

(a cross-linked polystyrene, 1% or 2% divinylbenzene, used as a reagent in Wittig reactions)

Alternate Names: methylenetriphenylphosphorane, polymer-supported.

Physical Data: the ylide on solid support is usually highly colored.

Solubility: this is an insoluble polymer-bound reagent that is incompatible with solvents that do not swell gel-type polystyrene (for example, H₂O, ethanol, isopropanol). The phosphorous ylide is usually prepared in THF and the subsequent reactions are run in the same solvent. However, the reagent is compatible with DMF, THF, DCM, benzene, and other non-acidic solvents that swell gel-type polystyrene.

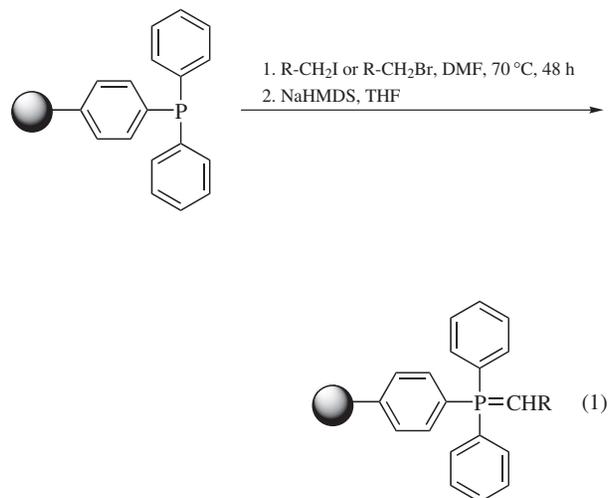
Form Supplied in: not commercially available but the precursor polystyrene-supported triphenylphosphine is commercially available in various loadings (1–3 mmol/g).

Analysis of Reagent Purity: combustion analysis, Fourier transform infrared spectroscopy. Although the ylide has not been directly analyzed, it is possible to quantify the amount of phosphonium salt by ion-exchange analysis.²

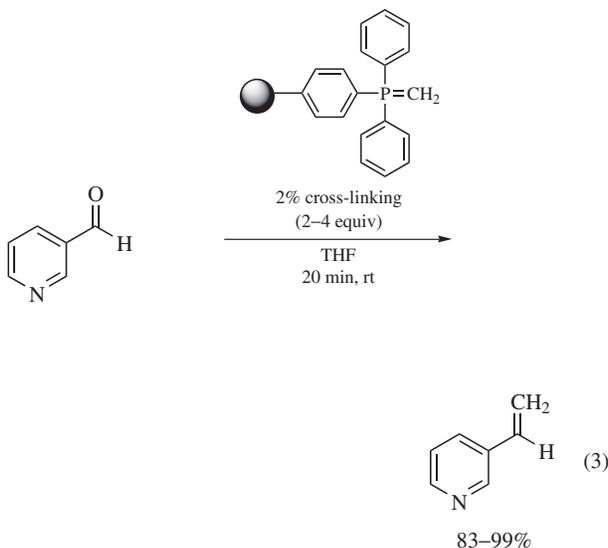
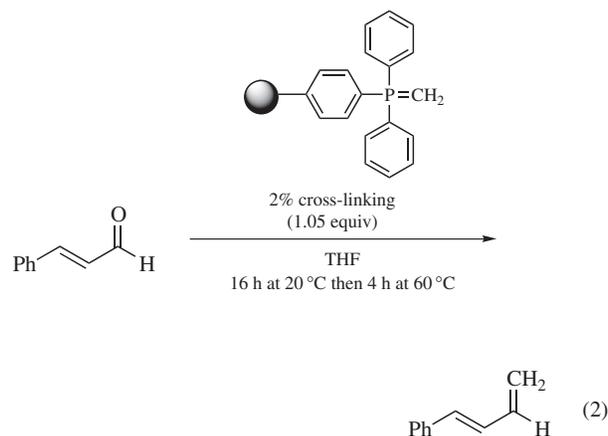
Preparative Methods: the reagent is prepared in two steps from commercially available polystyrene-supported triphenylphosphine.^{2–4} Alkylation of the phosphine followed by deprotonation of the corresponding phosphonium salt provides the ylide which is usually used directly in a subsequent reaction.

