

Organophosphorus Intermediates

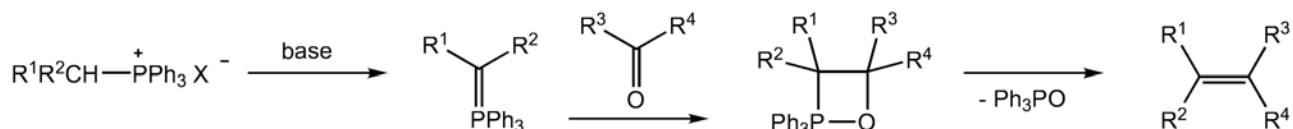


The Alfa Aesar Catalogue includes a wide range of organophosphorus compounds. This section groups together organophosphorus intermediates from the Catalogue which are capable of participating in carbon-carbon bond forming reactions via α -phosphorus-stabilised anions or ylides and provides a brief outline of their chemistry.

Phosponium salts and phosphoranes

Phosponium salts, formed by alkylation of triaryl or trialkyl phosphines, have applications, for example as metal complexing agents or phase-transfer catalysts, but of greatest interest in synthesis are those which can be deprotonated to give ylides (alkylidenephosphoranes). The reaction of these ylides with aldehydes or ketones, first reported by Wittig in 1953,¹ continues to be among the most valuable and general methods for regiospecific alkene formation. Mechanistically, the Wittig reaction is known to involve a four-center (1,2-oxaphosphetane) intermediate and the strength of the P=O bond (typical² bond energy 134 kcal mol⁻¹; 560 kJ mol⁻¹) is the driving force for alkene formation, with elimination of the phosphine oxide (Scheme 1). There has been much debate³ over the possible initial formation of an ionic (betaine) species which was then thought to cyclize to the oxaphosphetane, but evidence for such betaines appears to be lacking, and the likelihood of a cycloaddition mechanism has been postulated by Vedejs and others.⁴

Scheme 1



The mechanism of the reaction and stereochemistry of the alkene produced have been discussed in depth in the reviews of Vedejs and Peterson.^{5,6}

The stereochemical outcome of the Wittig reaction depends on many factors including the base and solvent system. For example, with potassium carbonate as base, simple alkyl phosphonium salts give predominantly (*E*)-alkenes in the protic solvent methanol, but predominantly (*Z*)-isomers in the aprotic solvent dioxane.⁷ However, many other factors influence the stereochemistry of the alkene including temperature, phosphorane structure and presence or absence of salts or other additives. The situation is undoubtedly a complex one and for any given example there are often a number of competing effects. In general, however, stabilized anions tend to give the (*E*)-alkene, whereas non-stabilized anions have a greater tendency to give the (*Z*)-alkene.

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The influence of the so-called "lithium salt effect" on the (*E*):(*Z*) ratio has been much studied. In non-polar media, addition of, for example, lithium iodide increases the (*E*):(*Z*) ratio, whereas under "salt-free" conditions (using non-lithium bases) the (*Z*)-isomer is favoured.⁸ Salt-free ylides can be isolated as crystalline solids, even in unstabilized cases, using sodium or potassium amide in THF as the base.⁹ They can also be generated by complexation of the metal ions with crown ethers: in THF, the (*Z*)-alkene again predominates, but in dichloromethane, the major product is the (*E*)-isomer.¹⁰ The lithium salt effect on stereochemistry has also been found to be strongly concentration dependent.¹¹ Carrying out the reaction under conditions of daylight lamp irradiation has been shown to maximize the yield of the (*E*)-isomer.¹²

Typical experimental protocols for the Wittig reaction are well described in several sources.¹³⁻¹⁶ Numerous reviews and monographs covering various aspects of the reaction have also been published.^{5,6,15-26,38}

Alfa Aesar offers the following alkyl triphenylphosphonium salts, $RPPH_3^+ X^-$, which are classified according to the nature of the alkyl group, R:

α -Unsubstituted primary alkyl phosphonium salts

Ylides without stabilizing substituents are generally the most reactive with a wide range of aldehydes and ketones:

