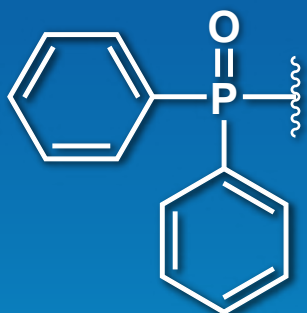


Protecting Group (Ph₂P(O)) for Terminal Acetylenes in Electronic Materials Synthesis



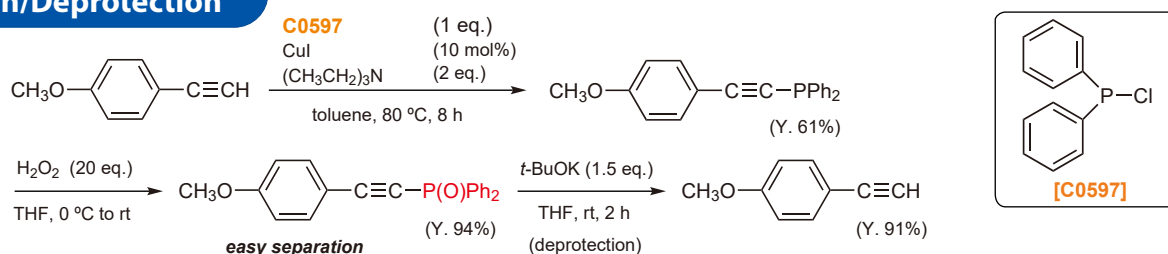
Ph₂P(O) group

Advantages

- Useful for the protection of terminal ethynes
- Stable under coupling and acidic conditions
- Applied for the synthesis of phenyleneethynylenes

Ph₂P(O) is a new terminal acetylenes protecting group, developed by Orita and Otera *et al.* This protecting group can be introduced readily to terminal acetylenes by CuI catalyzed phosphination using chlorodiphenylphosphine [C0597] and subsequent oxidation with H₂O₂. The high polarity of the phosphoryl group enables easy separation of the desired products from the lower polar hydrocarbon byproducts. The Ph₂P(O)-protected acetylenes can be easily deprotected by treatment with *t*-BuOK.¹⁾

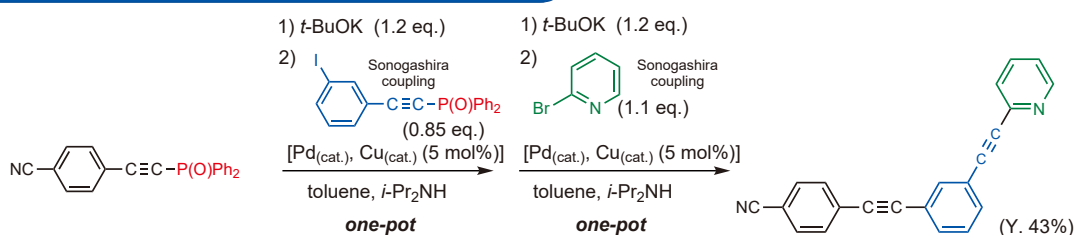
Protection/Deprotection^{1a)}



- 1) a) X. Yang, D. Matsuo, Y. Suzuma, J.-K. Fang, F. Xu, A. Orita, J. Otera, S. Kajiyama, N. Koumura, K. Hara, *Synlett* **2011**, 2402.
b) X. Yang, S. Kajiyama, J.-K. Fang, F. Xu, Y. Uemura, N. Koumura, K. Hara, A. Orita, J. Otera, *Bull. Chem. Soc. Jpn.* **2012**, 85, 687.

The deprotected acetylenes can be transformed to more expanded arylethylenes by the Sonogashira coupling with aryl halides. This synthetic approach is applicable to a one-pot synthesis of phenyleneethynylenes used for electronic devices by deprotection followed by coupling reactions.²⁾ In addition, HC≡C-P(O)Ph₂ [E1310], a mono-protected acetylene, is also used.

A Synthesis Example of Phenyleneethynylene^{2a)}



- 2) a) L. Peng, F. Xu, Y. Suzuma, A. Orita, J. Otera, *J. Org. Chem.* **2013**, 78, 12802.
b) L. Peng, F. Xu, K. Shinohara, A. Orita, J. Otera, *Chem. Lett.* **2014**, 43, 1610.
c) L. Peng, F. Xu, K. Shinohara, T. Nishida, K. Wakamatsu, A. Orita, J. Otera, *Org. Chem. Front.* **2015**, 2, 248.