Handling, Storage, and Precautions: the reagent is prepared in situ from polystyrene-supported methyl triphenylphosphonium halide which is stable at room temperature; the ylide should be used immediately after its formation.

Preparation. All the solid-supported phosphorous ylides are prepared from the corresponding polystyrene-supported triphenylphosphine by the following general procedure (eq 1). Commercially available polystyrene-supported triphenylphosphine (1.8–3 mmol/g) is suspended in dry DMF (10–20 mL/g of polymer) and 2–4 equiv of the alkylating agent are added. The alkylation usually proceeds smoothly at 70 °C over 48 h. Filtration and extensive successive washing with toluene, dichloromethane, and diethyl ether provide a powder that is dried in vacuo. The polystyrene-supported phosphonium iodide or bromide is suspended in dry THF and deprotonated with excess base (NaHMDS solution in THF or with sodium methylsulfinylmethylide). The highly colored ylide resin is washed with dry THF to remove excess base and is used immediately in the subsequent reaction.

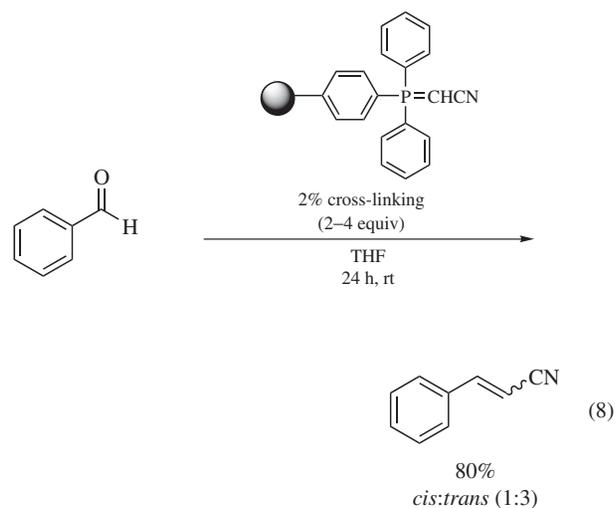
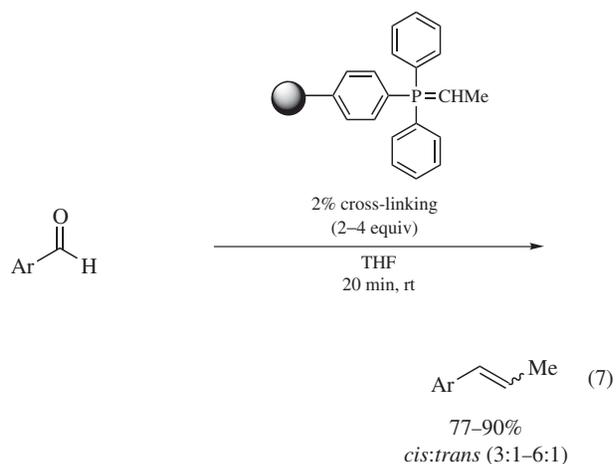
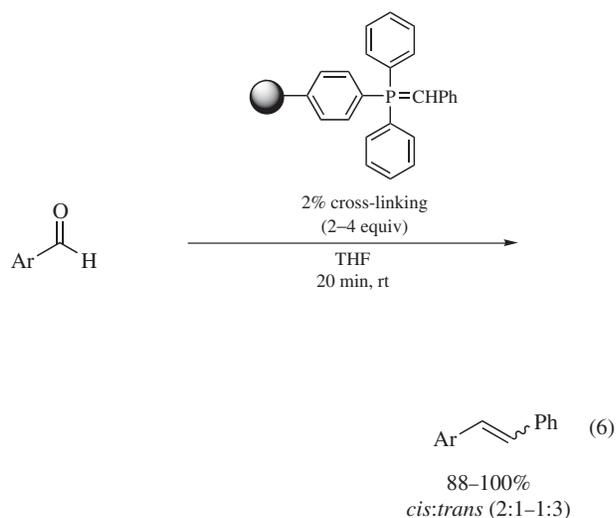
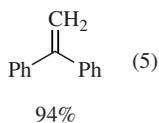
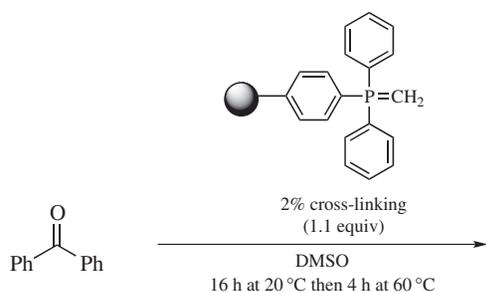
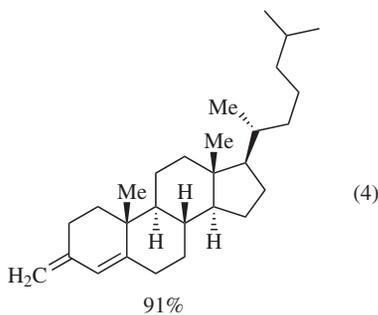
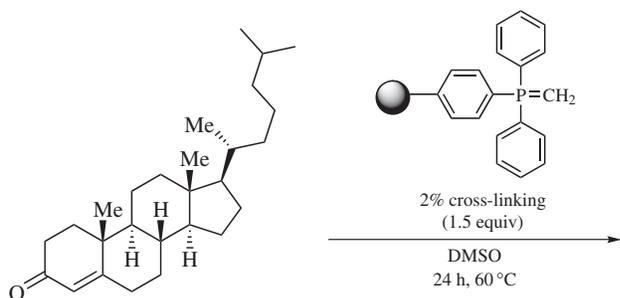