- | | |
|---|---|
| B23040 4-Bromobutyl)triphenylphosphonium bromide | A11021 (1-Decyl)triphenylphosphonium bromide |
| B24833 (2-Bromoethyl)triphenylphosphonium bromide | L04909 [2-(1,3-Dioxan-2-yl)ethyl]triphenyl phosphonium bromide |
| A13041 (3-Bromopropyl)triphenylphosphonium bromide | A14295 (1-Dodecyl)triphenylphosphonium bromide |
| A10504 (1-Butyl)triphenylphosphonium bromide | L05911 (4-Ethoxycarbonylbutyl)triphenyl phosphonium bromide |
| A12023 (4-Carboxybutyl)triphenylphosphonium bromide | A12190 Ethylenebis(triphenylphosphonium bromide) |
| B25609 (2-Carboxyethyl)triphenylphosphonium chloride | B23096 Ethyltriphenylphosphonium bromide |
| B20588 (5-Carboxypentyl)triphenylphosphonium bromide | B23015 Ethyltriphenylphosphonium chloride |
| A19302 (3-Carboxypropyl)triphenylphosphonium bromide | A17533 Ethyltriphenylphosphonium iodide |
| L00538 (2-Chloroethyl)triphenylphosphonium bromide | B25424 (1-Heptyl)triphenylphosphonium bromide |
| L01145 (Cyclopropylmethyl)triphenylphosphonium bromide | A15180 (1-Hexadecyl)triphenylphosphonium bromide |
| L00917 (2-Dimethylaminoethyl)triphenyl phosphonium bromide | A13826 (1-Hexyl)triphenylphosphonium bromide |
| | L00679 (2-Hydroxyethyl)triphenylphosphonium bromide |
| | A17881 Isobutyltriphenylphosphonium bromide |
| | A11322 Isopentyltriphenylphosphonium bromide |
| | A15878 Methyltriphenylphosphonium bromide |
| | A15644 Methyltriphenylphosphonium iodide |
| | L02341 (1-Nonyl)triphenylphosphonium bromide |

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α -Unsubstituted primary alkyl phosphonium salts con't

- L02412** (1-Octyl)triphenylphosphonium bromide
L00997 Pentamethylenebis(triphenylphosphonium bromide)
L01950 (4-Pentenyl)triphenylphosphonium bromide
A12534 (1-Pentyl)triphenylphosphonium bromide
A12669 (3-Phenylpropyl)triphenylphosphonium bromide
B22421 (4-Phthalimidobutyl)triphenylphosphonium bromide
B25034 (6-Phthalimidohexyl)triphenylphosphonium bromide

- A12968** (1-Propyl)triphenylphosphonium bromide
L04311 (1-Tetradecyl)triphenylphosphonium bromide
A14214 Tetramethylenebis(triphenylphosphonium bromide)
B25165 Trimethylenebis(triphenylphosphonium bromide)
L00788 (Trimethylsilylmethyl)triphenylphosphonium iodide

RELATED PRODUCT

- A18599** Methyltriphenylarsonium iodide
B25102 Cyclopropyltriphenylphosphonium bromide
A12881 Isopropyltriphenylphosphonium iodide

Secondary alkyl phosphonium salts

- L01532** (2-Butyl)triphenylphosphonium bromide
A14298 Cyclohexyltriphenylphosphonium bromide
A14647 Cyclopentyltriphenylphosphonium bromide

Allylic and benzylic phosphonium salts

Allyl and benzyl groups confer some stability on the ylide but not usually sufficient to permit its isolation. These ylides usually react with both aldehydes and ketones:

Allylic phosphonium salts

- A14490** Allyltriphenylphosphonium bromide
A16012 Allyltriphenylphosphonium chloride
L00534 2-Butene-1,4-bis(triphenylphosphonium chloride)
L00502 (2-Butenyl)triphenylphosphonium chloride

- A16220** Cinnamyltriphenylphosphonium bromide
L00513 (3,3-Dimethylallyl)triphenylphosphonium bromide
A13173 (2-Methylallyl)triphenylphosphonium chloride
A12753 Propargyltriphenylphosphonium bromide