Chlorodiphenylphosphine
Ethynyl(diphenyl)phosphine Oxide

25g / 100g / 500g [C0597]

100mg / 1g [E1310]

Protecting Group (Ph₂P(O)) for Terminal Acetylenes in Electronic Materials Synthesis

Related Products (Ar-C≡CH)

3-Ethynylaniline	5g / 25g	[A1122]	1-Ethynylpyrene	200mg / 1g	[E0939]
1-Butyl-4-ethynylbenzene	5g / 25g	[B2301]	1-Ethynyl-4-(phenylethynyl)benzene	200mg / 1g	[E0967]
1-Bromo-4-ethynylbenzene	1g / 5g	[B3701]	4-Ethynylbenzaldehyde	1g	[E0987]
1-Bromo-2-ethynylbenzene	1g / 5g	[B4608]	1-Ethoxy-4-ethynylbenzene	1g / 5g	[E1029]
1-Chloro-4-ethynylbenzene	1g / 5g	[C2670]	5-Ethynyl-1,2,3-trifluorobenzene	1g	[E1078]
1-Chloro-2-ethynylbenzene	1g / 5g	[C2750]	4-Ethynylbenzenesulfonamide	200mg / 1g	[E1130]
1,4-Diethynylbenzene	1g / 5g	[D2151]	1-Ethynyl-2,4-difluorobenzene	1g / 5g	[E1169]
1,3-Diethynylbenzene	1g / 5g	[D2496]	1-Ethynyl-4-(trifluoromethoxy)benzene	1g / 5g	[E1170]
4,4'-Diethynylbiphenyl	200mg / 1g	[D4233]	1-Ethynyl-3,5-dimethoxybenzene	200mg / 1g	[E1175]
1,5-Diethynyl-2,4-dimethylbenzene	1g / 5g	[D4878]	1-Ethynyl-4-fluorobenzene	1g / 5g	[F0470]
Ethynylbenzene	25mL / 100mL / 500mL	[E0196]	1,3,5-Triethynylbenzene	1g / 5g	[T2760]
4-Ethynylaniline	10g / 25g	[E0505]	Tetrakis(4-ethynylphenyl)methane	100mg / 1g	[T3151]
1-Ethynyl-4-pentylbenzene	5g / 25g	[E0563]	3,6-Diethynylcarbazole	200mg / 1g	[D4275]
1-Ethynyl-4-hexylbenzene	5g / 25g	[E0564]	2,6-Diethynylpyridine	200mg / 1g	[D5097]
4-Ethynylanisole	1g / 5g / 25g	[E0603]	2-Ethynylpyridine	1mL / 5mL	[E0340]
1-Ethynyl-4-(trifluoromethyl)benzene	1g / 5g	[E0626]	3-Ethynylpyridine	1g / 5g	[E0560]
1-Ethynyl-2-fluorobenzene	5g	[E0654]	4-Ethynylpyridine	100mg / 500mg	[E0561]
4-Ethynyltoluene	5g / 25g	[E0655]	4-Ethynylphthalic Anhydride	1g / 5g	[E0579]
3-Ethynyltoluene	1g 3,900円 / 5g / 25g	[E0665]	3-Ethynylthiophene	1g / 5g	[E0892]
1-Ethyl-4-ethynylbenzene	5g / 25g	[E0749]	2-Ethynylthiophene	1g / 5g	[E0915]
1-Ethynyl-4-propylbenzene	5g / 25g	[E0750]	4-Ethynylpyridine Hydrochloride	1g / 5g	[E1043]
4-Ethynyltriphenylamine	1g	[E0894]	9-(4-Ethynylphenyl)carbazole	1g / 5g	[E1055]
2-Ethynyl-naphthalene	100mg	[E0933]			

Introduction of the Researcher

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Faculty of Engineering, Okayama University of Science



Professor **Akihiro Orita**



content of the research

Orita's laboratory has been working on the development of these methodologies.

- 1) Developing functional materials through acetylene derivative synthesis
- 2) Selective synthesis using organotin compounds

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