

ittig Reagei

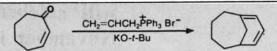
Wittig reagents1-4 have proven to be a very important class of synthetic tools in organic chemistry. Reaction with carbonyl groups leads to olefins, vinyl halides, vinyl ethers, esters, ketones and many other compounds depending upon the Wittig reagent used.

Cyclopropyltriphenylphosphonium bromide or (3bromopropyl)triphenylphosphonium bromide react with carbonyl compounds in the presence of a base to yield the corresponding cyclopropylidene derivatives.5

Reaction of α-hydroxymethylene ketones with (carbethoxymethylene)triphenylphosphorane gives α -methylenesubstituted ketones.6

Schweizer's Reagent, vinyltriphenylphosphonium bromide, has been used in the synthesis of a variety of heterocyclic compounds.7 It has also been employed as a dienophile and the resulting cycloadduct used as a Wittig reagent.8

Highly strained bridgehead dienes have been prepared9 from α,β -unsaturated ketones and allyltriphenylphosphorane via a Michael-type addition followed by an intramolecular Wittig reaction.



The ylides derived from alkoxyphosphonates have been used for the same type of olefination as the phosphoranes. Representative reactions of diethyl (cyanomethyl)phosphonate,10 diethyl (ethylthiomethyl)phosphonate11 and dimethyl (2-oxoheptyl)phosphonate (used in prostaglandin synthesis) are as follows:

$$\{ \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \\ R_{z} \\ \downarrow = 0 \end{array} + \underbrace{(EtO)_{z}PCH_{z}CN} \xrightarrow{NaH} \{ \begin{array}{c} \downarrow \\ \downarrow \\ \downarrow \\ R_{z} \\ \downarrow = 0 \end{array} + \underbrace{(EtO)_{z}PCH_{z}SEt} \xrightarrow{BuLi} \begin{array}{c} R_{1} \\ \downarrow \\ R_{z} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{z} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{z} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{z} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{z} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{z} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ R_{2} \\ \downarrow = 0 \end{array} + \underbrace{(CH_{z}O)_{z}PCH_{z}CO(CH_{z})_{z}CH_{z}} \xrightarrow{NaH} \begin{array}{c} R_{1} \\ L_{2} \\ L_{$$

A partial list of our wide spectrum of phosphoranes, phosphonates, phosphonium halides and some of their deuterated analogs is shown below.

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