Benzylic phosphonium salts

- B22299** Benzhydryltriphenylphosphonium chloride
B24567 Benzyltriphenylphosphonium bromide
A14034 Benzyltriphenylphosphonium chloride
A15220 (4-Bromobenzyl)triphenylphosphonium bromide
A17563 [4-(Bromomethyl)benzyl]triphenyl phosphonium bromide
A11769 (4-Chlorobenzyl)triphenylphosphonium chloride
L12187 (4-Cyanobenzyl)triphenylphosphonium chloride
A17651 (2,6-Dichlorobenzyl)triphenylphosphonium chloride
L08304 (4-Ethoxybenzyl)triphenylphosphonium bromide

- L00794** (9-Fluorenyl)triphenylphosphonium bromide
A10852 (4-Fluorobenzyl)triphenylphosphonium chloride
L00778 (2-Hydroxybenzyl)triphenylphosphonium bromide
L00594 (4-Methoxybenzyl)triphenylphosphonium chloride
L09423 (4-Methoxycarbonylbenzyl)triphenyl phosphonium bromide
B21729 (4-Methoxycarbonylbenzyl)triphenyl phosphonium chloride
A10719 (2-Methylbenzyl)triphenylphosphonium chloride
A11611 (3-Methylbenzyl)triphenylphosphonium chloride

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Benzylic phosphonium salts con't

- L01562** (4-Methylbenzyl)triphenylphosphonium bromide
- A12447** (4-Methylbenzyl)triphenylphosphonium chloride
- L00666** (1-Naphthylmethyl)triphenylphosphonium chloride
- L05650** (2-Nitrobenzyl)triphenylphosphonium bromide monohydrate
- A15288** (4-Nitrobenzyl)triphenylphosphonium bromide
- L03103** o-Xylylenebis(triphenylphosphonium bromide)
- A18241** p-Xylylenebis(triphenylphosphonium bromide)
- L01334** p-Xylylenebis(triphenylphosphonium chloride)

α -Hetero substituted alkylphosphonium salts

Phosphoranes with alkoxy or alkylthio substituents on the α -carbon yield enol ethers or enol thioethers which can readily be hydrolyzed to the corresponding carbonyl compounds. In the case of α -substituted methyl phosphonium salts, this reaction sequence permits aldehyde homologation.

Alkylphosphonium salts and phosphoranes α -substituted with an electron-withdrawing group

Ylides of this type are often sufficiently stable to be isolated. The reactivity is correspondingly reduced and in general, such ylides react only with aldehydes. Reaction with ketones has been accomplished, for example by the use of microwaves.²⁷ Abstraction of a further proton from the ylide with strong base gives a carbanion which may then be sufficiently nucleophilic to react with ketones.^{28,29} In many cases we offer both the phosphonium salt and the corresponding ylide.

- L04009** (Chloromethyl)triphenylphosphonium iodide
- A18615** (Hydroxymethyl)triphenylphosphonium chloride
- A14380** (Methoxymethyl)triphenylphosphonium chloride
- L00687** (Methylthiomethyl)triphenylphosphonium chloride
- A13229** (Phenylthiomethyl)triphenylphosphonium chloride

Phosphonium salts

- B22434** Acetyltriphenylphosphonium bromide
- A14691** Acetyltriphenylphosphonium chloride
- L15165** (tert-Butoxycarbonylmethyl)triphenyl phosphonium bromide
- L12245** (tert-Butoxycarbonylmethyl)triphenyl phosphonium chloride
- A13096** (Cyanomethyl)triphenylphosphonium chloride
- A18305** (1-Ethoxycarbonylcyclopropyl)triphenyl phosphonium tetrafluoroborate
- A13023** (1-Ethoxycarbonylethyl)triphenyl phosphonium bromide
- A16347** (Ethoxycarbonylmethyl)triphenyl phosphonium bromide
- A19494** (Ethoxycarbonylmethyl)triphenylphosphonium chloride
- A15733** (Formylmethyl)triphenylphosphonium chloride
- A16301** (Methoxycarbonylmethyl)triphenyl phosphonium bromide
- A17775** (Methoxycarbonylmethyl)triphenyl phosphonium chloride
- B24845** (2-Triphenylphosphonio)propiophenone bromide
- A10443** Methyl 4-(triphenylphosphonio)crotonate bromide
- B23614** (Benzoylmethyl)triphenylphosphonium bromide