Wittig Olefination. Polystyrene-supported methylenetriphenylphosphorane has been used in the Wittig olefination reactions of aldehydes and ketones. Aldehydes are converted to terminal alkenes in high yields in THF using either the ylide prepared with NaCH₂S(O)CH₃ (eq 2)² or NaHMDS (eq 3)⁴ as the base. The reaction proceeds very well, and usually only a slight excess of ylide is required.

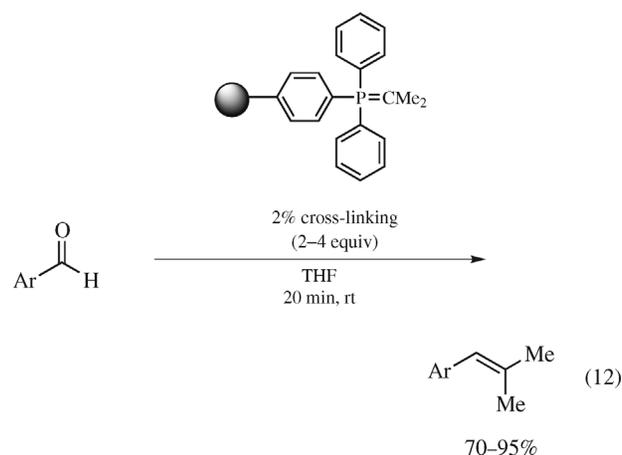
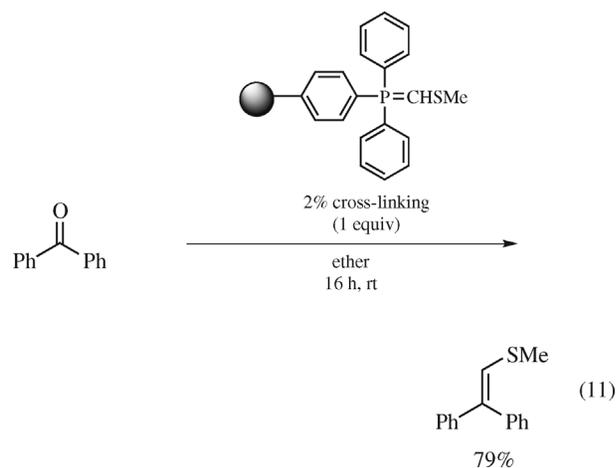
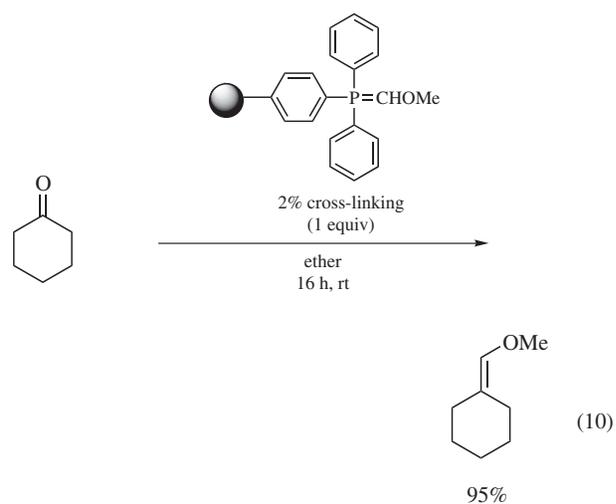
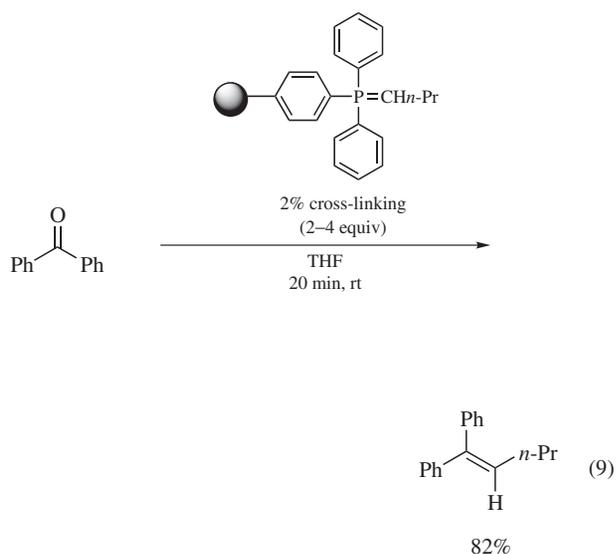