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PHOSPHORANES

- A11410** (Acetylmethylene)triphenylphosphorane
A12184 (Benzoylmethylene)triphenylphosphorane
L15144 (tert-Butoxycarbonylmethylene)triphenyl phosphorane
A15619 (1-Ethoxycarbonylethylidene)triphenyl phosphorane

- A12896** (Ethoxycarbonylmethylene)triphenyl phosphorane
A11709 (Formylmethylene)triphenylphosphorane
A14020 (Methoxycarbonylmethylene)triphenyl phosphorane

Vinylphosphonium salts

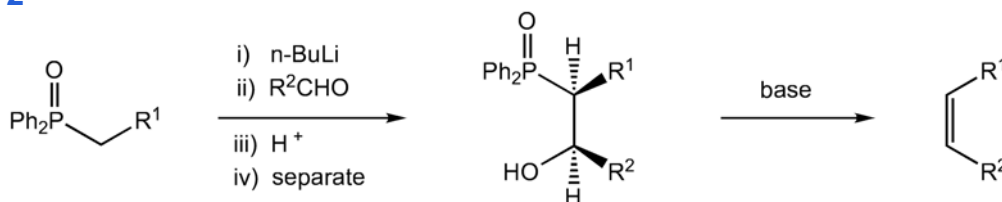
L00956 1,2-Vinylenebis(triphenylphosphonium bromide)

L00708 Vinyltriphenylphosphonium bromide

Alkyl diphenylphosphine oxides

Alkyl diphenylphosphine oxides can be metalated and reacted with aldehydes or ketones to give stable α -hydroxy phosphine oxide intermediates. These undergo stereospecific anti-elimination on treatment with strong base to give alkenes. This reaction is usually known as the Horner or Horner-Wittig reaction.³⁰ In contrast to the Wittig reaction with phosphoranes, where separation of the product from triphenylphosphine oxide can be a problem, the by-product (a diphenylphosphinate salt) is often water-soluble.

Scheme 2



A further major advantage over other Wittig-type reactions is that the intermediate adduct is isolable and can often be purified by crystallization or flash chromatography, allowing much more predictable control of the alkene stereochemistry.³¹ The scope of the chemistry of diphenylphosphine substituted molecules has since been further extended, particularly by Warren's group, further details of which can be found in the review literature.^{15,21,23,32}

Alkyl diphenylphosphine oxides

- L00698** Cyclohexyldiphenylphosphine oxide
L01336 Diphenylethylphosphine oxide

- L00912** (Methoxymethyl)diphenylphosphine oxide
A11484 Methylidiphenylphosphine oxide

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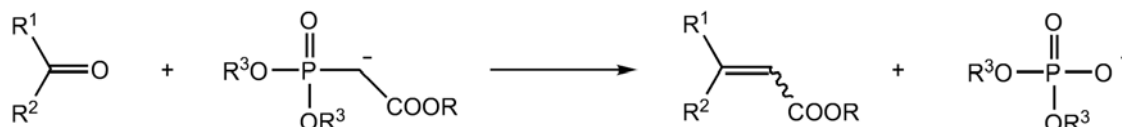
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Phosponates

Phosponate esters and related compounds with a second stabilizing group form anions which react with both aldehydes and ketones (Scheme 3). This reaction, first reported by Horner *et al*³⁰ as a variation of the phosphine oxide reaction (see preceding section) and subsequently studied in more detail by Wadsworth and Emmons,³³ is variously known as the Horner-Emmons, Wadsworth-Emmons, or Horner-Wadsworth-Emmons ('HWE') olefination reaction. In most cases, separation of the by-products is straightforward, since they are water-soluble and of relatively low mass, and it has become one of the most widely used methods of alkene synthesis:

Scheme 3



The mechanism again involves a four-center intermediate, and the stereochemistry is usually (*E*)-selective.

In general, phosphono-groups confer less stability on the anion than does the positively-charged triphenylphosphonio-group, with the result that Horner-Wadsworth-Emmons reagents are more reactive than the corresponding Wittig ylides. The versatility of this reaction can be extended by prior alkylation, *in situ*, of the phosphonate anion. Addition of a second mole of base leads to a new phosphonate anion, which can then be used in the olefination reaction. Typical experimental protocols^{15,34} for the reaction and reviews^{15,21,23,35-37} are available.

The phosphonates listed below are classified according to the nature of the stabilizing group and, in many cases, further information and reaction schemes are given in the main section of the Catalogue:

Phosponates α -substituted with an electron-withdrawing group

- | | |
|---|--|
| L17651 tert-Butyl diethylphosphonoacetate | A14120 Triethyl phosphonoacetate |
| A10218 Diethyl cyanomethylphosphonate | L09329 Triethyl 2-phosphonobutyrate |
| B22163 Diisopropyl cyanomethylphosphonate | A10995 Triethyl 2-phosphonocrotonate |
| L00537 Dimethyl acetylmethylphosphonate | 30413 Triethyl 2-phosphonopentanoate |
| A10644 Methyl (diethylphosphono)acetate | B23261 Triethyl 2-phosphonopropionate |
| A14532 Tetraethyl methylenediphosphonate | A13301 Trimethyl phosphonoacetate |
| A13484 Tetraisopropyl methylenediphosphonate | A12399 Trimethyl 4-phosphonocrotonate |
| A13441 Tetramethyl methylenediphosphonate | L00959 Trimethylsilyl diethylphosphonoacetate |

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Hetero substituted phosphonates

B21156 Diethyl 2-bromoethylphosphonate
L16715 Diethyl (bromodifluoromethyl)phosphonate
A12461 Diethyl 2,2-diethoxyethylphosphonate
L11025 Diethyl 2,2-dimethoxyethylphosphonate
L13341 Diethyl 5-hydantoylphosphonate
B21215 Diethyl hydroxymethylphosphonate
A13697 Diethyl iodomethylphosphonate
L00579 Diethyl methylthiomethylphosphonate

A13660 Diethyl phenylthiomethylphosphonate
B21096 Diethyl (phthalimidomethyl)phosphonate
L13763 Diisopropyl bromomethylphosphonate
L02840 Dimethyl phthalimidomethylphosphonate
A14581 Tetraethyl (dimethylaminomethylene)-diphosphonate
L17913 Triethyl 2-fluoro-2-phosphonoacetate

Allylic phosphonates

10365 Diethyl allylphosphonate
B21108 Diethyl cinnamylphosphonate

L10567 Dimethyl allylphosphonate

Benzylic phosphonates

B22279 Diethyl 4-aminobenzylphosphonate
A10645 Diethyl benzylphosphonate
L00965 Diethyl 4-chlorobenzylphosphonate

L05226 Diethyl 4-methoxybenzylphosphonate
A15190 Diethyl 4-methylbenzylphosphonate
L05286 Diethyl 1-naphthylmethylphosphonate

Alkyl phosphonates

Phosphonates with only simple alkyl groups on the α -carbon form anions which add readily to carbonyl compounds, but the adducts do not spontaneously undergo the *syn*-elimination required to complete the olefination sequence. However, it has recently been reported that dehydration to the alkene can be successfully accomplished by treatment with $MgBr_2$ and diisopropylcarbodiimide.³⁹

30467 Di-n-butyl methylphosphonate
B23997 Diethyl 1-butylphosphonate
L13038 Diethyl 1-decylphosphonate
A11046 Diethyl ethylphosphonate
A14772 Diethyl methylphosphonate
L18588 Diethyl 1-octylphosphonate
A17105 Diethyl 1-propylphosphonate
B21426 Diethyl 1-tetradecylphosphonate
44643 Diisobutyl methylphosphonate

A12904 Diisopropyl methylphosphonate
44364 Dimethyl cyclohexylphosphonate
44642 Dimethyl ethylphosphonate
A14268 Dimethyl methylphosphonate, 97%
89999 Dimethyl methylphosphonate, 99+%
L00983 Methylphosphonic bis(dimethylamide)
L10488 Triethyl 4-phosphonobutyrate
L10190 Triethyl 3-phosphonopropionate

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