Ketones also react with polystyrene-supported methylenetriphenylphosphorane to generate the 1,1-disubstituted alkenes in high yields (eqs 4 and 5). In these cases, higher temperatures and longer reaction times are usually necessary.

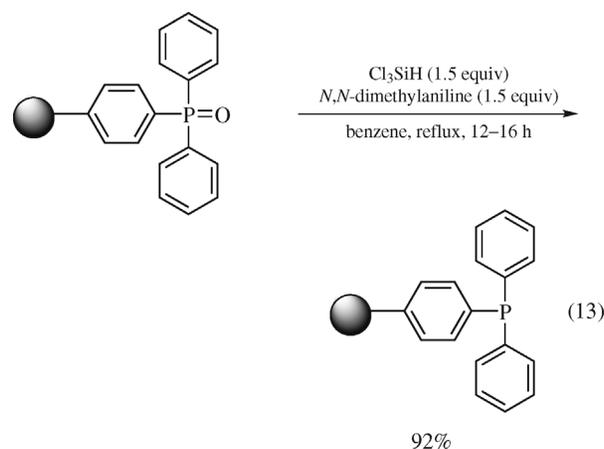
Substituted Ylides. It is also possible to prepare α -substituted ylides by the procedure shown in eq 1.⁵ Primary alkyl halides (2–4 equiv of iodides or bromides) react smoothly with polystyrene-supported triphenylphosphine to generate the corresponding phosphonium salt that can be deprotonated with sodium hexamethyldisilazide to generate the ylide.⁴ Deprotonation under phase transfer conditions has been reported.⁶ Both aldehydes and ketones react with alkyl substituted ylides to generate di- or trisubstituted alkenes in good yields (eqs 6–9).^{2,4,7}



The *cis:trans* ratio is comparable to the one found when the reaction is carried out under homogeneous conditions. Several other ylide reagents have been prepared to provide access to vinyl ethers and thioethers.⁸ α -Methoxymethyl- and α -methylthiomethylphosphonium chloride are deprotonated with phenyllithium in ether and the subsequent addition of aldehydes and ketones provides access to vinyl ethers and thioethers in good yields (eqs 10 and 11).



Recovery of Polystyrene-supported Triphenylphosphine. The by-product of the olefination reaction, polystyrene-supported triphenylphosphine oxide, can be recycled into polystyrene-supported triphenylphosphine upon treatment with trichlorosilane and *N,N*-dimethylaniline (eq 13).²



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It is also possible to alkylate secondary alkyl iodides and react their corresponding ylides with aldehydes (eq 12).⁴